The 18th International Congress on Marine Corrosion and Fouling – ICMCF 2016

University of Toulon
19-24 June 2016 - Toulon - France

ORGANIZED ON BEHALF OF

COMITE INTERNATIONAL PERMANENT POUR LA RECHERCHE SUR LA PRESERVATION DES MATERIAUX EN MILIEU MARIN (COIPM)

The COIPM Committee consists of:

Chair:	Tony CLARE	Newcastle University, UK
Vice Chair:	vacant	
Treasurer:	Claire HELLIO	Université de Bretagne Occidentale, France
Secretary:	Maureen CALLOW	University of Birmingham, UK

Committee Members:

Christine BRESSY	Université de Toulon, France
Sergey DOBRETSOV	Sultan Qaboos University' oman
Steve McELVANY	Office of Naval Research, USA
Kevin REYNOLDS	International Paint, Ltd, UK
Axel ROSENHAHN	University of Bochum, Germany
Emily RALSTON	Florida Institute of Technology, USA
Kiyoshi SHIBATA	Chiba Institute of Technology, Japan
Dominique THIERRY	Institut de la Corrosion, Brest, France
Serena TEO	National University of Singapore, Singapore

Student Committee:

Marlène LEJARS	Université de Toulon, France
Kody LIEBERMAN	Florida Institute of Technology, USA

Organising & Scientific Committee:

Laboratoire MAPIEM, Université de Toulon (Toulon, France)

Christine BRESSY, *Chair*

Emmanuel ARAGON
Lénaïk BELEC
Yves BLACHE
Jean-François BRIAND
Hugues BRISSET
Gérald CULIOLI
Anne DELARUE
Marlène LEJARS
André MARGAILLAN
Maëlle MOLMERET
Annick ORTALO-MAGNÉ
François-Xavier PERRIN

Pôle Mer Méditerranée (Toulon, France)
Christophe AVELLAN

Unité Recherches et Développements Technologiques, IFREMER (Brest, France)
Chantal COMPÈRE

DCNS Research / Centre Français de l'Anticorrosion (CEFRACOR)
Anne-Marie GROLLEAU

Laboratoire LEMAR, Université de Bretagne Occidentale (Brest, France)
Claire HELLIO

Institut de la Corrosion (Brest, France)
Dominique THIERRY

Sponsors:

LONZA
INTERNATIONAL
HEMPEL
DCNS
NORDOX
SELEKTOPE
JOTUN
SPIESS-URANIA
JANSSEN PMP
BOERO Yatch coatings
IMAREST : Institute of Marine Engineering, Sciences and Technology
Université de Toulon- axe MEDD
American Chemet Corporation

Financial support:

TPM (Communauté d'Agglomération Toulon Provence Méditerranée)
Région PACA (Provence Alpes Côte d'Azur)
Société Chimique de France

Financial support for travel provided by grants from:

The Office of Naval Research
The office of Naval Research Global

Financial support for best oral & poster prizes:

Biofouling
The European Society for Marine Biotechnology
Journal for Marine Science and Engineering
Biointerphases

Exhibitors:

EUROCORR 2016
Byefouling & SeaFRONT
TECAN

TABLE OF CONTENTS

MONDAY June 20, 2016

WEDNESDAY June 22, 2016

New antifouling responsive and textured surfaces

Impact & Applications of marine fouling and corrosion research and technologies

Adhesion, signaling & Biofilm formation

Novel environmentally friendly antifoulants

FRIDAY June 24, 2016

Biosecurity, risk management & Prediction in marine protection

Marine corrosion: Materials & Coatings

POSTER SESSION

JOINT WORKSHOP

MONDAY June 20, 2016

Plenary- 1 Fouling in times of global change

Martin WAHL

GEOMAR, Kiel, Germany.

mwahl@geomar.de

Fouling, i.e. the colonization of hard substrata by sessile organisms, is a typically marine phenomenon. Abiotic properties of the medium, such as density and viscosity and its suitability as a universal solvent and as a vector of suspended matter have permitted the evolution of sessile animals and determine the intensity and composition of fouling exerted by their dispersal stages.

Many properties in the shallow marine system fluctuate stochastically or regularly, but also exhibit anthropogenic directional shifts. The quality and quantity of fouling changes with these abiotic shifts, and so do the challenges fouling poses to maritime engineers or potential organismic hosts to epibionts (i.e. foulers attaching to living surfaces).

Global change in the sea comprises a simultaneous shift of numerous environmental traits such as temperature, precipitation, CO_2 concentration, nutrient status, stratification, salinity, pollution, prevalence of invasive species and many more. Warming may enhance the reproductive output of sessile organisms and, thus, the fouling pressure exerted by their dispersal stages. Warming may also lead to shifts in the reproductive phase or to a change in the length of the fouling season. It may also affect the composition of fouling-modulating biofilms, accelerate growth after settlement but also favour the spread of diseases. Shifting salinity in coastal areas and intensifying eutrophication will affect the composition of fouling communities and, possibly, enhance algal foulers which in turn may protect calcifying foulers from global acidification. Local pollution may select for hardy species predisposed for bioinvasions, a process which may be facilitated by the effects of environmental stress on native taxa. Global spread of invasive species, which frequently are particularly « tough » foulers, may further enhance the need for novel, efficient but non-polluting protection.

Potential hosts to foulers, i.e. most long-lived and large marine organisms, face the double challenge of a shifting target (new and/or more fouling) and of the direct stress of a shifting environment often jeopardizing their defenses. Their evolved protection systems, however, are composed of multiple, often independent, mechanisms which might provide a certain elasticity to the protection and, ultimately, the capacity to adapt to a shifting challenge. Biological antifouling systems are highly efficient, flexible and non-polluting. It might be increasingly rewarding for engineers to going fishing for ideas in the catalogue of biological defenses – especially so in times of global change.

Session 6: Biofilms & Microbial fouling - Auditorium Vauban

Keynote 1A

Understanding the microbiome of the seaweed holobiont

Peter STEINBERG

Sydney Institute of Marine Science, Mosman NSW;
School of Biological, Earth and Environmental Science, University of New South Wales Australia, Sydney, NSW; Australia

** p.steinberg@unsw.edu.au*

Increasingly marine eukaryotes such as sponges, corals or seaweeds – the living surfaces of the sea - are viewed as “holobionts”, or associations between a host organism and the microbial communities (the “microbiome”) which live in or on the host. The interaction between hosts and their microbiomes has fundamental consequences to the performance of the host and also mediates interactions between the external world, including interactions with fouling organisms and other natural enemies. In the context of understanding fouling of marine holobionts, two key questions have emerged. First, what governs the community patterns and development of microbiomes on hosts, and second, how do these microbiomes affect subsequent colonization of the host’s surfaces by other micro- or macro- organisms? The first question has been investigated by our lab and others using modern environmental sequencing tools, and in particular has focused on patterns of spatial and temporal variation of microbiomes on hosts, and the relationship between the taxonomic structure and the functional structure of these communities. Our initial studies in this area suggested a surprising mismatch in these structure/function relationships, but more recent studies and more rigorous analysis suggests a tighter coupling. Experimental studies have also showed the importance of interactions between different members of the microbiome for the temporal sequence of colonization of different bacterial taxa onto the host. With respect to the second question posed, perturbing this temporal sequence of colonisation can result in disease and infection of the host. However, the detailed mechanistic role of the microbiome in mediating subsequent colonization of these hosts more generally remains poorly understood. It is clear that removing or perturbing seaweed associated surface microbiomes can affect colonisation by invertebrate larvae such as those from corals or sea urchins. However, the specific microbial taxa, metabolites or structures which are responsible remain unclear, and the strongest evidence for specific deterrents or inducers of settlement from seaweed holobionts indicates that they are host derived.

Oral 1A

Metagenomic analyses of ship hull biofouling communities

Seongwon KIM[1], Regina Z. CER[2,3], Robert W. LI[4], Joseph ANDERSON[2], Vishwesh P. MOKASHI[2], Anne W. KUSTERBECK[5], Dagmar H. LEARY[5], Kimberly A. BISHOP-LILLY[2,3], and Gary J. VORA*,[5]

[1]*National Academy of Sciences, National Research Council, Postdoctoral Research Associate, US Naval Research Laboratory, Washington, D.C., USA*
[2]*Biological Defense Research Directorate, US Naval Medical Research Center, Frederick, MD, USA*
[3]*Henry M. Jackson Foundation for the Advancement of Military Medicine, Bethesda, MD, USA*
[4]*Bovine Functional Genomics Laboratory, US Department of Agriculture, Beltsville, MD, USA*
[5]*Center for Bio/Molecular Science and Engineering, US Naval Research Laboratory, Washington, D.C., USA*

* *gary.vora@nrl.navy.mil*

When biofouling communities form on the hulls of U.S. Navy ships, despite the use of antifouling coatings, they create a diverse range of problems that include an increase in frictional drag and fuel consumption, microbiologically influenced corrosion, and the potential introduction of invasive species to new environments. Informed solutions have been difficult to develop as our understanding of the formation, biological composition and function of these natural assemblages has been limited by a lack of analytical tools that are capable of deconvoluting the inherent complexity of these physically-associated and mostly non-culturable multi-species communities. To begin to provide a more comprehensive understanding of these communities, metagenomic sequencing analyses were utilized to determine the organismal composition and potential biological function of air–water interface biofilms sampled from the hulls of five U.S. Navy ships (USS *Arleigh-Burke*, USS *Laboon*, USS *Bainbridge*, USS *Nicholas*, USS *Elrod*). Prokaryotic community analyses using 16S rDNA profiling revealed five significantly different and taxonomically rich biofilm communities (1,242 to 3,258 taxa/ship) in which the majority of unique taxa were ascribed to members of the Rhodobacteraceae, Erythrobacteraceae, Alteromonadaceae and Flavobacteriaceae. Interestingly, beta diversity analyses revealed five distinct communities that could not be grouped based on the type of ship (destroyer or frigate) from which the biofilms were sampled. Complimentary whole metagenome sequencing analyses also revealed the tremendous taxonomic complexity and varying functionality of these communities despite having ~75% of sequences demonstrate e-values > 1e-5 (i.e. likely DNA sequences/genes that have not been previously described). Although harvested from identical anti-fouling substrates (controlled depletion polymer Interspeed 640 – BRA series [BRA640/BRA642] polishing antifouling), the findings demonstrated significant qualitative and quantitative differences in the organismal and potential funtional profiles of these communities suggesting that these properties were reflective of the different geographic environments in which these ships had travelled. Overall, the data described in this study provide a baseline for understanding the microbial composition of soft fouling communities that form on the hulls of U.S. Navy ships under dynamic conditions and in operational settings.

Oral 2A

Responses of marine microbial biofilm communities to contrasted antifouling coatings in two French Mediterranean sites

Thomas POLLET[1], Laurie FAVRE[1], Christine BRESSY[1], Benjamin MISSON[2], Didier DEBROAS[3], Cédric GARNIER[2], Gérald CULIOLI[1], Jean-François GHIGLIONE[4] & Jean-François BRIAND[1]

[1] Laboratoire MAPIEM, Université de Toulon, France
[2] Laboratoire PROTEE, Université de Toulon, France
[3] Laboratoire microorganismes : génome et environnement, Université Blaise Pascal, Clermont-Ferrand, France
[4] Laboratoire d'océanographie microbienne, Université Pierre et Marie Curie, Banyuls-sur-Mer, France

** thomas.pollet@univ-tln.fr*

Two main types of antifouling coatings (AC) are currently used to reduce organism colonization on ship hulls: the self-polishing coatings (SPC) and silicone or fluorine based fouling release coatings (FRC). SPC are composed of booster biocides, known to be potentially toxic for non-targeted species. With their mechanical properties and the lack of biocides, FRC are less toxic for environment but their efficiency remains greatly unknown. Microbial biofilm communities are pioneer organisms that colonize immersed surfaces but studies dealing with the impact of AC on their structure and dynamics remain scarce. We thus conducted experiments to determine the effect of SPC and FRC on microbial community abundance, diversity and composition. Immersions were conducted under static conditions in two French coastal sites, Toulon and Banyuls-sur-Mer (North-Western Mediterranean Sea), with contrasted physicochemical and hydrodynamic characteristics. Samplings were performed from 1, 4, 8, 12, 20, 28 days of immersion at Toulon and after 2.5 months in both sites. For each sample, microbial community abundances (heterotrophic prokaryotes and Nano/Picophytoplankton) were estimated by flow cytometry. Composition and diversity of prokaryotes (bacteria and archaea) were determined using high throughput sequencing. Finally, several environmental parameters and surface properties of coatings were measured. Unexpectedly under static conditions, our quantitative analysis suggested that FRC would be more efficient and consequently that surface properties of AC coatings would play a fundamental role in the first steps of microorganism colonization. Otherwise, results obtained simultaneously at Toulon and Banyuls after 2.5 months showed that the effect of both AC was significantly higher at Banyuls suggesting that hydrodynamics would be a limiting factor in microbial capacity to colonize these surfaces. Note that all results have been associated with metabolomics and environmental parameters (e.g. temperature, organic matter, nutrients, heavy metals…) in a statistical meta-analysis that will be presented during the congress.

Keywords: biofilm, antifouling coatings, microbial ecotoxicology

Oral 3A

Biofilm community structure and associated drag penalties on groomed ship hull coatings

Kelli HUNSUCKER*[1], J. Travis HUNSUCKER[12], Harrison GARDNER[1], Geoffrey SWAIN[1], Dasha LEARY[3] and Gary VORA[3]

[1]*Center for Corrosion and Biofouling Control, Florida Institute of Technology, Melbourne Florida USA*
[2] *SHIPWRIGHT LLC, Port Everglades, FL, USA*
[3]*Center for Bio/Molecular Science & Engineering, Naval Research Laboratory, Washington D.C. USA*

* *khunsucker@fit.edu*

Grooming is a proactive method utilizing frequent and gentle wiping of the hull surface to prevent the settlement of fouling organisms (Tribou and Swain 2010). It has been estimated that the US Navy could save 12 million US dollars per DDG-51 over a 15-year period, if the hull is actively groomed to maintain a light biofilm layer (Schultz et al. 2011). During several studies to test the efficacy of grooming, it was observed that a tenacious biofilm developed on surfaces that had been actively groomed (Hearin et al. 2015). For grooming to be a viable option, it is important to understand the composition of tenacious biofilms and their associated drag penalties. A study was designed to determine the community composition and drag penalties of tenacious biofilms grown on commercially available coatings. Coatings were groomed twice a week to develop tenacious biofilms. A second set of replicates were also deployed and remained un-groomed throughout the course of the study. After the development of a tenacious biofilm, the drag forces were measured on groomed and ungroomed coatings using a floating element balance. Biofilm samples were collected before and after hydrodynamic testing. Diatom taxonomy was performed using microscopic techniques; taxonomic diversity and structure of the biofilm communities were also analyzed by 16S and 18S ribosomal RNA gene sequencing. Rarefaction analyses were used to determine the species richness within communities (alpha diversity) and to analyze the dissimilarity between communities (beta diversity). Results showed differences in the biofilm communities on groomed versus ungroomed surfaces. The drag penalties associated with these communities will also be discussed.

Acknowledgements: This research was funded by the Office of Naval Research (Grant No. N00014-02-1-0217).

[1] M. Tribou and G. Swain. *Biofouling*. **2010**, 26, 47-56.
[2] M.P. Schultz, J.A. Bendick, E.R. Holm, W.M Hertel. *Biofouling*. **2011**, 27, 87-98.
[3] J. Hearin, K. Hunsucker, G. Swain, A. Stephens, H. Gardner, K. Lieberman, M. Harper. *Biofouling*. **2015**, 31, 625-638.

Oral 4A

Bubbles vs biofilms: a new method for biofilm removal

Maria SALTA[1*], LR GOODES[2], BJ. MAAS[3], SP. DENNINGTON[2], TJ. SECKER[4], TG. LEIGHTON [5,6]

[1]*Faculty of Sciences, School of Biological Sciences, University of Portsmouth, Portsmouth, UK*
[2]*Faculty of Engineering and the Environment, National Centre for Advanced Tribology at Southampton (nCATS), University of Southampton, Southampton, UK*
[3]*Faculty of Technology, School of Engineering, University of Portsmouth, Portsmouth, UK*
[4] *Faculty of Natural & Environmental Sciences, Centre for Biological Sciences, University of Southampton, UK*
[5]*Faculty of Engineering and the Environment, University of Southampton, Southampton, UK*
[6]*Institute of Sound and Vibration Research, University of Southampton, Southampton, UK*

[*] *maria.salta@port.ac.uk*

The accumulation of marine microorganisms (e.g. bacteria, diatoms) on a range of underwater surfaces is often termed as microfouling (or biofilms) [1]. Biofilms tenaciously adhere on ship hulls and result in increase of the surface roughness and therefore the vessel's drag. Current antifouling coatings, such as Foul Release Coatings (FRCs) only inhibit colonization of larger organisms (such as barnacle and algae, collectively termed biofouling), however biofilms remain the main issue and significantly contribute to drag increase on ships. Recent findings demonstrated that biofilms (up tp up to ~500 μm) were responsible for an up to 70% increase in skin-friction when FRC systems were tested [2]. Here we report the use of a newly developed biofilm removal system utilising an Ultrasonically Activated Stream (UAS) which enhances the cleaning properties of bubbles in a freely flowing water stream and effectively removes biofilms. Commercially available FRCs were immersed in the marine environment where biofilms were formed (~600μm thickness). The UAS was then applied on FRCs and surface roughness and bio-volume removal was evaluated (through 3D microscopy), illustrating total removal of detectable biofilm and zero damage to the coating.

[1] M. Salta, JA Wharton, Y Blache, KR Stokes, JF Briand, *Environmental Microbiology* **2013**, 15 (11), 2879-2893.
[2] MP Schultz, JM Walker, CN Steppe, KA Flack - *Biofouling* **2015**, 31(9-10), 759-773.

Session 3: Cathodic protection in marine environment
Room Colbert

Keynote 1B

Cathodic protection and marine organisms: what are the interactions?

Anne-Marie GROLLEAU[1 *]

[1] *DCNS Research, Cherbourg, France.*

anne-marie.grolleau@dcnsgroup.com

Corrosion control of immersed marine structures is ensured by the used of cathodic protection (CP) systems, whether galvanic (GACP) or impressed current cathodic systems (ICCP). CP is often used in conjunction with paint systems to reduce the size of the CP system as well as improve potential distribution on the protected structure.
Cathodic protection effectiveness relies on the application of the relevant protective potential, which in turn is related to current density requirements. In the case of submerged structures, cathodic protection has been applied with success using -800 mV vs. SCE as a protective potential. However, in the presence of microorganisms and where risks of microbial corrosion are identified, different criteria as the one cited above are recommended by a number of international standards.
This presentation will first review the basics requirements of CP in sea water and then focus on the influence of calcareous deposits and biofilms that form on cathodically protected surfaces on the current density required to maintain protective cathodic potentials. The protection criteria in case of anaerobic conditions will be also discussed.

Finally the use of anti-fouling systems and their impact on cathodic protection will be also illustrated.

Oral 1B

Harbour of Calais - Cathodic protection monitoring of marines structures

Jérôme CROUZILLAC[1,*], Alexandre DENIS[2], Julien MICHEL[3]

[1]Bac Corrosion Control, France, j.crouzillac@bacfrance.com
[2]Bac Corrosion Control, France, a.denis@bacfrance.com
[3]Bac Corrosion control, France, j.michel@bacfrance.com

* *j.crouzillac@bacfrance.com*

Authorities of Calais Harbour (Industry Commerce Chamber) have decided to protect against corrosion in immersed parts all their marine structures on a period of 3 years. It concerns 20 quays in total with piles of different diameters and sheet piles with different characteristics.
Cathodic protection system is by galvanic anodes in indium activated aluminum alloy. It has been designed according to European standard 13174 « Cathodic protection of harbour installations » to obtain a potential of -900mV Ag/AgCl sea water.
To get information for study a monitoring system has been installed on all marine structures. Several elements as monitoring anodes, zinc permanent reference electrodes and calibrated steel coupons will be used.
In finality we could get general informations on potential and current evolution during polarization phase and all along life of cathodic protection system.

Keywords: monitoring anodes, reference electrode, potential, current

Oral 2B

Compositional, environmental and accelerated testing considerations for the development of new cathodic delamination-resistant coatings for marine hardware

Thomas RAMOTOWSKI*, Wayne TUCKER, Matthew RICE and Adam DUSZKIEWICZ

Naval Undersea Warfare Center, Division Newport, Newport, RI, 02841, U.S.A.

* *thomas.ramotowski@navy.mil*

Most polymeric coatings debond rapidly from cathodically polarized, conductive substrates in the marine environment. This process is known as “cathodic delamination” or “cathodic disbondment” and it is estimated to cause billions of dollars of damage worldwide each year to commercial and military vessels and their associated hardware and support infrastructure. This undesirable debonding is a by-product of the cathodic protection systems used to prevent metals immersed in seawater from undergoing anodic corrosion; it is believed to be caused by the development of highly alkaline conditions on cathodically polarized surfaces due to the reduction of dissolved oxygen naturally present in seawater and the subsequent generation of hydroxyl $(OH)^-$ anions thereon. Despite many years of research, it has proven difficult to develop coatings with long term (>15 years) resistance to cathodic delamination. To develop new and better coatings, more needs to be known about the mechanism and kinetics of the cathodic delamination process itself. As a guide for future work and new coatings development, technical issues and possible opportunities for performance improvement related to coating and substrate composition, as well as to the state of the immediate physical environment of the coating will be discussed. The importance of being able to subject newly developed and possibly cathodic delamination-resistant coatings to realistic accelerated life testing to verify their long-term resistance is extremely important, but often the necessary testing protocols cannot be found in the literature. Different approaches for designing and running accelerated life tests on coatings highly resistant to cathodic delamination (for which the standard, Arrhenius-based approaches do not work) will be presented, along with actual test results for coatings that have demonstrated long-term resistance to cathodic delamination. A better understanding of how and why these coatings are able to resist cathodic delamination for long periods of time may result in the development of new coatings that will perform better/last longer than their predecessors.

Acknowledgements: Funding and support for this work has been received from the U.S. Navy’s Office of Naval Research/NUWC Division Newport Independent Applied Research (IAR) Program.

Oral 3B

Ensure effectiveness of marine applications of cathodic protection by using standardization and certification of competence

Marcel ROCHE[1 *]

[1] *CEFRACOR, Paris, France.*

marcel.roche@orange.fr

The effectiveness of cathodic protection for preventing corrosion of metallic or reinforced concrete structures has been improving a lot during the last decades thanks to company specifications, industrial recommendations, and national, regional or international standards. A complementary approach has been introduced for ensuring at the best the quality in design, implementation and control of cathodic protection systems through the verification of the competence of persons with a third-party scheme, i.e. certification.
In the marine environment, cathodic protection of ships, offshore structures and pipelines is systematic. Its use is developing for harbour facilities but remains to be better known by their owners and operators. It is essential to spread awareness on the requirements and recommendations to apply, and to insist on the importance of selecting appropriate and competent actors for the tasks required.
The paper will first make the status on the relevant standards, published or in preparation. Then, it will present a short history of certification in the field of cathodic protection. In France, the CFPC (*Conseil Français de la Protection Cathodique*) was created by the CEFRACOR (*CEntre FRAnçais de l'antiCORrosion*) in 1996 and commissioned in 1998 by *AFNOR Certification* for the operation of the mark "*AFNOR Competence*" for the cathodic protection persons in application of NF A05-690 and NF A05-691 standards, with 3 competence levels and 4 application sectors (*Underground and immersed metallic structures*, *Marine metallic structures*, *Reinforced concrete structures*, and *Inner surfaces of metallic container structures*). The first certificate has been delivered in 2000 for *Underground and immersed metallic structures* and 2008 for *Marine metallic structures.* Since July 2011, the CFPC operates directly certification of cathodic protection persons under the mark "*CEFRACOR Certification / Protection Cathodique*", in accordance with EN ISO / IEC17024: 2012, which defines the general requirements for bodies operating certification of persons, and EN 15257: 2007, which provides a harmonized framework for defining and verifying competence of persons in cathodic protection. CEFRACOR CFPC is accredited by COFRAC (COmité FRançais d'ACcréditation) from Feb. 2014 for *Underground and immersed metallic structures* and *Marine metallic structures* application sectors.
Scientific and technical information on cathodic protection as well as the management of certification is available on the web site *www.protectioncathodique.net*, which also manages the certification process. The scheme is operational in French, but also in English for level 3 for all application sectors, and for levels 1 and 2 for *Marine metallic structures* application sector. Any information or support can be obtained using the email address *cfpc@cefracor.org*. The name of certified persons is available on the website.
In the near future, EN ISO 15257, in preparation, should ensure equivalence of certification systems in the world for the same 4 application sectors but for 5 competence levels.

N°4-0558

Oral 4B

Oil and gas subsea equipment - CP challenges in Australia

Paul GEORGESON[1], Oddbjorn GJERDE*[2]

[1] Wood Group, Perth, Australia.
[2] SEAR JIP, Perth, Australia

** Oddbjorn.Gjerde@woodgroup.com*

Oil and gas operators in Australia are facing a number of challenges with regard to cathodic protection of their subsea equipment. Subsea systems are designed to have a number of retrieval items which can be changed out, i.e. Subsea Control Modules, shown in Figure 1.

Fig. 1: Subsea Manifold, Retrievable Subsea Control Module (SCM) and Sacrificial Anodes

Fig. 2: SCM Mounting Base Underside

Increasing equipment design life durations (up to 40 years) has meant that a significant volume of sacrificial anode material is being added to structures to ensure corrosion protection. This in turn is creating issues with regard to retrieval of replaceable components, whose surfaces are generally left uncoated, due to the formation of calcareous deposits. Costly vessel and ROV time is required to perform acid baths or physical separation of components by vibrating or pulling items with forces well above design limits.

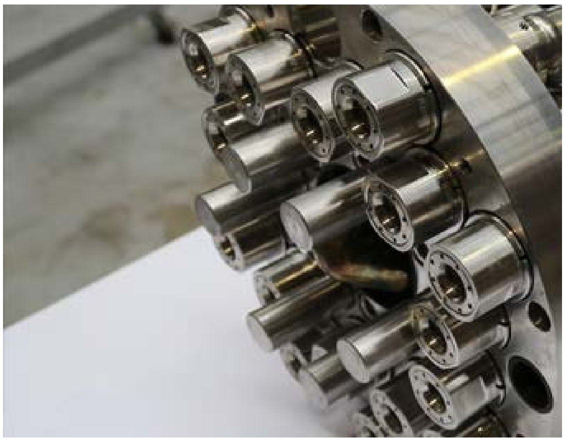


Fig. 3: Hydraulic Couplings

Fig. 4: Calcareous Deposits on EFL and SCMMB

The challenge for the industry is to find smarter CP designs, materials, equipment interfaces or coatings to address these issues.

Session 6: Biofilms & microbial fouling - Room Colbert

Oral 5A

Regulation of the epibiotic bacterial community by the surface metabolome of the brown alga *Taonia atomaria*

Ahlem OTHMANI[1], Jean-François BRIAND[1*], Mireille AYE[1], Maëlle MOLMERET[1], Robert BUNET[2] and Gérald CULIOLI[1*]

[1] Université de Toulon, MAPIEM, EA 4323, La Garde, France.
[2] Institut Océanographique Paul Ricard, Ile des Embiez, Six-Fours-les-Plages, France

** briand@univ-tln.fr, culioli@univ-tln.fr*

The goal of this work was to better understand the ecological mediation between the Mediterranean ochrophyta *Taonia atomaria* and bacterial communities colonizing its surface. A specific extraction protocol dedicated to surface metabolites using the dipping technique in organic solvents was developed without causing cell lysis of the outer layer. MeOH and MeOH/CH_2Cl_2 were demonstrated by fluorescent microscopy to be suitable solvents for the surface-metabolites extraction for a time of exposure less than 15s. These results were validated by a metabolomic approach which allowed the discrimination of solvent-dipped and whole-cell extracts. The extraction of surface-associated metabolites led to the detection of six compounds identified by comparison of their spectral data with those of compounds previously purified from algal whole-cell extracts. The hypothesis of a chemical selection of epibiotic bacteria, which belong to a more global chemical defense strategy, is proposed following several complementary information: (i) the surface of *T. atomaria* is free of macrofouling in its natural environment, (ii) some components at its surface were capable to selectively (**B** and **C**) or not (**A**) inhibit the adhesion of bacteria, (iii) compounds **A**, **B**, and **C** inhibit the attachment of bacteria at concentrations close to the ones naturally found at the surface of the algae, (iv) the active surface compounds **A**, **B** and **C** could be released into the surrounding seawater, (v) taking into account the overall chemical defense strategy, the settlement of barnacle larvae was prevented by some of the surface compounds (**B** and **D**).

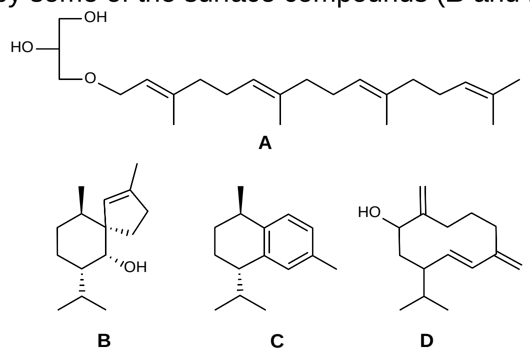


Fig. 1. Compounds isolated from *Taonia atomaria*

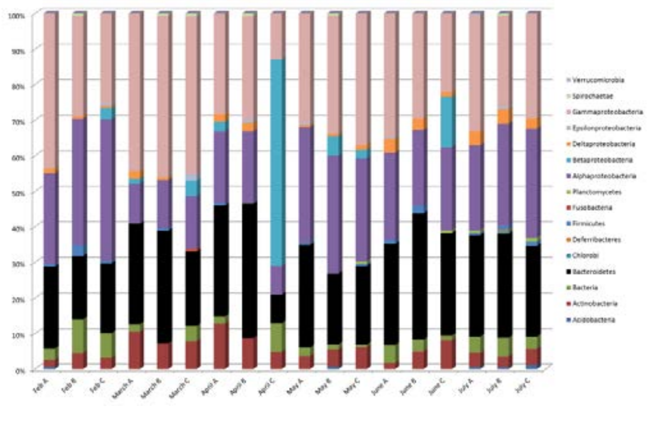


Fig. 2. Epibiotic bacterial communities

A seasonal monitoring of both the surface metabolome (LC-MS) and the bacterial communities (16S rDNA / MiSeq) was performed during the occurrence of *T. atomaria* from February to July on the collection site near Toulon. Bacterial communities remained relatively comparable at a high taxonomic level with the co-dominance of Bacteroidetes (mainly Sphingobacteria), α- and β-proteobacteria. The link between bacterial communities and exometabolomes did not appear at the global scale but should be found for specific molecules.

Oral 6A

Fluctuating defence with fluctuating time: temporal variation in the antifouling defence of the brown alga *Fucus vesiculosus*

Mahasweta SAHA[1]* and Martin WAHL[1]

[1] *Helmholtz center for Ocean research, Kiel, Germany.*

* *sahamahasweta@gmail.com*

The important role of marine epibiotic biofilms in the interactions of the host with its environment has been acknowledged recently. Studies from the temperate brown macroalga *Fucus vesiculosus* have identified surface based polar and non-polar compounds that have the potential to control such biofilms. Furthermore, both the fouling pressure and the composition of the epibiotic bacterial communities on this macroalga is known to vary seasonally. The extent to which this reflects a seasonal fluctuation of the fouling control mechanisms of the host is, however, unexplored in an ecological context. The present study investigated seasonal variation in the anti-settlement activity of surface extracts of *F. vesiculosus* against a set of biofilm-forming bacteria isolated from rockweed-dominated habitats, including replication of two populations from two geographically distant sites. The anti-settlement activity at both sites was found to vary temporally, reaching a peak in summer/autumn. Anti-settlement activity also showed a consistent and strong difference between sites throughout the year. This study is the first to report temporal variation of antifouling defence originating from ecologically relevant surface-associated compounds.

Oral 7A

Deep-sea bacterial biofilm communities growing on oceanographic instruments

Nikoleta BELLOU[1*], Juan Antionia GARCIA[2] and Gerhard J. HERNDL[2]

[1] Hellenic Centre for Marine Research, Institute of Oceanography, Anavyssos, Greece
[2] University of Vienna, Department of Limnology and Oceanography, Vienna, Austria

** bellou@hcmr.gr*

The colonization of surfaces and biofilm formation of microbial communities has been widely investigated in coastal marine systems while in the deep open sea only one *in situ* study has reported the presence of biofilm on artificial substrate and characterized the bacterial composition applying a fingerprinting method [1]. Due to the increasing number of deployments of oceanographic instrument in the deep sea, there is increasing interest into biofilm formation in deep-sea environments and on the microbial community composition in these biofilm.

In this study, pyrosequencing was used to characterize the bacterial communities in deep-sea biofilms developing on oceanographic instruments, which were deployed at the deepest point of the Mediterranean Sea, the Hellenic Trench, at 4500m depth for 155 d (October 2007 May to 2008). Samples were taken from the surface of OCEANO deep-sea acoustic releaser (Aluminum Alloy -Hard Anodized/+Epoxy Paint, Aluminum – 50μm hard eloxadize), the basic biofilm sampling platform, the connection rod of the platform (stainless steel) and from the Neutrino telescope glass. Immediately after retrieving, the samples were put into a sterile tube and stored in a -20°C freezer until further processing in the laboratory.

A total of 101194 individual sequence reads longer than 200bp were obtained from all analyzed samples with 87122 BLASTn hits against the bacterial database (http://ncbi.nlm.nih.gov) with an identity greater than 70%. The average sequence identity was 90.74%. A total of 21658 sequences had an identity of 89%, thus suggesting the presence of uncharacterized Bacteria with an amount of 21%. In total, 14 different taxa were identified. Overall, the most abundant were Proteobacteria (78%), Planctomycetes (11%), Bacteroitedes (7%), and other (6%) and with less than 1% Firmicutes, Chloroflexi, Actinobacteria, Fusobacteria, Acidobacteria, Verrucomicrobia, Nitrospirae, Lentisphaerae, Gemmatimonadetes and Cyanobacteria and others.

[1] Bellou, N., Papathanassiou, E., Dobretsov, S., Lykousis, V., & Colijn, F. *Biofouling* **2012**, 199–213.

Oral 8A

Biofilm ecology of antifouling surfaces in tropical marine environments

Siti Zarina ZAINUL RAHIM[1], Peter TODD[1], and Serena TEO*[,2]

[1] *Department of Biological Sciences, National University of Singapore, Singapore.*
[2] *Tropical Marine Science Institute, Nationa University of Singapore, Singaporel.*

* *tmsteolm@nus.edu.*

Singapore experiences the world's highest fouling pressures due to its tropical waters and high biodiversity. The fouling process usually begins with the formation of a microbial biofilm that can induce or retard subsequent settlement of various marine organisms based on its age, composition and density. Surface properties, temperature and other factors can all play a role in altering the early biofilm. In this work, we observe seasonal variations in the early biofilm community of anti-fouling (AF) coatings over the course of a year, using Singapore as a model for tropical waters. Fouling biofilm volume and community was also compared to macrofouling during this period. Biofilm abundance was analysed via confocal laser scanning microscopy (CLSM) and diversity via terminal restriction fragment length polymorphism (TRFLP). Understanding biofilm community development and its interaction with other marine organisms will help inform both anti-fouling and restoration ecology solutions.

Oral 9A

Structure of bacterial and diatoms communities on artificial substrata

Sergey DOBRETSOV[1]*, Priyanka SATHE[1, 2], Thirumahal MUTHUKRISHNAN[1] and Mario De STEFANO[3]

[1] Department of Marine Science & Fisheries, College of Agriculture & Marine Sciences, Sultan Qaboos University, Muscat, Oman.
[2] Chair in Nanotechnology, Water Research Centre, Sultan Qaboos University, Muscat, Oman.
[3] Second University of Naples, Naples, Italy

** sergey@squ.edu.om*

Every substrata submerged in aqueous environments are quickly foul with microbial biofilms mainly composed of bacteria and diatoms. Traditionally, bacteria on artificial substrata have been investigated using culture dependent techniques, which provide only limited information about diversity of species. High-throughput sequencing platforms, such as MiSeq Illumina and 454 pyrosequencing, allow identification of thousands of bacterial species in a biofilm sample. Diatoms on artificial substrata have been studied using light microscopy, while only scanning electron microscopy (SEM) can correctly identify diatom species. In this study bacteria and diatoms colonized artificial substrata in the Sea of Oman have been studied using MiSeq Illumina and 454 pyrosequencing, light and SEM microscopy approaches. Metagenomic sequencing revealed a high diversity of bacteria on artificial substrata. In total, more than 16 different bacterial classes have been identified. More than 80% of the sequences in each biofilm on every substrate were affiliated to the classes *Alphaproteobacteria*, *Flavobacteria* and *Gammaproteobacteria* and in some cases to the phylum *Cyanobacteria.* Other groups of bacteria were less dominant and varied among tested substrata. A total of 21 genera of fouling diatoms were identified using SEM. Some diatom genera, like *Berkeleya*, *Extubocellulus*, *Fragilaria*, *Grammatophora*, *Thalassiosira*, *Nanofrustulum*, *Toxarium* and *Surirella,* were observed only using SEM but not light microscopy. While some bacterial and diatom species were found on a particular substratum, environmental conditions had a strong influence on formation of microbial communities. Overall, our data highlighted the importance of using metagenomic sequencing and SEM to study fouling microbial communities.

Acknowledgements: This work was supported by The Research Council (TRC) grant RC/AGR/FISH/16/01 and an internal SQU grant IG/AGR/FISH/15/02.

Session 9 – Novel methods to evaluate antifouling efficacy and detect biofouling - Room Bonaparte

Keynote 2B

Metabolomic and genomic imaging of marine biofilms as tools for the study and control of marine biofouling

Iwona B. BEECH*,[1], Akiko OGAWA[1], Sukriye CELIKKOL-AYDIN, Zakari MAKAMA[1], Jonathan BRAUER[1], Egemen AYDIN[1], Vincent BONIFAY[1], Anjumala HERRAT[1], Matthew KOWALSKI[1], Jan SUNNER[1]

University of Oklahoma, Norman, OK, USA
** ibeech@ou.edu*

Understanding mechanisms governing various stages of marine biofilm development, from irreversible bacterial cell adhesion events, through formation of a microbial community, to biofilm detachment, is of paramount importance to the development of effective antifouling strategies. While considerable progress has been made in elucidating phenomena governing attachment of microbial cells to inanimate surfaces, there is still relatively poor understanding of the effect physico-chemical properties of the surface exerts on the initial cell adhesion process, including metabolic response of colonizing organisms. The near/surface environment experienced/sensed by a cell and the metabolic response of the cell to these queues would govern not only the strength of cell/surface adhesion but most likely, also the subsequent development of the, often complex, biofilm community. Identification of such metabolomic responses offers a promise of developing novel approaches to controlling cell adhesion events. Of equal relevance in combating biofouling is knowledge of microbial community structure in respect to its co-operative metabolism. Detection and identification followed by selective elimination of key players and/or their metabolic products involved in e.g. maintaining stability of a biofilm matrix or acting as surface “anchors” could open up possibilities of developing new ways of biofouling control. This latter aspect is of importance when designing laboratory experiments aimed to evaluate and test novel targeted antifouling measures, such as antimicrobial compounds or antifouling coatings. An overview of selected laboratory and field studies, is presented, demonstrating the application of advanced mass-spectrometry based metabolomics and ambient metabolomic imaging (LASCA) platform [1,2] developed at the University of Oklahoma to investigate marine biofilms. Moreover, a new laser ablation nucleic acid recovery method (LANAR) [3] that offers the promise of genomic imaging of biofilms will be presented and its relevance and advantages to the study of biofouling discussed. It is demonstrated that combining metabolomics and genomics is desirable when elucidating biofouling processes. The studies also reveal that care needs to be taken when attempting to reproduce field conditions and metabolic activity of biofilms, in laboratory experiments. Moreover, caution needs to be exercised when reporting fouling community structure based solely on DNA profiles.

Acknowledgements: This work was funded by ONR under contract N000141010250, DURIP N00014-09-1-0797 and MURI N00014-10-1-0946.

[1] J. I. Brauer, I.B. Beech, and J. Sunner, *J Am Soc Mass Spectrom* **2015**, 26,1538-1547.
[2] J. I. Brauer, Z. Makama, V. Bonifay, E. Aydin, E.D. Kaufman, I.B. Beech and J. Sunner, *Biointerphases* **2015**, 10.
[3] Sunner, J. and Beech, I.B. **2016**. Patent pending.

Oral 5B

3D scanning to capture configuration and arrangement of fouling roughness

Scott STORMS*[1], Eric HOLM[2]

[1] Naval Surface Warfare Center – Philadelphia Division, Philadelphia, PA, United States.
[2]Naval Surface Warfare Center – Carderock Division, West Bethesda, MD, United States.

** scott.storms@navy.mil.*

Fouling organisms on ship hulls affect performance of the ship by increasing drag and shaft horsepower output to compensate for the losses encountered. Although the general effects of hull fouling on ship performance are well documented, the effects of particular types of fouling organisms, their distribution, and abundance, are poorly understood. Hydrodynamic testing of actual fouling communities is helpful, but difficult due to issues associated with maintaining, replicating, or scaling the organisms of interest.

The Naval Surface Warfare Center – Philadelphia Division's advanced data acquisition, prototyping technology, and virtual environments (ADAPT.VE) lab uses laser metrology to digitally capture shipboard environments. Using the 3D scanning technologies, fouled testing panels provided by the Florida Institute of Technology were scanned to capture the geometric shape of the organisms. The panels had various types of fouling organisms including, but not limited to, barnacles, encrusting bryozoans, arborescent bryozoans, tubeworms, and sponges (Figure 1). The data is collected by the laser scanner as X-Y-Z coordinates in 3D space and then converted into a polygon mesh. This polygon mesh is where the data can be manipulated to account for any noise that may have been captured as a result of unfavorable conditions during the scanning process—wet surfaces causing laser refraction or high levels of sunlight exposure interfering with the laser. Next, exact surfacing of the mesh generates a Non-Uniform Rational B-Spline (NURBS) surface on top of the mesh. During the NURBS surface creation, the organic nature of the objects is accounted for and the surface is optimized for this type of scan data. The NURBS surface is sent to 3D CAD software to generate the 3D CAD file. Finally, any long wavelength deformations (for example, curvature or warping of the substrate) is corrected using wavelet theory approaches developed at the Naval Surface Warfare Center—Carderock Division. The wavelet algorithms successively flatten the panel by removing the largest features from the dataset, and re-create the dataset without that feature. The resulting surface includes only roughness elements due to fouling, and can be used for generation of physical models for hydrodynamic testing by means of 3D printing, or for simulation and modeling by methods of computational fluid dynamics.

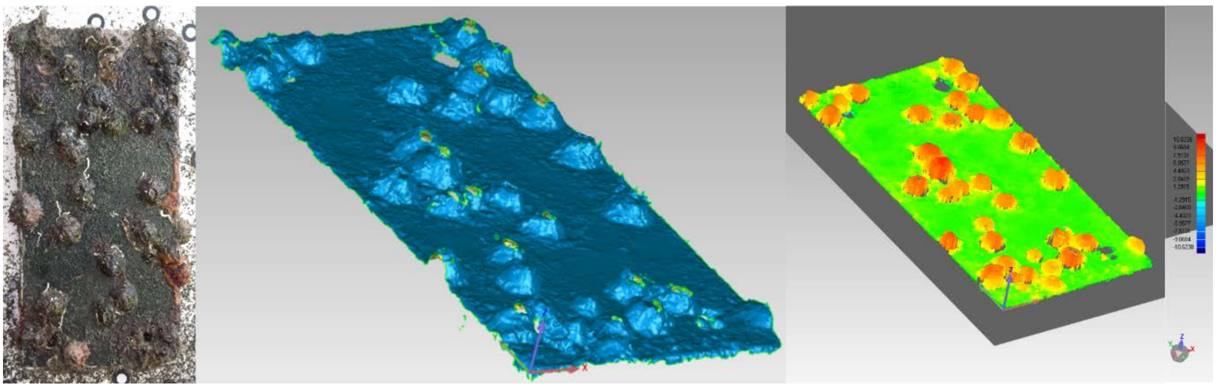


Fig. 1: [LEFT] Photo of biofouled panel. [MIDDLE] Scan data results. [RIGHT] Deviation analysis results.

Oral 6B

Rapid performance testing of commercially available hull coatings for navy ships

Job KLIJNSTRA*[1], Mark BAKKER[1], Claire MARTIN[2], Sandra MARCEAUX[2], André MARGAILLAN[2] & Christine BRESSY[2]

[1] Endures BV, Den Helder, The Netherlands
[2] Laboratoire MAPIEM, Toulon, France

* *Job.Klijnstra@Endures.nl*

In the EDA project “Antifouling Coatings for War Ships” (ACWS) investigations were made into development of methods for rapid performance testing of hull coatings. The ACWS project, funded through the European Defence Agency, was a collaborative research project between the navies of France, United Kingdom and The Netherlands involving navy representatives and 7 research partners. On the long run the project results should provide test protocols for identifying hull coatings with enhanced performance during increased docking intervals (6-10 years) for navy ships.

For self-polishing paints the polishing properties are the major determinant for long term performance. Six commercially available SPC’s were applied in recommended thickness for navy ships and investigated for about 1 year on polishing behaviour at 25 kn and 25 °C in natural seawater. Four products would easily reach a docking interval longer than 5 years and two systems could even cover 7.5 years from polishing point of view. Two out of the six products showed too high polishing to get even at a lifetime of 5 years, despite recommended thickness.

Friction drag properties of 6 SPC’s and 3 FRC’s with and without fouling were investigated in a laboratory based rotating disk test set up. The difference in drag between fouled and clean condition can be attributed to the specific fouling pattern on the disk. A protocol was used that discriminates between drag effects of initial fouling and drag effects of remaining fouling. This allows direct comparison of biocidal and biocide-free hull coatings on a major performance criterion.

Initial fouling growth after 12 weeks and associated added drag did not differ very much between SPC’s and FRC’s. The drag penalty of remaining fouling was lower on FRC’s showing their better foul release properties. In longer term raft tests all 3 FRC’s were found fully covered with a thick mixed biofilm (but no barnacles) that initially gives very high added drag. This drag effect disappears rapidly at higher rotation speeds and the low remaining fouling gave a drag penalty between 3 and 11 %. The SPC’s after 11 months raft exposure showed slime and animal fouling at lower % coverage than FRC’s. Drag penalty of this condition was between 37 - 55 % and not very different between products. Remaining fouling on the SPC’s, however, was found to give high drag penalty between 20 - 30 %.

Long term static exposure tests of commercial products were done both in France and in The Netherlands for benchmark with results of rapid performance tests. Results will be presented.

Advanced test protocols for rapid comparative performance testing of hull coatings for navy ships should include static/dynamic and rotation ageing methods to screen polishing and friction drag properties of candidate products prior to ship testing.

Oral 7B

LimnoMar's RotoMarin® - A new opportunity for dynamic field testing

Bernd DAEHNE*[1], Burkard T. WATERMANN[2], and Constanze FÜRLE[1]

[1] *LimnoMar, Laboratory for Aquatic and Marine Research, Experimental Station Norderney, Germany*
[2] *LimnoMar, Laboratory for Aquatic and Marine Research, Hamburg, Germany*

* *daehne@limnomar.de*

The RotoMarin® test rotor for dynamic testing of antifouling coatings is the first output of the three year German R&D project FoulProtect, which started in 2014. As a first step LimnoMar designed the RotoMarin® to provide an advanced method for dynamic antifouling testing at simulated field conditions, which is an ideal extension in the range of test facilities at the Marine Station of LimnoMar on the island Norderney (North Sea). Furthermore laboratory tests with cypris larvae and biofilm adhesion as well as static simulated field tests permanently submerged in the harbour and in the tidal zone at the exposed beach side of the island to simulate offshore conditions were conducted in the project.
At the RotoMarin® 16 test panels shaped like a segment of a circle are arranged horizontally around a vertical axis (Fig. 1). The speed can be adjusted correct to a minute with a switch box for 14 days in advance. Consequently it is possible to simulate an individual activity on customer request. The speed of rotating test panels increases with distance to the axis. At the outside the maximum speed is 19.1 knots.
Another great advantage of RotoMarin® in comparison to other test systems like rotating drums or rotating discs is the possibility to define the critical speed for self-cleaning performance of test coatings more exactly. For this purpose the distance of the outmost fouling coverage to the axis has to be measured and converted into the speed at this zone.
During the fouling season 2015 the first prototypes of test coatings developed by the project partners were tested successfully.
The mode of action of RotoMarin® as well as first results will be presented.

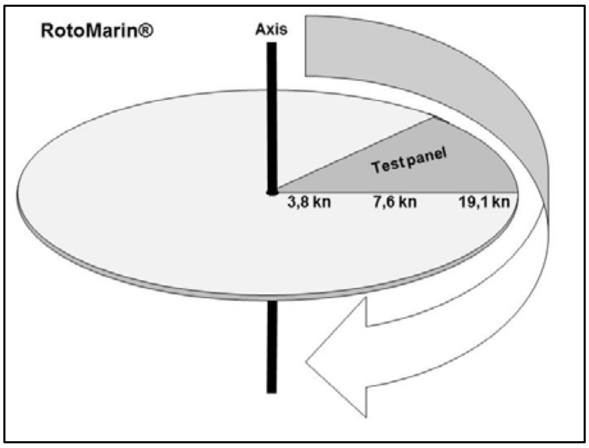


Fig. 1: Shape of test panels and maximum speed.

Acknowledgements: The work presented in this study has been funded by the German Federal Ministry for Economic Affairs and Energy, R&D Project FoulProtect (Grant Agreement No. 03SX370).

Oral 8B

How clean is this surface? Rapid and quantitative methods to assess biofouling

Curtis LARIMER[1], Eric WINDER[2], Robert JETERS[2], Jiyeon PARK[2], Matthew PROWANT[1], Ian NETTLESHIP[3], R. Shane ADDLEMAN[1], and George T. BONHEYO[2]*

[1] Pacific Northwest National Laboratory, Richland, USA.
[2] Marine Science Laboratory—Pacific Northwest National Laboratory, Sequim, USA.
[3] University of Pittsburgh, Pittsburgh, USA.

** George.Bonheyo@pnnl.gov*

Quantitative assessment of the early stages of biofouling is difficult using existing standard methods. A new method was developed to enhance the visibility and subsequent quantification of biofouling. First, broad spectrum biomolecular staining was used to enhance the visibility of the cells, nucleic acids, and proteins found in conditioning films and biofilms. Then a novel image analysis algorithm was developed to objectively and quantitatively measure biofouling accumulation from digital photographs of the stained surfaces. This new staining and analysis method was used to quantify the biofouling growth intensity (BGI) on coatings and materials fouled in natural seawater from Sequim Bay in the northwestern United States. The method was also tested with a biomedically relevant bacterial biofilm. Results were compared to independent measurements of cell counts and total organic carbon (TOC) analysis of fouling attached to the sample surfaces.

The TOC method was developed to allow thorough extraction of biomass from solid, porous, and fibrous surfaces without damaging underlying coatings and substrates or mineralizing the organic carbon. These methods are simple, fast, and high throughput for studies involving hundreds of coupons. The staining and image analysis can be scaled easily from small test coupons to large areas. Stained and processed images also facilitate assessment of spatial heterogeneity of a biofilm across a surface. This new approach to biofilm analysis could be applied in studies of natural, industrial, and environmental biofilms.

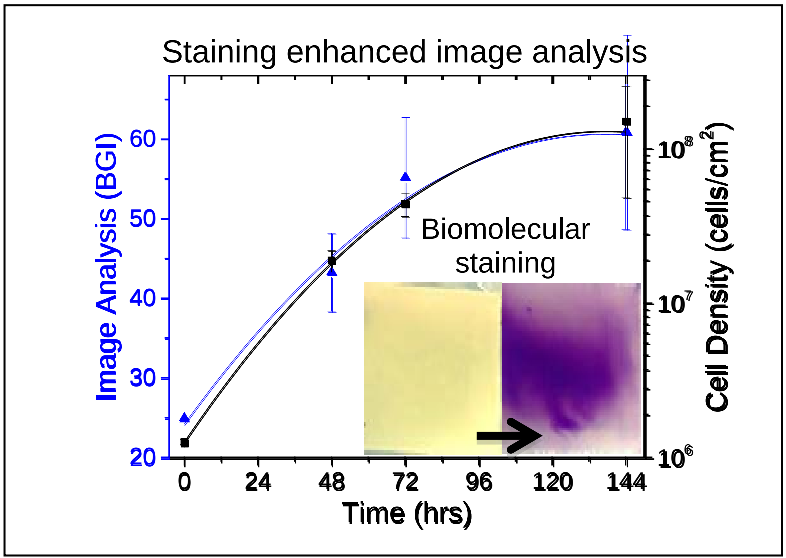


Fig. 1: Comparison of BGI measure of biofilm growth to cell density measured by optical density. BGI is shown on a linear scale (left) and cell density is shown on a log scale (right). Image analysis accurately and quickly measured accumulation of biofouling on the samples.

Session 13: Advances in fouling release technologies
Room Colbert

Keynote 2A

The future of fouling release: performance, practicality & new opportunities

Kevin REYNOLDS[1]*

[1] *AkzoNobel Performance Coatings, Gateshead, UK*

* *kevin.reynolds@akzonobel.com*

The current state of the art fouling control coatings such as Intersleek® 1100SR are the result of decades of research, development, testing and optimisation. As a result, the magnitude of their fouling release performance is close to optimum with them displaying high removal of microbial, weed and animal fouling at low hydrodynamic shear. This results in significantly improved fuel efficiency and reduced CO_2 emissions for shipping vessels.
Despite the reduced drag and fuel consumption, enhanced environmental profile (biocide free and high volume solids), superior aesthetics (ultra-smooth surface and excellent colour retention) and operational flexibility that Intersleek® 1100SR delivers to a customer (in comparison to a typical self-polishing antifouling product) the vast majority of the world shipping fleet continue to use biocidal based products. In other industries and end-uses such as oil & gas exploration and extraction, underwater surveying and marine renewable energy generation, at present in the majority of cases no fouling control technology is employed. The factors that contribute to these situations are based upon historic precedent, product perceptions, practical considerations and cost. The marine shipping market is conservative and risk averse and as a consequence is generally slow to abandon established practices and adopt new technologies. Fouling release coatings are rightly perceived as highly advanced technologies although they are also sometimes incorrectly viewed as being unsuitable for certain vessel types and operational profiles based upon isolated experience with earlier iterations of the technology. Whilst this is the case, some practical considerations including the complexity of the scheme and impact on yard throughput at new building and maintenance and repair still remain to be addressed.
The purpose of this presentation is three fold:

- To review the attributes of the current state of the art in fouling release technologies and examine the perceived barriers to widespread adoption.
- To highlight the opportunities for fouling release technologies outside of the marine shipping market.
- To showcase new fouling control concepts which may address existing concerns, deliver further enhancement of fouling control performance and initiate the expansion of the use of fouling release technologies in marine shipping and in new market sectors.

Oral 10A

Antifouling properties of surface-active borate glasses

Kenan FEARS[1 *], Jenifer SCANCELLA[1], Beatriz ORIHUELA[2], Daniel RITTSCHOF[2], Kathryn WAHL[1]

[1] Naval Research Laboratory, Chemistry Division, Washington, DC USA
[2] *Duke University Marine Laboratory, Beaufort, NC USA*

* *Kenan.fears@nrl.navy.mil*

Concern about the ecological impact of biocide-releasing materials has encouraged the Navy to seek novel strategies to prevent biofouling in an environmentally friendly manner. Here, we developed surface-reactive glasses as a targeted approach to mitigating barnacle adhesion. When exposed to seawater, the glass surfaces hydrolyzed and released ions. These ions either diffused into solution, or precipitated at the interface, forming reaction layers (< 15 microns) that limited glass dissolution without hampering the broad spectrum optical transparency. While sodium aluminoborate glasses were partly successful (78%; N=32) at resisting barnacle adhesion in 14 day re-settlement assays, a higher success rate (100%; N=16) was achieved by incorporating Mg—an essential mineral, abundant in seawater, but toxic at high concentrations. Since high Mg concentrations were localized at the interface, barnacles in direct contact with these glasses were adversely affected and did not permanently adhere, whereas barnacles on adjacent commercial window glass displayed no adverse effects and permanently adhered.

Oral 11A

Amphiphilic copolymers for fouling-release coatings

Albert CAMÓS NOGUER[1], Stefan M. OLSEN[2], Søren HVILSTED[1], Søren KIIL[1,*]

[1]Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Kgs. Lyngby, Denmark
[2]Department of Fouling Release Systems, Hempel A/S, Kgs. Lyngby, Denmark

** sk@kt.dtu.dk*

Polydimethylsiloxane (PDMS) resins are extensively used as binder in fouling-release coatings due to the low critical surface energy and low elastic modulus of PDMS. These properties result in poor adhesion of the fouling organisms, which are therefore detached by hydrodynamic forces during navigation [1,2,3]. Other compounds are usually mixed together with the binder (e.g. silica and pigments) in order to improve the mechanical, thixotropic and visual properties of the coatings. It has ben shown, however, that these ingredients have a negative effect on the fouling-release properties of the coatings [1,2,4].
Together with the PDMS-system, non-reactive polymers have been used to improve the fouling-release properties of the coatings. Initially, hydrophobic siloxane-based polymers were used, which aimed to increase the hydrophobicity of the PDMS surface [5,6]. However, copolymers comprising hydrophilic, amphiphilic and zwitterionic chemistries have been recently introduced due to their resistance to protein adsorption [7,8]. As a result, most of the current commercial fouling-release coatings contain either amphiphilic or hydrophilic copolymers to improve the fouling release properties of the coatings [9,10,11].
This work shows the effect of an amphiphilic copolymer that induces hydrophilicity on the surface of the silicone-based fouling release coatings. The behaviour of these copolymers within the coating upon immersion and the interaction of these surface-active additives with other compounds of the coatings are adressed.

[1] R. F. Brady, I. L. Singer, *Biofouling* **2000**, 15, 73-81.
[2] M. Lejars, A. Margaillan, C. Bressy, *Chem. Rev.* **2012**, 112, 4347-4390.
[3] A. G. Nurioglu, A. Catarina C. Esteves, G. de With, *J. Mater. Chem. B* **2015**, 3, 6547-6570.
[4] J. Stein, K. Truby, C. D. Wood, M. Takemori, M. Vallance, G. Swain, C. Kavanagh, B. Kovach, M. Schultz, D. Wiebe, E. Holm, J. Montemarano, D. Wendt, C. Smith, A. Meyer, *Biofouling* **2003**, 19, 87-94.
[5] K. Truby, C. Wood, J. Stein, J. Cella, J. Carpenter, C. Kavanagh, G. Swain, D. Wiebe, D. Lapota, A. Meyer, E. Holm, D. Wendt, C. Smith, J. Montemarano, *Biofouling* **2002**, 15, 141-150.
[6] A. Milne, *US Patent* 4,025,693, **1977**
[7] R. G. Chapman, E. Ostuni, S. Takayama, R. E. Holmlin, L. Yan, G. M Whitesides, *J. Am. Chem. Soc.* **2000**, 8303-8304
[8] C. J. Kavanagh, G. W. Swain, B. S. Kovach, J. Stein, C. Darkangelo-Wood, K. Truby, E. Holm, J. Montemarano, A. Meyer, D. Wiebe, *Biofouling* **2003**, 19, 381-390.
[9] P. C. W. Thorlaksen, A. Blom, U. Bork, WO Patent 076856A1, 2011.
[10] D. C. Webster, R. B. Bodkhe, WO Patent 052181A2, 2013.
[11] K. J. Reynolds, B. V. Tyson, WO Patent 131695A1, 2014.

Oral 12A

Tough and durable amphiphilic fouling-release coatings

Dean C. WEBSTER,[1*] Teluka GALHENAGE,[1] Augusto M. S. Moreira,[1] Ryan BURGETT,[1] Shane J. STAFSLIEN,[1] Lyndsi VANDERWAL,[1] John A. FINLAY,[2] Sofia FRANCO,[2] Tony CLARE[2]

[1] North Dakota State University, Fargo, North Dakota, USA
[2] Newcastle University, UK

** dean.webster@ndsu.edu*

Coatings having amphiphilic surfaces are being recognized as an approach to non-fouling or fouling-release marine coatings that can deter the settlement and adhesion of a wide variety of marine organisms. Several commercial coating systems have been recently introduced that have amphiphilic character, but they are still based on silicone elastomers, which are known to be soft materials that are challenging to adhere to a marine epoxy primer. Over the past several years, we have been exploring the concept of a self-stratified coating system where the properties of the bulk material and the surface are decoupled. Thus, the siloxane-polyurethane system results in a coating having the low surface energy of poly(dimethylsiloxane) (PDMS) while maintaining the tough and durable properties of a polyurethane. However, as in all siloxane-based systems, it is prone to fouling by slimes.

To address this issue, we have been exploring a number of different methods to create self-stratified coatings having amphiphilic surfaces. In several studies it has been found that by attaching hydrophilic groups to the siloxane component of the coating system that both the siloxane and the hydrophilic groups are expressed on the surface [1-3]. However, in these systems it proved challenging to achieve the appropriate balance of hydrophilicity-hydrophobicity. A new approach is appearing to be highly promising. In this approach, an isocyanate prepolymer is synthesized containing both PDMS and polyethylene glycol (PEG) oligomers. This prepolymer is then combined with a polyol and additional polyisocyanate to form the coating system. A range of PDMS and PEG molecular weights were explored and the overall content of PDMS and PEG were kept at 5 and 10 weight percent of the total coating system. Water contact angle data indicated that the surfaces were hydrophobic in nature. Laboratory fouling-release assays were carried out using a variety of marine organisms. For the green alga *Ulva*, a number of the amphiphilic coatings had release performance better than the control non-amphiphilic siloxane-polyurethane coating and also better than a siloxane elastomer and a commercial fouling-release coating. For the diatom *Navicula incerta*, which tends to have good adhesion to silicone surfaces, removal was better than that of commercial fouling-release coatings. Thus, coatings that had good removal of *Ulva* with simultaneous good removal of *Navicula* are indicative of the presence of a suitable amphiphilic surface. These coatings showed low barnacle adhesion values, as well. Thus, it seems that an approach to amphiphilic siloxane-polyurethane coatings with broad fouling-release performance has been identified.

[1] R. B. Bodkhe; S. J. Stafslien; J. Daniels; N. Cilz; A. J. Muelhberg; S. E. M. Thompson; M. E. Callow; J. A. Callow; D. C. Webster, *Prog. Org. Coat.* **2015**, 78, 369-380.
[2] D. C. Webster; R. Bodkhe, **2015**, U. S. Pat. No. 9,169,359.
[3] R. B. Bodkhe; S. J. Stafslien; N. Cilz; J. Daniels; S. E. M. Thompson; M. E. Callow; J. A. Callow; D. C. Webster, *Prog. Org. Coat.* **2012**, 75, 38-48.

Oral 13A

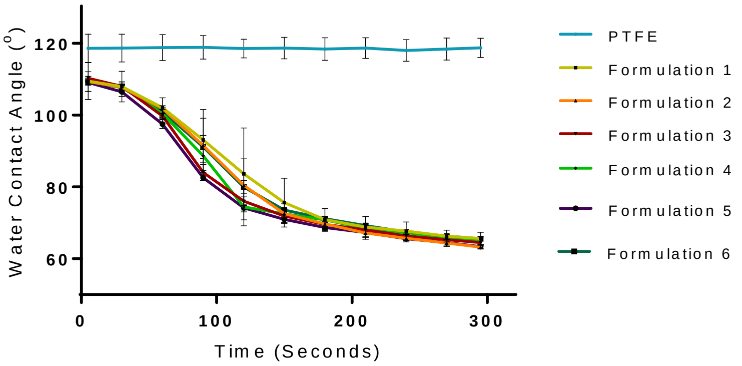
Preventing bacterial adherence utilising reorienting foul-release coatings

Stephen KENNY[1], Michael TAYLOR[1], David PIERRE[2], Stuart LEADLEY[2], Stephanie ALLEN[1], Morgan ALEXANDER[1] and Clive J ROBERTS[1*]

[1] *School of Pharmacy, Boots Science Building, University Park, The University of Nottingham, United Kingdom*
[2] *Dow Corning Europe SA, Seneffe, Belgium*

** clive.roberts@nottingham.ac.uk*

Since the ban on biocides such as organotin compounds in 2008 there has been demand for environmentally benign marine micro-organism foul-resistant coatings. Silicone is a robust and potent material for preventing bacterial adherence but is only effective against a limited number of bacterial species. Amphiphilic coatings containing both hydrophobic and hydrophilic groups have been shown to have improved foul-release properties. Utilising *Pseudomonas Aeruginosa* (PA01) as a model foulant, a novel silicone-based resin containing a reactive binder comprised of hydrophilic material was demonstrated *in vitro* to be more effective at preventing biofilm formation than pure poly(dimethyl siloxane) (PDMS). This is due to its ability of the coating to molecularly reorient from a hydrophobic surface to a more hydrophilic one when immersed in water. This was ascertained by examining the surface using surface analysis techniques including sessile-drop Water Contact Angle (WCA) measurement, Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) and Atomic Force Microscopy (AFM). The surface is initially dominated by PDMS (CA > 100°) in ambient conditions, but over a period of five minutes on exposure to water the coating shows an increase in wettability (CA ~ 65°). This is likely due to a reorientation and swelling of the polymer, with groups formerly buried in the bulk moving towards the surface. This proposal is consistent with AFM imaging and ToF-SIMS data.



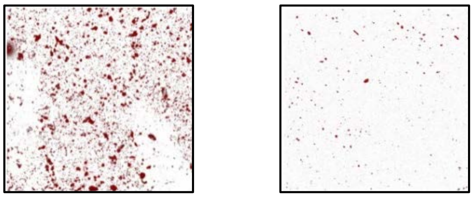


Fig. 1: (*Top*) Graph depicting change in water contact angle with time. The graph shows a trend of decreasing contact angle on the novel material until around 200s before plateauing. PTFE was used as a hydrophobic control. (*Bottom Left*) Plain PDMS sheet covered in *Pseudomonas Aeruginosa* (PA01) (30% total coverage). (*Bottom Right*) Novel amphiphilic coating with PA01 (2% coverage).

Oral 14A

FOULPROTECT: development of new coating concepts for achieving a long-lasting protection against marine fouling and biocorrosion

Thorsten FELDER*,[1], Gunnar HOFFMUELLER[1], Wen LIAO[1], Bernd DAEHNE[2], Andreas BRINKMANN[3], Deniz DOGAN[4], Simon RUTHMANN[4] and Oliver SEEWALD[4]

[1] Momentive Performance Materials GmbH, Leverkusen, Germany
[2] LimnoMar, Laboratory for Aquatic and Marine Research, Experimental Station Norderney, Germany
[3] Fraunhofer Institute for Manufacturing Technology and Advanced Materials, Bremen, Germany
[4] University of Paderborn, Group Prof. Wolfgang Bremser, Paderborn, Germany

The Foulprotect Consortium: Fraunhofer IFAM, LimnoMar, Norden-Frisia, Muehlhan, Nordseetaucher, Salzgitter Mannesmann Line Pipe, University Duisburg-Essen, University Paderborn, German Dry Docks, Ginco, Mankiewicz, Federal Maritime and Hydrographic Agency (BSH), Momentive

** thorsten.felder@momentive.com*

Marine fouling and biocorrosion is an unavoidable process occurring to all exposed surfaces which are immersed for a prolonged time in the sea and related water areas. The economic impacts of fouling and biocorrosion are significant on the shipping industry with respect to fuel consumptions and the CO_2 balance as well as for holders of off-shore constructions due to elevated maintenance costs. However, the ecologic consequences resulting from the incumbent most frequently used, namely biocide containing anti-fouling solutions has proven to be problematic, since the leaching chemicals from these technologies interfere strongly with the aquatic environment.

The FOULPROTECT consortium, consisting of 12 partners from academia, research organizations and industry, anticipates developing novel systematic approaches to achieve a biocides-free non-leachable fouling and biocorrosion protection. The approaches followed in the project will make use of new polymer chemistries leading to improved coatings and surface treatment methods that allow readily removing the occurred fouling from the surface. Subsequently, another part of the systematic approach is to develop instrumental procedures for cleaning surfaces protected with the new anti-fouling paint formulations. The ultimate objective in the project is to use the developed anti-fouling systems for the imprinting of riblet-structured surfaces (sharkskin morphologies) that are easy-to-clean and which provide an optimized flow-friction for various types of marine applications and beyond.

The presentation will give an introduction into the collaboration project and will mainly highlight the research results with respect to the biocide-free anti-fouling paint development.

Acknowledgements: The work presented in this study has been funded by the German Federal Ministry for Economic Affairs and Energy, R&D Project FoulProtect (Grant Agreement No. 03SX370).

Session 9: Novel methods to evaluate antifouling efficacy and detect biofouling - Room Bonaparte

Oral 9B

Probing diatom adhesion by microfluidics

Kim Alexander NOLTE*[1], Axel ROSENHAHN[1]

[1] *Analytical Chemistry - Biointerfaces, Ruhr-University Bochum, Germany*

* *kim.nolte@rub.de*

During the last years, novel materials were developed with environmentally benign fouling-release properties. To test the efficiency of new fouling release chemistries, several techniques are accessible that quantify, how easy fouling organisms can be removed. Among the established methods are calibrated, turbulent flow channels, push-off tests, water jets and microfluidic devices [1]. We developed a microfluidic assay that allows to test coating candidates against algal cell adhesion. Diatoms are driven through a micro-channel at a precisely controlled flow rate and at a constant concentration. The accumulation of adherent algal cells on the surfaces is monitored by video microscopy. Using self-assembled monolayers as model surfaces and diatoms as model organisms we were able to show that the adhesion strength [1] correlates with the accumulation dynamics if an appropriate shear stress is applied. Similar to the identification of a suitable flow for removal assays, a shear force range was identified within which the discrimination between the surfaces is maximized. We also present a parallelized version that allows sequential, quick testing of coating candidates. Due to the modular assembly of the device, not only model surfaces and thin organic films, but also practical coatings can be tested.

[1] M. Alles, A. Rosenhahn, *Biofouling.* **2015,** 31, 469–480.

Oral 10B

Screen-printed 96 well-microplates for screening electroactive coatings

Jean-François BRIAND*,[1], Raphaëlle BARRY-MARTINET[1], Aurore FAYARD[1], Guillaume DEMOL[1], The Hy DUONG[1], Hugues BRISSET[1], Pierre FRERE[2], Frédéric GOHIER[2], Philippe LERICHE[2], and Christine BRESSY[1]

[1] MAPIEM EA 4323, University of Toulon, La Garde, France.
[2] MOLTECH-ANJOU, University of Angers, Angers, France.

** briand@univ-tln.fr*

Several alternatives are currently investigated to prevent and control the natural process of colonization of any seawater submerged surfaces by marine organisms. The approaches under development include the use of (1) biocidal coatings [1], (2) PDMS-based fouling release coatings [2], (3) nanotextured or hierarchical slippery surfaces [3], and (4) conductive coatings [4]. Redox addressable polymers bearing 3,4-ethylenedioxythiophene (EDOT) lateral groups are under development in our laboratory through the AF-Electrocoatings project (ANR ASTRID, 2013-2016). To assess the potential of these electroactive coatings to prevent the adhesion of marine bacteria isolated from the Mediterranean sea [5], a screen-printed plate formed by 96 three-electrode electrochemical cells was used (Fig. 1). This novel platform is intended to control and record the redox properties of the electroactive coating in each well during the bioassay (15h), and to allow screening the antiadhesion activity of electroactive coatings with enough replicates to support significant conclusions. The activity of polymers synthesized during the AF-Electrocoatings program will be presented.

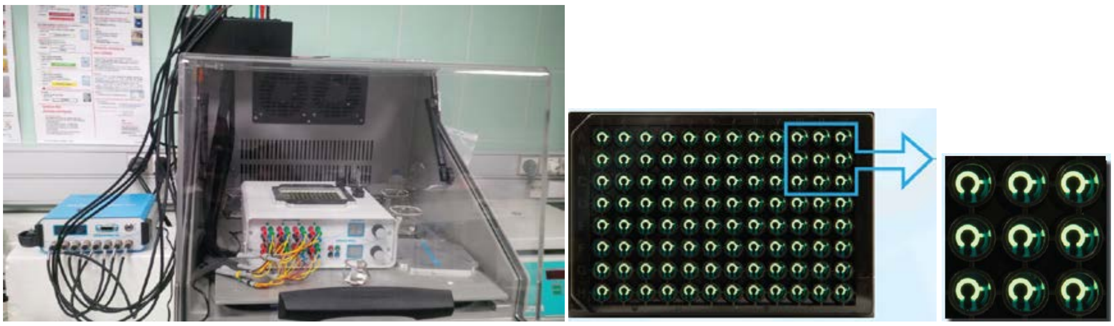


Fig. 1: new screen-printed electrochemical array formed by 96 three-electrode electrochemical cells with carbon-based working electrodes from DROPSENS

[1] C. Bressy *et al*. "Tin-free self-polishing marine antifouling coatings" in Advances in Marine Antifouling Coatings and Technologies; Woodshead Publishing: Cambridge, UK, **2009**.
[2] M. Lejars, A. Margaillan, C. Bressy, *Chemical Reviews* **2012**, 112, 4347.
[3] A. J. Scardino, H. Zhang, D. J. Cookson, R. N. Lamb, R. de Nys, *Biofouling* **2009**, 25, 757.
[4] C. Jr Bohn, A.B. Brennan, R.H. Baney, WO 2006/025857 A2.
[5] M. Camps, J-F. Briand, L. Dombrowsky, G. Culioli, A. Bazire, Y. Blache, *Marine Pollution Bulletin* **2011**, 62,1032.

Oral 11B

Short- and long-term efficacy mesocosm tests: a novel approach

Eldad GUTNER-HOCH[1,2], Rachel MAILICK[1], Michal WEIS[1], Martin AXELSSON[3], Aikaterini-Flora A. TROMPETA[4], Costas A. CHARITIDIS[4], Frederico MAIA[5], João TEDIM[5], Tania TEIXEIRA[6], Severine B. LARROZE[6], Yehuda BENAYAHU*[1]

[1]*Department of Zoology, Tel Aviv University, Ramat Aviv, Tel Aviv, Israel*
[2]*Interuniversity Institute for Marine Science in Eilat, Eilat, Israel*
[3]*Jotun A/S Sandefjord, Norway*
[4]*Research Unit of Advanced, Composite, Nano-Materials & Nanotechnology, School of Chemical Engineering, National Technical University of Athens, Zographos, Athens, Greece*
[5]*Smallmatek - Small Materials and Technologies, Lda Rua Canhas, Aveiro, Portugal*
[6]*AquaBioTech Group, Naggar Street, Targa Gap, Mosta, Malta G.C.*

* yehudab@tauex.tau.ac.il

Following the ban on tributyltin (TBT) as a marine antifoulant, the marine sector has intensively sought low-toxic, cost-efficient, and environmentally-friendly antifouling materials [1, 2]. Mesocosm tests have been commonly used to gain rapid information on the efficacy of new biocide-based paint prototypes, incorporating nanomaterials such as carbon nanotubes [3] and smart micro/nanoreservoirs. Traditionally, this is done by introducing a large number fouling organism larvae into tanks supplied with running seawater, and then examining their settlement and metamorphosis on test panels. To examine the efficacy of such products, a new approach was applied by adopting both short- and long-term mesocosm experiments. For the former we used the mussel *Brachidontes pharaonis* over a 96-hour period, with daily retrieval of panels and examination of mussel mortality and the development of byssus threads. For the latter, on days 10 and 20 of the experiment we examined biomass accumulation (dry weight) on the panels as well as chlorophyll content. The incorporation of BYEFOULING products into a commercial antifouling paint system, yielded meaningful results and demonstrated significantly greater efficacy compared to the control. The advantages of our experimental approach are evident: it lacks seasonal constraints, displays simplicity, and enables test repeatability. It is thus recommended to apply these tests in mesocosm experiments as an indicative tool for the efficacy of biocide-based paint prototypes and especially when nanomaterials are incorporated.

Acknowledgements: This research is supported by the EU FP7 Programme/ THEME [OCEAN 2013.3] within the collaborative project “BYEFOULING - Low-toxic, cost-efficient, environment-friendly antifouling materials” (www.byefouling-eu.com) under Grant Agreement no. 612717.

[1] D. M. Yebra, S. Kiil, K. Dam-Johansen, *Prog. Org. Coat.* **2004**, 50, 75–104.
[2] I. Omae, *Appl. Organometal. Chem.* **2003**, 17, 81-105.
[3] M.F. De Volder, S. H. Tawfick, R. H. Baughman, A. J. Hart, Science, **2013**, 339, 535-359.

Oral 12B

An evaluation method of antifouling efficacy in the laboratory using *Mytilus galloprovincialis* with flow-through systems

Ryuji KOJIMA *[1], Seiji KOBAYASHI [2], Cyril Glenn Perez SATUITO [3], Ichiro KATSUYAMA [2], Hirotomo ANDO [1], Yasuyuki SEKI [4], and Tetsuya SENDA [1]

[1] National Maritime Research Institute, Mitaka, Tokyo, Japan
[2] Japan NUS Co., Ltd, Shinjuku, Tokyo, Japan
[3] Nagasaki University, Nagasaki, Japan
[4] Chugoku Marine Paints, Ltd, Otake, Hiroshima, Japan

** kojima@nmri.go.jp*

A test method for evaluating the efficacy of antifouling (AF) paints by released biocide was established for reproducible and effective laboratory bioassay using *M. galloprovincialis* with flow-through systems. In this method, six different formulations of AF paints were designed with a graded AF character by varying content of cuprous oxide (Cu_2O), which is the most commonly used AF substances, from 0 to 40 wt. %.
A dynamic aging of test plates was conducted by the apparatus that held test plates on a 14 polygon section cylinder drum inside a water tank. During the aging process, test plates were rotated by a motor at a plate surface speed of 10 knots for 45 days under controlled condition. After dynamic aging, a behavioral test was conducted using five mussels pasted onto one coating surface of the test plate for each formulation of the paints. The results with high reproducibility were obtained by normalizing the number of formation of byssus threads with control groups. The paint systems varied cuprous oxide (Cu_2O) content showed an inverse correlation between Cu_2O contents of the paints and the byssus threads production of mussels.
In order to validate the laboratory experiment, field experiments (raft trial test) were conducted in August, October, December in 2013, and May in 2014 at two experimental sites located in the inland sea of Japan. The results showed that fouling on the plates generally exhibited a similar tendency regardless of the immersion site. Moreover, the degree of fouling on the plates decreased with increasing Cu_2O content of the paints used. These field experiments showed a good agreement with the case of laboratory bioassay.

In conclusion, the highly senstive laboratory bioassay used mussels which was examined in this study would be applicable as one of the method for universally evaluating the efficacy of AF paints.

Oral 13B

Laboratory disc rotors for measuring drag and observing the release of attached organisms from fouling release coatings

Simon DENNINGTON*[,1], Jennifer LONGYEAR[2], Paul STOODLEY[1,3] and Keith STOKES[1,4]

[1] University of Southampton, Southampton SO17 1BJ, UK.
[2] International Paint Ltd, Gateshead NE10 0JY, UK.
[3] The Ohio State University, Ohio 43210, USA.
[4] Defence Science and Technology Laboratory (Dstl), Salisbury SJ4 0JQ, UK.

** s.p.dennington@soton.ac.uk*

Disc rotor rigs are an established means of measuring the hydrodynamic drag experienced by rough or fouled marine hull coating surfaces [1, 2]. We have published [3] details of a prototype bench-top method using a sensitive analytical rheometer to measure the torque on 25 mm diameter plastic discs spinning in seawater. The test geometry has been refined, including the use of thinner and larger diameter (4 cm) discs to increase the sensitivity, and gives highly reproducible results. Although the torque (τ) developed at the maximum rotational velocity (300 $rad\cdot s^{-1}$, 2865 rpm) is low (< 5 mN·m even for fouled discs), the method is sufficiently sensitive to distinguish between the amounts of microfouling formed on duplicate sets of plastic test discs immersed at 2 week intervals over an 8 week period in estuarine waters. The coefficient of momentum (C_m) of rotating discs bearing various sandpaper grits was correlated with the surface roughness measured by optical profilometry. Larger discs (28 cm diameter) coated with fouling release coatings (FRC) were also immersed at the same exposure site for up to 4 years, followed by testing using a conventional disc rotor rig. The τ developed by the fouled discs rotated in seawater was continuously recorded at increasing rpm, and the drop in τ caused by organisms detaching from the foul release coatings was apparent. The discs were removed at 100 rpm intervals and photographed. At maximum rpm (1400) the peripheral speed of these discs is 40 knots, thus the test covers a full range of operating speeds of interest to most commercial vessels. The speed needed to release various fouling organisms could be estimated from the rpm and the radial position. Calcareous tubeworms (*Pomatoceros*) were the most resistant to removal and some specimens required a water velocity of ≥ 20 knots for release. The extent of tubeworm removal was increased by prolonging the time that the discs were held at maximum speed. Similarity law scaling [2] on data from the 4 cm and 28 cm discs coated with sandpaper of varying grits will be used to calibrate the two methods to each other.

Fig. 1: Fouled FRC-coated disc (*left*); rotated at 700 rpm (*middle*); held at 1400 rpm for 15 mins (*right*)

[1] P.S. Granville, *J. Fluids Eng.* **1982**, 104, 373-377.
[2] M.P. Schultz, J.M. Walker, C.N. Steppe, K.A. Flack, *Biofouling* **2015**, **31**:9-10, 759-773.
[3] S.P. Dennington, P. Mekkhunthod, M. Rides, D. Gibbs, M. Salta, V. Stoodley, J.A. Wharton, P. Stoodley, *Surf. Topog.: Metrol. Prop.,* **2015**, 3, 034004.

Oral 14B

Development of experimental hydrodynamic facilities to evaluate the "long-term" performance of marine coatings

Irma YEGINBAYEVA[1*], Mehmet ATLAR[1], Barry KIDD[2]

[1] *School of Marine Science and Technology, Newcastle University, UK*
[2] *International Paint Ltd, Gateshead, UK*

* *i.yeginbayeva@ncl.ac.uk*

Under the current challenging market conditions there is an obvious need for ship owners to maintain a high level of vessel operational efficiency. Without an effective fouling control coating, the accumulation of biofouling on ships hulls can increase the frictional resistance, fuel consumption, greenhouse gas emissions while significantly reduce vessel operational efficiency [1], [2]. The challenge for marine coatings suppliers is to provide commercially viable fouling control products that maintain low frictional resistance throughout the full in-service period from initial application to next recoat. While, the Emerson Cavitation Tunnel has a long history of supporting the coating industry [3], [4], it is recognised that a new generation of experimental facilities are required. Within this context, new experimental hydrodynamic test facilities have been developed that replicate the turbulent flow characteristics of the surface of a ship hull in service. These state of the art experimental facilities include a multipurpose flume [5], a laboratory-based dynamic slime farm and a strut system deployed on a research vessel that allows the collection of in-service dynamically grown biofilms [6], [7]. The multipurpose flume enables both the long term dynamic exposure of fouling control coatings and the measurement of their frictional resistance via boundary layer and pressure drop measurements. Collectively, the facilities allow the frictional resistance associated with changes in physical micro and macro roughness and the accumulation of biofouling over time to be accurately quantified.

The presentation will provide an overview of the new experimental test facilities as well as provisional results that have been generated for a series of foul release and biocidal fouling control coatings. The results will be interpreted in relation to the impact substrate preparation and coating choice on ship powering requirements and operational efficiency.

[1] IMO*, International Convention on the Control of Harmful Anti-Fouling Systems on Ships*. **2001**.

[2] IMO, *Prevention of Air Pollution from from Ships: Second IMO GHG Study* **2009***.* Marine Environment Protection, 9-April, 2009. 59 session.

[3] Unal, U.O., Unal, B., Atlar, M., *Experiments in Fluids* **2012***,* 52(6), 1431-1448.

[4] Atlar, M., Ünal, B., Ünal, U. O., Politis, G., Martinelli, E., Galli, G., Davies, C. & Williams, D. *Biofouling* **2013***,* 29, 39-52*.*

[5] Politis, G., Atlar, M. and Kidd, B. (**2013**)*. "A multi-purpose flume for the evaluation of hull coatings", 3rd International conference on advanced model measurement technology for the maritime industry (AMT'13), Gdansk, Poland.*

[6] Yeginbayeva, I., Atlar, M., Serkan, T. (**2015**)*, "Biofilm (slime) growth farm design". 4th International conference on advanced model measurement technology for the maritime industry (AMT'15), Istanbul, Turkey.*

[7] Atlar, M., Bashir, M., Turkmen, S., Yeginbayeva, I., Carchen, A., Politis, G. (**2015**)*. "Design, manufacture and operation of a strut system deployed on a research catamaran to collect samples of dynamically grown biofilms in-service". 4th International conference on advanced model measurement technology for the maritime industry (AMT'15), Istanbul, Turkey.*

TUESDAY June 21, 2016

Plenary- 2 Ambiguous surfaces: antifouling and fouling release coatings based on self-assembly

Brandon WENNING, David CALABRESE and Christopher K. OBER*[1]

[1] *Cornell University, Ithaca, NY, USA.*

* *cko3@cornell.edu*

Functionalized block copolymers allow for systematic control of surface chemistry and structure in environmentally benign antifouling coatings. Block copolymer structure can be used to control surface chemistry and morphology, mechanical properties, as well as temporal response to environmental conditions [1]. Dynamic and chemically ambiguous surfaces which resist marine fouling are made by incorporating polar, non-polar, and chemically active components into a block copolymer design. Block copolymers produced using anionic polymerization can be modified via efficient chemistries such as thiol-ene “click” chemistry to create architecturally diverse materials with a wide range of properties. As an example, sequence controlled peptide chemistry has been utilized to precisely control chemical structure [2]. These surfaces limit settlement behavior of a diverse range of marine organisms by employing protein-resistant components such as poly(ethylene glycol) (PEG) to deter settlement, low surface-energy materials including siloxanes and fluoro-oligomers to reduce adhesion strength [3], and targeted structures such as antioxidants to inhibit both settlement and biological adhesive curing processes by marine organisms. Surface chemical composition and structure has been investigated *ex situ* using X-ray spectroscopy techniques including X-ray photoelectron spectroscopy (XPS) and near-edge X-ray fine structure (NEXAFS) spectroscopy. Additionally, surface chemical rearrangement can be observed in real time using in situ time-resolved bubble contact angle measurements. Coatings were evaluated as antifouling coatings by studies of settlement and adhesion of marine algae, diatoms, and barnacles, which each have significantly different mechanisms of attachment. Correlation of this biological response to surface properties and copolymer design allows for rational design of antifouling coatings based on chemical structure.

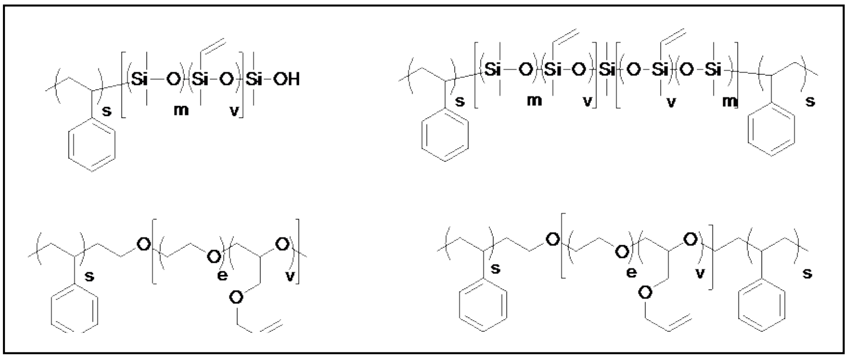


Fig. 1: AB and ABA block copolymers used as backbone materials in the formation of antifouling coatings modified using thiol-ene chemistry.

[1] S. Krishnan, C. J. Weinman, C K. Ober, *J. Mater. Chem.*, **2008**, 18(29), 3405-3413
[2] D. R. Calabrese, B. Wenning, J. A. Finlay, M. E. Callow, J. A. Callow, D. Fischer, C. K. Ober, *Polymers for Advanced Technologies*, **2015**, 26(7), 829-836.
[3] H. S. Sundaram, Y. Cho, M. D. Dimitriou, C. J. Weinman, J. A. Finlay, G. Clay, M. E. Callow, J. A. Callow, E. J. Kramer, C. K. Ober, *Biofouling*, **2011**, 27(7), 6, 589-601.

Session 12 – Biocidal antifouling technologies - Auditorium Vauban

Keynote 3A

Inhibition of marine biofouling by self-renewal surface consisting of biodegradable polymers

Chunfeng MA, Wentao XU, Liguo XU, Guangzhao ZHANG*

Faculty of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, P. R. China

** msgzzhang@scut.edu.cn*

Marine anti-biofouling is important for marine industry and activities. To develop environment-friendly anti-biofouling systems is a challenge. We have prepared biodegradable polymers for marine anti-biofouling, whose degradation leads to a self-renewal surface. We have examined the enzymatic and hydrolytic degradation of the polymers in seawater and the anti-biofouling by marine field tests. Our studies demonstrate that the degradation rate and mechanical properties can be controlled by the composition and structure of the polymers. The degradable polymers show good antifouling ability due to its self-renewing property. Moreover, the polymers can serve as a carrier and release system of organic antifoulant. Such systems are promising in marine anti-biofouling.

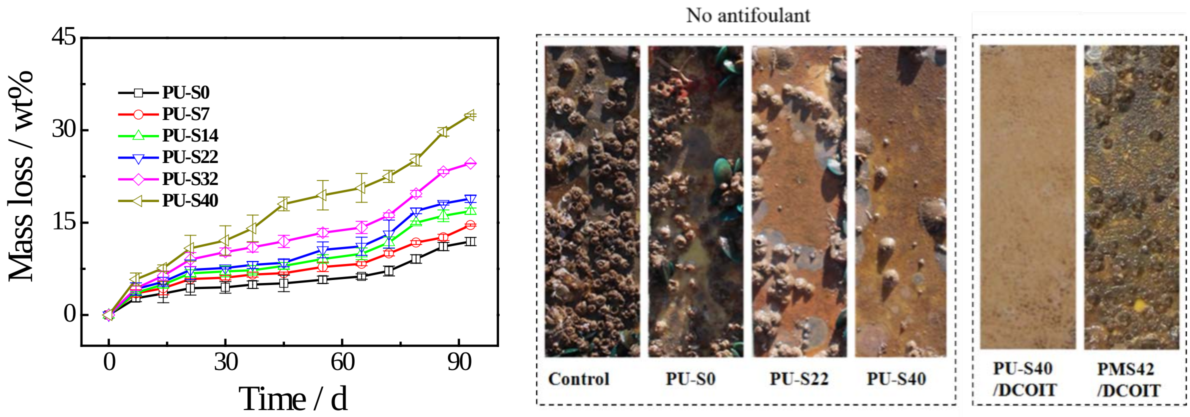


Fig. 1: Mass loss of the polyurethanes with different PTIPSA contents in artificial seawater and panels coated with the polymer and polymer carrying 10 wt % DCOIT after immersion in marine for 3 months

[1] Hellio, C.; Yebra, D. M. Advances in Marine Antifouling Coatings and Technologies. Woodshead Publishing; Cambridge, UK: **2009**.

[2] Ma, C. F.; Xu, L. G.; Xu, W. T.; Zhang, G. Z. Degradable Polyurethane for marine anti-biofouling. *J. Mater. Chem. B* **2013**, *1*, 3099-3106.

[3] Xu, W. T.; Ma, C. F.; Ma, J. L.; Gan, T. S.; Zhang, G. Z. Marine Biofouling Resistance of Polyurethane with Biodegradation and Hydrolyzation, *ACS Appl. Mater. Interfaces* **2014**, *6*, 4017-4024.

[4] Yao, J. H.; Chen, S. S.; Ma, C. F.; Zhang, G. Z. Marine anti-biofouling system with poly(ε-caprolactone)/clay composite as carrier of organic antifoulant. *J. Mater. Chem. B*, **2014**, *2*, 5100-5106.

Oral 15A

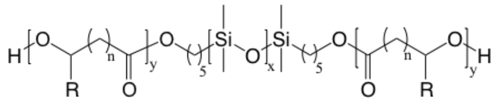
Development of new hybrid antifouling coatings ecofriendly

Fabrice AZEMAR[1]*, Fabienne FAŸ[1], Karine RÉHEL[1], Isabelle LINOSSIER[1]

[1] *Laboratoire de Biotechnologie et Chimie Marines (LBCM), Lorient, France.*

* *azemar.fabrice@gmail.com*

Antifouling paints are the main system used against the development of organisms (bacteria, micro and macroalgae, mussels, barnacles, etc.) on immerged surface and the most studied. Since the 19th century and the use of first antifouling paints, lots of researches have been done to increase efficiency against the biofouling. However, these improvements have been done to the detriment of the environment. Nowadays two strategies were used: the biocide release system based on the incorporation of natural or synthetic biocides less harmful for the environment [1] and the fouling release strategy based on paints with physico-chemical surface properties to limit durable colonization by organisms [2]. But, the development of new biocides and new paints have greatly increased the paints price without increase their efficiency. Moreover, both kinds of paints have shown other disadvantages. In the aim to develop a new kind of antifouling paint, the two strategies will be combined to design an hybrid binder. To do that, two polymers families seem appropriate. Polyesters and silicones have been already used separately as binder for antifouling paints and environmental applications.



$n = 0$ to 5 and $R = H$ or CH_3

Fig. 1: Structure of triblock copolymers used as binder.

The objectives of this study are to measure the efficiency of an hybrid system for antifouling paint and to observe the influence of the physico-chemical properties of the binder on the antifouling activity. The use of a block copolymer (Fig. 1) should allow mixing the properties of erosion and hydrophobicity to obtain a more efficient paint with a reduced environmental impact [3]. For this purpose, molecular weight of polyester blocks and different ester monomers were studied. Several parameters were followed during the immersion of binders and paints like the water absorption of the coating, the degradation of the binder and the surface properties. Moreover, paints containing triblock copolymer were immersed in seawater in Lorient harbour to evaluate their antifouling activities. These two studies have allowed the understanding of the influence of the binder properties in the resulting antifouling coating efficiency. The hybrid paints have shown efficiency close to a commercial paint during their immersion in situ in spite of inadequate static conditions of test (Fig. 2) [4].

a) b)

Fig. 2: MEB of hybrid paint after 24 weeks in seawater. b) Pictures of coatings without paint, with a commercial paint and with the hybrid paint after 18 months in seawater

[1] C. Bressy, A. Margaillan, F. Faÿ, I. Linossier, K. Réhel, Advances in Marine Antifouling Coatings and Technologies **2009**, Woodshead Publishing, Cambridge, p. 445.
[2] C.M. Magin, S.P. Cooper, A.B. Brennan, *Mater.Today* **2010**, 13, 36-44.
[3] F. Azemar, F. Faÿ, K. Réhel, I. Linossier, *J. Appl. Polym. Sci.* **2014**, 131, 40431.
[4] F. Azemar, F. Faÿ, K. Réhel, I. Linossier, *Prog. Org. Coat.* **2015**, 87, 10-19.

Oral 16A

Degradable Silyl Acrylate Copolymer: a novel design for self-polishing antifouling coatings

Chunfeng MA*, Guangzhao ZHANG

Faculty of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, P. R. China

* *msmcf@scut.edu.cn*

Silyl acrylate copolymers are promising materials for marine anti-biofouling. However, their structures need optimizing to improve their erosion and mechanical properties. We have prepared copolymer of 2-methylene-1,3-dioxepane (MDO), tributylsilyl methacrylate (TBSM) and methyl methacrylate (MMA) via radical ring-opening copolymerization. Such polymer has a degradable backbone and hydrolysable side chains. Our study demonstrates that as the ester units in the backbone increase, the degradation rate increases but the swelling decreases in seawater. Moreover, such polymer can serve as a carrier and controlled release system for organic antifoulants. Marine field tests show that the system consisting of the copolymer and organic antifoulant can effectively inhibit the colonization and growth of marine organisms when MDO content is above 20 wt %.

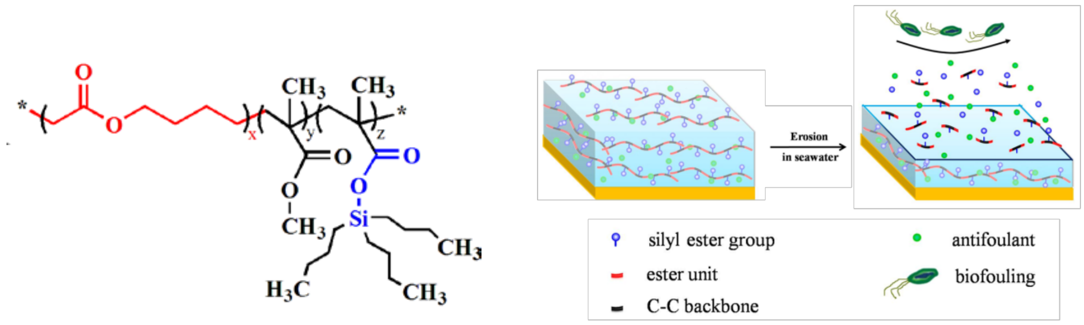


Fig. 1: The structure of degradable silyl acrylate copolymer and its antifouling mechanism

Ma, C. F.; Xu, L. G.; Xu, W. T.; Zhang, G. Z. *J. Mater. Chem. B* **2013**, *1*, 3099-3106.
Xu, W. T.; Ma, C. F.; Ma, J. L.; Gan, T. S.; Zhang, G. Z., *ACS Appl. Mater. Interfaces* **2014**, *6*, 4017-4024.
Yao, J. H.; Chen, S. S.; Ma, C. F.; Zhang, G. Z. *J. Mater. Chem. B*, **2014**, *2*, 5100-5106.
Ma, J. L. ; Ma, C. F. ; Yang, Y. ; Zhang, G. Z. *Ind. Eng. Chem. Res.*, **2014**, *53*, 12753–12759
Zhou, X.; Xie, Q. Y.; Ma, C. F.; Chen, Z. J.; Zhang, G. Z. *Ind. Eng. Chem. Res.*, **2015**, *54*, 9559–9565.

Oral 17A

Antifouling coatings containing modified nanoparticles with dual antimicrobial effect

Marios MICHAILIDIS, Dmitry SHCHUKIN*

University of Liverpool, Liverpool, United Kingdom

* *D.Shchukin@liverpool.ac.uk*

Antifouling coatings containing mesoporous silica nanoparticles (MSNs) modified with quaternary ammonium salts (QAS) and loaded with biocide were investigated as low-toxic cost-efficient environment-friendly antifouling coatings for marine applications. For this purpose, spherical MSNs with average size of 500 nm were synthesized in room temperature [1]. The surface of the nanoparticles was modified with two different types of QAS which already indexed as biocides [2]. The QAS provide to the coatings the necessary hydrophobicity and antifouling properties, biocidal activity against marine microorganisms and resistance to microfouling in seawater immersion [3]. The advantage of the QAS-modified MSN in comparison with the classic biocide-release coatings is in their attached nature to the filler particles, which allows the biocide effect to be appeared without the release of the biocide material from the coating. Afterwards, the QAS-modified MSN were loaded with another liquid biocide for dual antimicrobial effect. The synthesized materials were incorporated into coating formulations and tested against gram positive and gram negative bacteria and marine microorganisms.

The successful surface modification of the nanoparticles was confirmed by FTIR, Thermogravimetric Analysis (TGA) curves, elemental analysis and Z-potential measurements. The homogenous dispersion of the modified MSNs inside the coating formulations was confirmed by cross section SEM images. The coating formulations containing the modified MSNs presented significant antibacterial performance in comparison with the coatings without the modified MSNs inside. At the antibacterial tests against *S. Aureus* and *E. Coli* the reduction was 99.9%. Furthermore, the synthesized coatings presented 100% inhibition attachment of mussels and 91% of the Artemia salina were dead after 24h of immersion. Finally, on the barnacles assays there was 100% inhibition attachment of cyprids after 72 h of immersion where approximately 70% of the cyprids were alive and 30% dead.

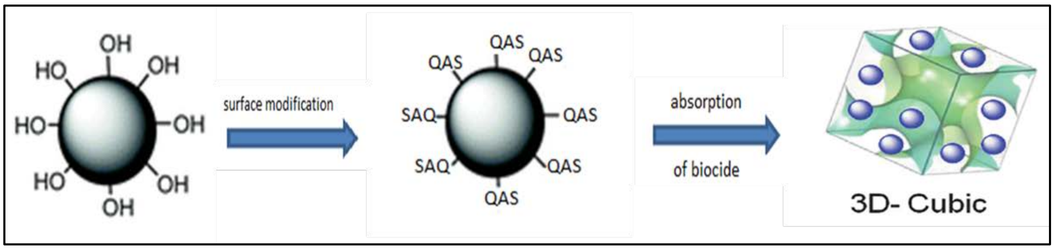


Fig.1: Schematic illustration of the experimental process for the synthesis of the modified MSNs.

[1] K. Schumacher, M. Grün, K. . Unger, *Microporous Mesoporous Mater.* **1999**, 27, 201.
[2] P. Majumdar, E. Lee, N. Patel, K. Ward, S. J. Stafslien, J. Daniels, B. J. Chisholm, P. Boudjouk, M. E. Callow, J. a Callow, S. E. M. Thompson, ***Biofouling*** **2008**, 24, 185.
[3] J. Song, H. Kong, J. Jang, *Colloids Surfaces B Biointerfaces* **2011,** 82, 651.

Oral 18A

Chitosan-ZnO nanocomposite coatings for the prevention of marine biofouling

Laila AL-NAAMANI[1,2]*, Sergey DOBRETSOV[1], Grant BURGESS[2], Joydeep DUTTA[3]

[1] *Department of Marine Science and Fisheries, Sultan Qaboos University, Oman*
[2] *School of Marine Science and Technology, Newcastle University, UK*
[3] *Functional Materials Division, KTH Royal Institute of Technology, Stockholm, Sweden*

* *lnaamani@hotmail.com*

Marine biofouling is a worldwide problem affecting maritime industries. The global concern about high toxicity of antifouling paints has highlighted the need to develop less toxic antifouling coatings. Chitosan is a promising material possessing antimicrobial, antifungal and antialgal properties could be obtained from partial deacetylation of crustaceans waste. Chitosan has high ability to form metal complexes with zinc which increase its functional property and particularly antimicrobial activity. In the present study, nanocomposite chitosan-ZnO nanoparticle hybrid coatings were developed. Coatings properties were characterized using water contact angle, SEM, and ATR-FTIR spectroscopy. Antibacterial assays showed that nanocomposite coatings inhibited growth of pathogens *Salmonella* sp., *Escherichia coli* and *Staphylococcus aureus* in laboratory experiments. Chitosan-ZnO nanoparticle coatings had an anti-diatom activity against *Navicula* sp. Further antifouling properties of the coatings were investigated in a mesocosm study using tanks containing natural sea water under controlled laboratory conditions. Every week for the duration of 4 weeks, biofilms were scrapped off the coatings and analyzed by flow cytometry to estimate total bacterial densities. Chitosan and ZnO nanoparticle coatings resulted in an inhibition of bacterial and diatom growth in comparison with chitosan coatings and controls (uncoated samples). Most of bacteria attached to the coatings were dead which was revealed by epifluorescence microscopy with life and dead staining. This study demonstrated the high antifouling potential of chitosan-ZnO nanocomposite coatings, which can be used for the prevention of biofouling in the future.

Oral 19A

The efficacy of grooming on antifouling coatings

Emily RALSTON *[1] and Geoffrey SWAIN[1]

[1]Center for Corrosion and Biofouling Control, Florida Institute of Technology
150 W University Blvd, Melbourne, FL 32901

* eralston@fit.edu

The majority of ships are coated with antifouling paints. These coatings can fail to completely protect from fouling due to mismatches between paint type and duty cycle, the presence of biocide tolerant fouling organisms, improperly applied, old or damaged paint, etc.
Grooming antifouling coatings can provide a solution. Results will be presented to illustrate how grooming maintains antifouling coatings in a clean condition.

Acknowledgements: This research was made possible with generous support from the Office of Naval Research and Naval Surface Warfare Center – Carderock.

Oral 20A

Anti-fouling paint based on gel encapsulated biocide technology for large vessels and ships

Eva WALLSTRÖM*

EnCoat ApS, Lersø Parkallé 38, DK-2100 Copenhagen, Denmark

** ewa@encoat.dk*

A silica aerogel encapsulated biocide to control the biocide leaching in an anti-fouling yacht paint without cuprous oxide or zinc oxide have been shown to have approximately the same technical properties as a commercial solvent-based anti-fouling paint. The test paint has during a summer season proven similar anti-fouling efficacy on rafts compared to a commercial product and to show the same effectivity against fouling on yachts in sea water.
This technology can be adjusted to larger vessels and ships where water absorption and the polishing rate is acceptable for a durability according to state of the art. Anti-fouling paints for larger vessels or ships contain large amounts of cuprous oxide. A reduction in cuprous oxide, which the encapsulation technology allows, will reduce the raw material cost of an anti-fouling paint as cuprous oxide currently is one of the most expensive raw materials in an anti-fouling paint.
The gel particles are hydrolysed/worn down throughout the polishing process thus giving a constant effective release of biocide in the coated surface layer. When a gel particle is opened by wear the biocide is already effective on the coating surface due to gel swelling when it is exposed to water. A constant release and wear contributes to keeping the hull clean and avoiding a rise in the fuel consumption.
Experiences from raft tests from different locations (in and outside Denmark) will be presented. Adjustments of water absorption and the biocide release will be discussed.

The aim is to show that it is possible, to use technical experiences gained within the area of yachts together with laboratory tests and initial raft tests with prototype products for large ships to achieve anti-fouling properties that are satisfactory for larger ships and at the same time to reduce the amount of cuprous oxide in the paint formulation.

Keywords: Gel encapsulation, Biocide, Silica gel, Anti-fouling

Session 2 - Microbiologically induced corrosion-Biocorrosion - Room Colbert

Keynote 3B

Effect of nutrient pollution on long-term microbiologically influenced corrosion of steel and cast iron infrastructure

Robert E Melchers

Centre for Infrastructure Performance and Reliability, The University of Newcastle, Newcastle, Australia.

**rob.melchers@newcastle.edu.au*

Microbiologically influenced corrosion (MIC) has long been suspected of involvement in marine corrosion of steels. It also has long been implicated in the corrosion of cast irons particularly when buried in wet soils. Largely this was based on observations of the presence of certain, easy-to-detect bacterial populations such as the sulphate reducing bacteria. Although much research effort is on-going for identification of microbial species that may be associated with corrosion, detailed understanding of 'who does what' is still not well-developed. An alternative approach used in recent research has focused on the availability of nutrients necessary for microbial metabolism, on the basis that both the possibility and the rate of metabolism are the links to corrosion and its severity. Recent marine corrosion field studies for steels have shown that corrosion loss can be correlated with the concentration of nitrates in the water immediately adjacent to the steel. This follows from nitrates being the critical nutrient in seawater exposures. In that environment organic carbon, sulphates etc. are readily available and the micro-nutrient Fe is supplied by the corrosion process.

The recent research outcomes for MIC of steels are reviewed, with special attention given to practical implications. This includes the phenomenon known as 'accelerated low water corrosion' (ALWC), critical for steel sheet and other piling in many harbours around the world. Attention then moves to the very severe corrosion observed for mooring chains for FPSOs (Floating Production Storage and Offloading) vessels increasingly being used in the offshore oil and gas industry.

Some results are given also for a recent study of the corrosion of cast iron bridge piers some 100 years old, all exposed close to the Pacific Ocean. These showed almost no corrosion in the atmosphere, and significant corrosion where the estuary waters were subjected to fertilizer contamination from upstream agricultural practices, including the presence of AWLC.

Finally, some comments are made about the external corrosion of cast iron water mains used in many older cities as the main mode of delivery of potable water. Their maintenance is costing the water utilities (and therefore societies) millions of dollars annually, yet the process of corrosion involved, and where corrosion will be most severe and why, currently are only poorly understood. To deal with the known involvement of MIC, the understanding gained from the importance of nutrients for immersion and tidal MIC is being transferred to in-ground MIC. However, the available data shows that MIC usually is not the main factor in the severe corrosion sometimes observed on pipe exhumation. This is discussed as part of on-going research.

Oral 15B

Formation mechanisms for iron-rich accretions from World War II shipwrecks in the Gulf of Mexico

Brenda J. LITTLE*,1, Jason S. LEE[1], Brandon R. BRIGGS[2] and Tammie L. GERKE[3]

[1] *Naval Research Laboratory. Stennis Space Center, MS 39525, United States*
[2]*University of Alaska-Anchorage, Anchorage, Alaska 99508, United States*
[3] *Miami University, Middletown, OH 45042, United States*

* *brenda.little@nrlssc.navy.mil*

Metal hulls, railings and machinery, especially substrata containing low alloy steels, on shipwrecks in oxygenated seawaters are covered with iron-rich accretions (FeRA). The Fe-rich encrustations have been referred to rusticles, based on shape and color. In several studies there has been an assumption that the iron in FeRA is derived from corrosion reactions at the wreck site. Consequently, the growth rate of the accumulations and the iron concentration within the accumulations have been used to predict degradation rates for the wrecks. In addition, the spatial relationship between bacteria and FeRA has been interpreted as one of cause and effect, i.e., bacteria are causing the corrosion, i.e., microbiologically influenced corrosion (MIC).

The physicochemical and microbiological properties of FeRA recovered from three WW II shipwrecks in the Gulf of mexico (GOM) were examined using a combination of physiochemical characterization techniques including synchrotron-based *in-situ* micro X-ray diffraction (μ-XRD), scanning electron microscopy, transmission electron microscopy, inductively coupled plasma – optical emission spectroscopy and DNA sequence analysis. Data from those investigations were used to evaluate claims of MIC.

GOM FeRA were goethite (α-FeOOH) with minor to trace amounts of lepidocrocite (γ-FeOOH) and concentrations of sulfur (4688 to 63124 parts per million). The presence of α-FeOOH and sulfur, unassociated with a sulfide mineral, is consistent with the oxidation of an unstable iron-deficient sulfide. Sulfate reducing bacteria, in addition to iron oxidizing and reducing bacteria and heterotrophic bacteria were identified in GOM FeRA by DNA sequencing. These groups of bacteria are fequently cited as causing MIC of low alloys steels in specific environments. In marine environments, sulfate is typically present > 2.0 grams/L, while nutrients and dissolved iron increase with depth to approximately 1000 m. Deep sea marine environments can support both microbial iron oxidation/reduction and sulfate reduction without degradation of low carbon steels. In addition, GOM FeRA lack the mineralogical differentiation typical of iron corrosion products. FeRA formation is best explained as biological and abiological accumulations of environmental iron and other cations. Data from archived GOM FeRA cannot be used to support claims of shipwreck corrosion.

Oral 16B

S.loihica PV-4: model organism to study biocorrosion and antifouling coating materials

Monica EPIFANIO[1], Alan BARRET[1], Fiona REGAN[1,2], Aoife MORRIN [1,2]

[1] *School of Chemical Sciences, Dublin City University, Dublin 9. Ireland.*
[2] *DCU Water Institue, Dublin City University, Glasnevin, Dublin 9. Ireland.*

* *Monica.epifanio@dcu.ie*

Many researchers are concerned about the phenomenon of microbially influenced corrosion (MIC) of iron and its alloys, that are the most represented materials which are in contact with water. The aim of this work is to gain a greater understanding of the mechanisms of corrosion impacting deployed structures. Accurate monitoring of MIC rates and its prevention is a must when viewed in terms of the maintenance and repair costs associated with corrosion and material failure. In this study, the corrosion behaviour of iron alloys (such as SS304L and SS316L) where undertaken in presence bacteria biofilms and different TEOS/DMDEOS silane mixtures fabricated using a sol-gel process where used to coat the diverse iron alloys surfaces. The characterization of the TEOS/DMDEOS silane mixtures coatings was performed by water contact angle (WCA) and scanning electron microscopy (SEM) while the biofilm developmental characterization was performed by electrochemical techniques and GC-MS.

Oral 17B

Electrochemical study of epoxy coated mild steel in different aqueous environment

Umadevi VADAMADURAI RATHINAVELU*, J.M.C. MOL, Y. GONZALEZ-GARCIA.

Delft University of Technology, Department of Materials Science and Engineering, Mekelweg 2, 2628 CD Delft, Netherlands

* *U.VadamaduraiRathinavelu@tudelft.nl*

The present study investigates microbiologically influenced corrosion (MIC) of marine coating systems on mild steel in three different aqueous environments: natural seawater, artificial seawater and 3.5 % sodium chloride (NaCl) electrolyte. Three types of epoxy-based coatings, in both intact and scribed condition, were investigated using electrochemical and microscopic techniques. Electrochemical impedance spectroscopy (EIS) was used to study the evolution of the capacitive and resistive behaviour of the intact and scribed coating systems with immersion time in various aqueous environments. Furthermore, the delamination behaviour of the scribed-coating systems after exposure was studied by measuring the surface potential of the coating/metal interface using Scanning Kelvin Probe (SKP). It was found that the reduction of impedance of the coatings that were exposed to natural seawater was significantly higher with time compared to that of those exposed to the artificial seawater and NaCl electrolytes. This is attributed to the formation of a marine biofilm on the surface of the coatings and possible increase in ingress of moisture due to the biofilm-coating interaction upon immersion in natural seawater. The biofilm population and morphology on the different coating surfaces were further analysed using scanning electron microscopy (SEM) and epifluorescence microscopy. Conventional corrosion research of marine coatings is performed by immersion in electrolytes that simulate the natural environment such as artificial seawater (containing only the soluble salts that are found in seawater) or NaCl solution. This study demonstrates that chloride-containing or artificial seawater environment does not fully represent the marine ecosystem exposure where microorganism are present, influencing the corrosion protective properties of the coating.

Oral 18B

Potential ennoblement of stainless steel in seawater: Influence of dissolved oxygen content and pressure

Charles LEBALLEUR[1], Dominique THIERRY[1], and Nicolas LARCHE*[1]

[1] Institut de la corrosion, Brest, France.

**Nicolas.Larche@institut-corrosion.fr.*

Biofilm formation in natural seawater is known to be one of the main parameter affecting the corrosion resistance of stainless steel. This results in the shift of the open circuit potential (OCP) of stainless steel to the noble direction (ennoblement), and to an increase in the efficiency of oxygen reduction reactions, increasing both the risk of initiation and propagation of localized corrosion.
In this study, the OCP and biofilm formation on stainless steel has been investigated as a function of the dissolved oxygen content (DO) and pressure in natural seawater. It exists a critical DO below which no ennoblement is measured. SEM observations were performed on UNS32750 coupons both at saturated DO and below 20 ppb in natural seawater continuously renewed. Bacteria was still present at low DO but a higher diversity of bacteria was observed at saturated DO. The activity of the bacteria (e. g. production of Extra-cellular Polymeric Substance) was also very different between the two conditions and these results may explain the differences in potential ennoblement (and consequent corrosion risk) between low and high DO conditions in seawater. However, more investigations are needed to better understand the nature of biofilms and their actual influence on the electrochemical behavior of passive films as well as their exact role in the potential ennoblement.
An autoclave has been adapted to allow continuous potential monitoring of stainless steel coupons in continuously renewed natural seawater. The results showed that at 180 bar (i.e. simulating the pressure at 1800 m depth in seawater) the potential ennoblement due to biofilm formation occurred in a similar way as at atmospheric pressure.

Oral 19B

SRB induce accelerated corrosion attack of high strength steel under - 0.85V vs SCE cathodic polarization potential

Fang GUAN[1], Jizhou DUAN*,[1], Xiaofan ZHAI[1], Baorong HOU[1]

[1] Institute of Oceanology, Chinese Academy of Sciences, Qingdao, China.
[2] University of Chinese Academy of Sciences, Beijing, China.

* *duanjz@qdio.ac.cn.*

The impact of cathodic protection on the *Desulfovibrio caledoniensis* metabolic activity and its influence on high-strength steel of EQ70 were studied by bacterial analyses, weight loss, polarization and electrochemical impedance measurements. It was shown that highest corrosion rate were found for EQ70 high-strength steel under $-0.85V_{SCE}$ cathodic protection (CP) potential than that without CP, $-0.95V_{SCE}$ and $-1.05V_{SCE}$ potentials. Application of cathodic protection also led to the transformation of corrosion products from green rusts (SO_4^{2-}) into green rusts (CO_3^{2-}) by surface advanced analysis techniques. This finding provided referential suggestions for proper cathodic protection potential choice of steel structures in presence of SRB.

Acknolegments: This work was funded by the National Key Basic Research Project (No. 2014CB643304).

Oral 20B

Local mooring chain corrosion- microbial analysis of *in-situ* samples

Nanni NOËL*[1], Merlina KRANENBURG[1], Mark BAKKER[1], Xialong ZHANG[1], Gabriele FERRARI[1], Job KLIJNSTRA[1] and Martijn HOOGELAND[2]

[1] Endures B.V., 1781 AT Den Helder, The Netherlands
[2]TNO, 2628 XE Delft, The Netherlands

* *nanni.noel@endures.nl*

Mooring chains are widely used to fix a floating production, storage and offloading (FPSO) system. Chain steel exposed to seawater is subjected to marine corrosion. The mean time of failure of most permanently installed FPSO mooring systems is 7.6 years, though design life is more than 20 years [1]. The LMCC project (Localized Mooring Chain Corrosion) has been set up by TNO/ ENDURES to investigate the causes of localized corrosion, ranging from electrochemical to microbial behavior in combination with the chain link surface conditions and environmental effects.
The presented data focus on the microbial study of this joint industry project. Biogeochemical data relevant for possible MIC processes in the mooring chain environment were analyzed next to in-situ samples taken from seawater, biofilms and corrosion products from the mooring chain and the corresponding environment. Different techniques, growth-based as well as molecular tools, were used to identify and quantify corrosion relevant microorganisms. Next to the most probable number (MPN) technique, quantitative polymerase chain reaction (Q-PCR) and next generation sequencing (NGS) were chosen for such approach.
Corrosion related microorganisms were frequently found in samples coming from the mooring chain environment. There is clear evidence of MIC processes occurring. Aerobic organisms in the outer biofilm layer, deliver necessary substrates and favor the environmental conditions for activity of anaerobic microorganisms. DNA- NGS data indicated that sulfur- oxidizing bacteria (SOB) and iron- reducing bacteria (IRB) were found in seawater, solid biofilm and swab biofilm sample, whereas sulfate- reducing bacteria (SRB) have only been found in the swab biofilm sample taken directly from the mooring chain surface. This indicates favored conditions for anaerobic microorganisms directly on the surface of the mooring chain. RNA- NGS data showed next to other energetic metabolisms that a nitrogen, methanogen and sulfur metabolism is present. All 3 cycles are relevant for corrosion.

Acknowledgments: The work presented in this study has been funded within the LMCC (Localized Mooring Chain Corrosion) project.

[1] A. Hall, and A. Trower, OTC Brazil, **2011**, OTC-22615-MS.

Session 8 – Macrofouling - Room Colbert

Keynote 4A

Progress in the study of adhesion by marine invertebrate larvae

Nick ALDRED*

School of Marine Science and Technology, Newcastle University, UK

* *nicholas.aldred@ncl.ac.uk*

The larval stages of sessile marine invertebrates are instrumental in the formation of fouling assemblages on immersed marine structures. Most fouling invertebrates have dispersal stages that are, to a greater or lesser degree, selective with regard to the surfaces to which they attach permanently. However, the mechanisms of surface selection and adhesion remain poorly understood for most species. Larvae present significant challenges to contemporary analytical approaches that have hindered progress to date. Foremost among these are the small scale and complexity of the adhesive materials/structures and the speed at which the adhesion processes occur. Recent advances in biomolecular technologies and the adoption of advanced imaging, spectroscopic and surface sensing techniques from the physical sciences have nevertheless provided new avenues for investigation. By adopting a broad, multidisciplinary approach, it seems increasingly likely that the fundamental principles of surface selection and adhesion in invertebrate larvae will be revealed.

This talk will cover two challenges in the field of study outlined above. First, how do we determine the influence of perceived adhesion strength on the decision by a larva to settle? Second, what are the bio-/physicochemical processes that occur at the adhesive interface and how well conserved are these phenomena between species or phyla?

For the first challenge, the temporary adhesion system of the barnacle cyprid will be used by way of example to illustrate progress towards the development of a system that can monitor and quantify the behaviour of larvae under different laboratory-controlled conditions, while simultaneously identifying surface specific behaviour and adhesive interactions. To address the second challenge, an example of the cyprid permanent adhesive system will be used to present a number of convergent, multidisciplinary routes towards an understanding of the process of adhesion on different experimental surfaces, and how this knowledge may inform the development of more effective fouling-resistant coatings.

Oral 21A

Stereoscopic tracking reveals responses of barnacle larvae to surface cues

Axel ROSENHAHN[1,2*], Stojan MALESCHLIJSKI[2], G. Hernan SENDRA[2], Stella BAUER[2], Michael GRUNZE[2], Bo LIEDBERG[3,4], Thomas EDERTH[4], Alessio Di FINO[5], Nicholas ALDRED[5], Anthony S. CLARE[5], Laura LEAL-TAIXE[6], Bodo ROSENHAHN[6]

[1] *Analytical Chemistry - Biointerfaces, Ruhr-University Bochum, 44801 Bochum, Germany*
[2] *Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany*
[3] *Nanjang Technological University, Singapore, Singapore*
[4] *Linköping University, Linköping, Sweden*
[5] *School of Marine Science and Technology, Newcastle University, Newcastle NE1 7RU, UK*
[6] *Leibniz University Hannover, Hannover, Germany*

* *axel.rosenhahn@rub.de*

A crucial step in surface colonization by marine biofouling organisms is surface exploration and settlement of the sessile stages (larvae, spores). For many species, attachment to surfaces is a highly selective process [1]. 3D stereoscopic tracking enables quantitative analysis of the pre-settlement behavior and thus to understand how larvae respond to chemical and physical surface cues [2]. We developed a transportable, submersible stereoscopic system which can be applied to record three dimensional video data and to extract swimming trajectories of multiple, label-free objects. The pre-settlement ritual can be classified into different motion patterns which vary in characteristic parameters, such as distance to the surface, velocity, or the curvature of the motion [3]. In general the larvae favor both, liquid-solid and liquid-air interfaces. The distribution within the water column and the fraction of larvae exploring the solid surface is determined by its chemistry. Using different self-assembled monolayers we found a positive correlation of the settlement probability with both, the fraction of larvae exploring the interface and their mean swimming velocity [4]. Thus, 3D tracking provides a predictor for settlement probability. A combination of stereoscopic tracking with imaging surface plasmon resonance allows to directly correlate deposition of temporary adhesive with the mechanosensing process [5]. It turned out that surfaces with high settlement probability and low swimming speeds tend to have a higher affinity to the temporary adhesive.

[1] N. Aldred, A.S. Clare, *Biofouling* **2008**, 24, 351–363
[2] S. Maleschlijski, G. H. Sendra, A. D. Fino, L. Leal-Taixé, I. Thome, A. Terfort, N. Aldred, M. Grunze, A. S. Clare, B. Rosenhahn and A. Rosenhahn, *Biointerphases* **2012**, 7, 50.
[3] S. Maleschlijski, S. Bauer, A. DiFino, H. Sendra, A.S. Clare, A. Rosenhahn, *Journal of the Royal Society Interface* **2015**, 12(102), 20141104
[4] S. Maleschlijski, S. Bauer, A. Di Fino, G.H. Sendra, A.S. Clare, A. Rosenhahn *Biofouling* **2014**, 30(9), 1055
[5] S. Maleshlijski, G.H. Sendra, N. Aldred, A.S. Clare, B. Liedberg, M. Grunze, T. Ederth, A. Rosenhahn *Surface Science* **2016**, 643, 172

Oral 22A

Developing a sensory architecture for response of larval barnacles *Amphibalanus amphitrite* to surface properties

Eric R. HOLM*[1], Caitlyn M. GATLEY[2], and Michael R. DETTY[2]

[1] *Naval Surface Warfare Center, Carderock Division, West Bethesda, MD, USA.*
[2] *Department of Chemistry, SUNY at Buffalo, Buffalo, NY, USA.*

* *eric.holm@navy.mil*

The attachment response of cypris larvae to materials with differing surface properties varies among and within species of barnacles. Previously we investigated whether variation in attachment in response to wettability, within a population of the barnacle *Amphibalanus amphitrite*, had a genetic basis, and found that 1) the proportion of larvae attaching to 4 surfaces varied significantly among maternal families, and 2) variation in the attachment response was correlated within surface types (hydrophilic vs. hydrophobic) but uncorrelated across surface types. These results suggested that response of barnacle cyprids to these surfaces was influenced by genetic or maternal effects, and that these effects differed between hydrophilic and hydrophobic surfaces.

We have expanded this initial analysis in an effort to develop a more detailed sensory architecture for the response of *Amphibalanus amphitrite* to surface properties. Cypris larvae from 30 maternal families were assayed for attachment in response to 6 surface treatments and a positive control (settlement factor). Surface treatments included glass and 5 xerogel coatings varying in their surface energy, charge, and other properties. Response to the positive control differed among maternal families, suggesting that genetic or maternal environmental influences on larval vigor, or timing of acquisition of competence, had the potential to affect patterns of attachment across surfaces. Identity of the maternal parent also affected attachment in response to all the surface treatments. Analysis of principal coordinates (PCO), based on mean values of attachment for each surface/maternal family, indicated that response to the glass surface was in part a function of larval vigor or competence, while response to the other surface treatments was not. Despite large differences among the xerogel coatings in a suite of surface properties, responses to these surfaces were all positively correlated, and variation in attachment could not be associated with any particular surface property. For these surfaces, variation in attachment among maternal families may instead be driven by genetic or maternal influences on larval physiological age, some unknown aspect of larval vigor not accounted for by the positive control treatment, or response to an unmeasured or unrecognized surface property.

Acknowledgements: This investigation was supported by funding from the Navy Undersea Research Program, Office of Naval Research.

Oral 23A

Colorful side of fouling: environmental benefit for coral reefs and beyond

Yehuda BENAYAHU[1]*, Camelia GOCHEV[1], Julia NOVAK[2], Gregory ZILMAN[2]

[1]Department of Zoology, Tel Aviv University, 69978 Tel Aviv, Israel
[2]School of Mechanical Engineering, Tel Aviv University, 69978 Tel Aviv, Israel

** yehudab@tauex.tau.ac.il*

Artificial submerged structures, such as jetties, pontoons, shipwrecks, and oil rigs, provide ample surface area for fouling communities. It has been long established that such structures can also function as artificial reefs (ARs) and can even mimic natural reefs. Various factors, especially time elapsed since deployment, have been considered to determine the features of fouling assemblages on an AR. Our survey of the supporting vertical steel pillars of the oil jetty at Eilat (northern Red Sea) revealed that colonies of the vibrant and colorful soft coral *Dendronephthya hemprichi* were distinctively aligned in vertical rows along depth. The hypothesis of the current study was that such unprecedented distribution of a fouling organism is related to the ambient water flow regime, which determines the larval settlement. A quantitative line transect survey conducted on the pillars revealed that *D. hemprichi* was the most abundant fouler, covering >50% of the surface. To understand the possible hydrodynamic effect on the soft-coral larvae, a flow chamber with vertical cylinders was designed, mimicking the pillar setting. Filming the larvae and passive particles in this chamber revealed that the particular pillar spacing affects the hydrodynamic regime taking place between pillars. The fouling larvae, which otherwise behaved like passive particles, in the boundary layer of the pillars also exhibited self-motion. When vorticity occurred between the pillars the larvae spent additional time there, facilitating their selection of an appropriate site for settlement and thus led to their exceptional fouling pattern. The findings provide novel predictive information regarding fouling species on submerged artificial surfaces, and also for the design of ARs for both nature conservation and recreational purposes.

Acknowledgements: This research was in part supported by the EU FP7 collaborative project “BYEFOULING - Low-toxic cost-efficient environment-friendly antifouling materials”, under Grant Agreement no. 612717 and by the Israel Cohen Chair in Environmental Zoology to YB.

Oral 24A

Importance of roughness for marine fouling-laboratory and field tests of algae and barnacles

Lena GRANHAG [1,*] and Elisabeth LUNDMARK [2]

[1] *Department of Shipping and Marine Technology, Chalmers University of Technology, Gothenburg, Sweden.*
[2] *Department of Biological and Environmental Sciences, University of Gothenburg, Gothenburg, Sweden.*

* *lena.granhag@chalmers.se*

Roughness (topography) is considered as an important factor for settlement and establishment of marine fouling. Roughness of different structure and spacing have previously been investigated for settlement of common ship hull fouling species [1-3]. Algae in slime-biofilms and invertebrate larvae differ in size, from typically 10 microns for spores of the green alga *Ulva* to mm sizes for invertebrate larvae. Therefore the optimal roughness for establishment (for firm adhesion and hydrodynamic shelter) will vary between fouling organisms. Natural fouling communities with settlement of both algal stages and larvae are representative of the mix of organisms growing on a ship hull. In this work, we in lab and field tests, studied settlement of common fouling algae and the barnacle *Amphibalanus improvisus*, to roughness including smooth to 1500 microns (spacing between depressions). Additionally, in field test the slime-biofilm development over time and species richness were investigated along a transect in Gothenburg harbour. A significantly lower settlement of *A. improvisus* was seen at roughness 300 microns compared to settlement on a smooth PVC panels. Finding a roughness with low settlement and establishment of multiple fouling organisms is challenging due to the varying propagule and larval sizes as well as interactions between organisms. Mapping of roughness impact for establishment of the most common fouling species, and comparing lab and field results, can however be useful information towards mitigation of the biofouling problem.

[1] K. M. Berntsson, P. R. Jonsson, M. Lejhall, P. Gatenholm. **2000**, *J of Exp Mar Biol Ecol,* vol 251: 59-83.
[2] J. F. Schumacher, M. L. Carman, T. G. Estes, A. W. Feinberg, L. H. Wilson, M. E. Callow, J. A. Callow, J. A. Finlay, A. B. Brennan, *Biofouling*. **2007**, vol 23: 55-62.
[3] L. H. Sweat and K. B. Johnson, *Biofouling*. **2013** vol 29, 879-890.

Oral 25A

Using environmental data to describe trends in fouling recruitment: an eastern Florida example

Kody LIEBERMAN*, Emily RALSTON, Kelli HUNSUCKER, Abraham STEPHENS and Geoffrey SWAIN

Florida Institute of Technology, Melbourne, FL, USA

* *klieberman2009@my.fit.edu*

Fouling community composition is dependent on the ecological (natural and anthropogenic) properties of the water body. This study describes seasonal, spatial and temporal fouling recruitment to polyvinyl chloride (PVC) control panels at two sites along the east coast of Florida: an oceanically influenced recreational and commercial harbour at Port Canaveral, and a remote natural site in the Indian River Lagoon estuary. These sites are approximately 60 km apart and differ significantly both ecologically and environmentally. Using environmental data, we can describe trends in timing of recruitment and may be able to estimate magnitude of fouling risk. By expanding recruitment and environmental monitoring sites, and with the addition of various antifouling coatings, we can move towards characterizing each site. This could allow users to make management decisions such as where and when to dock, perform cleanings and assess the risk of introducing nonindigenous species.

Acknowledgments: We would like to thank the Office of Naval Research (Grant no. N00014-02-1-0217) for their continuous support.

Oral 26A

Cement proteomics: shared traits and conserved chemistries in barnacle cement proteins from *Balanus amphitrite*

Christopher R. SO[1]*, Kenan P. FEARS[1], Dagmar H. LEARY[2], Zheng WANG[2], Jenifer M. SCANCELLA[1], Jinny LIU[2], Beatriz ORIHUELA[3], Dan RITTSCHOFF[3], and Kathryn J. WAHL[1]

[1]Chemistry Division, code 6176, US Naval Research Laboratory, 4555 Overlook Ave, SW, Washington, DC, USA
[2]Center for Biomolecular Science and Engineering, code 6900, US Naval Research Laboratory, 4555 Overlook Ave, SW, Washington, DC, USA
[3]Nicholas School of the Environment and Earth Sciences, Duke University Marine Laboratory, Beaufort, NC, USA

** christopher.so@nrl.navy.mil*

Sessile marine organisms such as barnacles adhere through a permanent proteinaceous interface developed between themselves and the marine environment throughout their adult life. These proteins play a dual role in adhering to both the native organism and a foreign substratum, which are often shell, cuticular exoskeleton or sedimentary minerals. Though much has been done to break down and sequence certain cement proteins, a complete picture of components remains missing and impedes a sequence-dependent understanding of barnacle bioadhesion. To this end, we have combined milligram-scale collection, effective non-covalent breakdown, and transcriptome-led[1] proteome sequencing of cement to reveal a full spectrum of proteins at the barnacle-substrate interface. In addition to known cement proteins, we identify a class of unique proteins that maintain sequence homology to previously identified components. To outline all potential members of this new cement family, conserved domains derived from cement samples are searched against the full mRNA transcriptome database. Our results indicate that barnacles utilize novel molecular strategies to construct the cement interface, where large proteins contain smaller homologous components. Further, deficiencies between certain residues in whole glue and the known cement components can be accounted for by incorporating newly sequenced proteins from this work. An informatics-led understanding of diverse barnacle cement components allows insight into highly conserved and functional molecular strategies used by barnacles to adhere to surfaces.

[1] Z. Wang, D. Leary, J. Liu, R. E. Settlage, K.P. Fears, S.H. North, A. Mostaghim, T. Essock-Burns, S.E. Haynes, K.J. Wahl and C.M. Spillmann. *BMC Genomics* **2015**, 16, 1–14.

Oral 27A

Spatial - biochemical organization of barnacle adhesive plaques following initial reattachment

Daniel E. BARLOW*[1], Kenan P. FEARS[1], Christopher R. SO[1], Jenifer M. SCANCELLA[1], Kedar MANANDHAR[1,2], Boris FEIGELSON[1], Beatriz ORIHUELA[3], Daniel RITTSHOF[3], Kathryn J. WAHL[1]

[1] US Naval Research Laboratory, Washington, DC, USA.
[2] National Research Council Post Doc
[3] Duke University Marine Lab, Beaufort, NC, USA

** daniel.barlow@nrl.navy.mil*

New advancements in barnacle adhesion proteomics are continuing to be made with progressing technologies. In efforts to better link these advances with the spatial – biochemical organization in barnacle adhesive plaques we will present spectroscopic and imaging analysis of the formation and multistep deconstruction of barnacle adhesive from 48 hour reattachment assays. Multiple internal reflection infrared spectroscopy (MIR-IRS), atomic force microscopy (AFM), and combined atomic force microscopy – nanoscale infrared spectroscopy (AFM-IR) were used to analyze the plaque formation and subsequent stepwise deconstruction. Either mica or Al_2O_3 coated substrata were used for reattachment assays. Consistent with previous work, AFM shows both amorphous and nano-fibrillar morphologies at 48 hours and MIR-IRS shows the emergence of an amyloid - like component. AFM-IR directly confirms individual nanofibrils as high beta sheet structures. Rinsing plaques with 80% acetic acid preferentially removed globular protein components, reducing overall protein content about 20%. Fibrillar structures remained but with a loss of segmented morphology. Further treatment of the plaques with hexafluoroisopropanol (HFIP) completely removed fibrillar morphologies and amyloid associated spectroscopic signatures, leaving an alpha-helical structure bound to the surface. Interactions between the remaining alpha helical component and hydroxyl terminated surfaces will be further discussed, as well as the analysis of the extracted cement components.

Oral 28A

Crack propagation in barnacle interfaces

Andrew B. GELTMACHER[1], William POGUE[1], James M. WOLLMERSHAUSER[1], Joel P. GOLDEN[1], Kenan P. FEARS[1], Christopher R. SO[1], Leonard M. TENDER[1], Christopher M. SPILLMANN[1], Richard K. EVERETT[2], Beatriz ORIHUELA[3], Daniel RITTSHOF[3], and Kathryn J. WAHL[1]*

[1] *US Naval Research Laboratory, Washington DC 20375, USA*
[2] *University of Maryland, Baltimore County, Baltimore MD 21250, USA*
[3] *Duke University Marine Laboratory Beaufort NC 28516, USA*

* *kathryn.wahl@nrl.navy.mil*

Acorn barnacles adhere to surfaces by secreting proteins which “cure” underwater to form a thin adhesive plaque or cement between their calcareous baseplate and whatever substrate they are living on. Prior work has shown that the nature of the barnacle base plate and adhesive may impact release characteristics. The adhesion process occurs in cyclic stages as the barnacle expands its periphery and is compositionally variable in a regular, concentric pattern in the interface. How the overall shape and shell microstructure and topography, as well as the variation in adhesive chemistry and composition, contribute to adhesion and release processes is part of ongoing research in this field. Here we report on a series of experiments designed to investigate the nature of the barnacle-substrate interface by (1) monitoring the development of the barnacle/substrate interface using surface plasmon resonance imaging (SPRi) and (2) measuring crack initiation and propagation with high speed videography. For the SPRi measurements [1], we monitor growth and development of barnacle interfaces on glass slides coated with a thin film of gold. Over a period of days to weeks, intensity changes in the SPR signals observed reveal secretory activity and variation in refractive index across the interface. For the latter experiments, we have settled and grown adult barnacles on plastic bars and tested them in four-point bending in order to propagate a crack in between the base plate and the substrate. We use high speed videography to capture the crack nucleation and propagation events, and image analysis to determine debonding area versus time. Ceramic rods and hollow forms have been tested as controls. We will discuss how these approaches allow insights into the adhesive and debonding processes of barnacles.

[1] J.P. Golden, D.K. Burden, K.P. Fears, D.E. Barlow, C.R. So, J. Burns, B. Miltenberg, B. Orihuela, D. Rittschof, C.M. Spillmann, K.J. Wahl, and L.M. Tender, *Langmuir* **2016** DOI:10.1021/acs.langmuir.5b03286M.

Session 5 – Regulation of AF/Corrosion products & Environmental issues - Room Bonaparte

Keynote 4B

Environmental issues associated with antifouling waste

Andrew TURNER [1,*]

[1] *SoGEES, University of Plymouth, UK*

* *aturner@plymouth.ac.uk*

Antifouling paint particles (APP) are generated during the maintenance of boats, the grounding of ships and the weathering of abandoned structures. However, little systematic study has been undertaken regarding the distribution, composition and effects of APP in the wider marine environment. This presentation reviews the state of knowledge in respect of APP, with particular emphasis on those generated by recreational boatyards and abandoned boats. The likely biogeochemical pathways of the biocidal and non-biocidal metals in current use (mainly Cu and Zn) and used historically (Sn and Pb) are addressed in light of recent research and an understanding of the more general behaviour of contaminants in marine systems. Analyses of individual paint fragments or composites thereof from recreational facilities and foreshores in the UK reveal chemical compositions that are similar to those of the original formulations; specifically, dry weight concentrations of Cu, Zn, Sn and Pb of up to about 35%, 15%, 5% and 70%, respectively. Elevated concentrations of other, non-biocidal trace metals, like Ba, Cr, Ni and Bi, also often occur. Metals leach more rapidly from APP than the painted hull itself due to the greater surface area of pigments and additives exposed to the aqueous medium. In suspension, APP are subject to greater and more rapid environmental variability (e.g. salinity, pH, dissolved oxygen) than hulls, while settled APP represent an important source of persistent and degradable biocides to poorly circulating environments. Through diffusion and abrasion, high concentrations of contaminants are predicted in interstitial waters that may be accumulated directly by benthic invertebrates. Animals that feed non-selectively and that are exposed to or ingest paint-contaminated sediment are able to accelerate the leaching, deposition and burial of biocides and other substances, and represent an alternative vehicle for contaminant entry into the marine foodchain. Clearly, an extensive understanding of biocide behaviour on painted surfaces is not sufficient for predictive or management purposes regarding APP and abandoned boats. Greater caution is required by boaters and boatyards during the removal and disposal of solid wastes, and more awareness or stricter enforcement of relevant codes of practice or legislation is recommended.

Oral 21B

Risk Assessment – Regional assessments of copper based antifouling paints

Kevin LONG [1]

[1] *Regulatory Compliance Limited, Loanhead, Scotland.*

* *klong@regcs.co.uk*

Generic EU-wide risk assessment procedures for antifouling substances are now enshrined in Guidance and have been applied for the approval of the active substances. However, while general scenarios have been defined to identify the potential for safe use of an active substance, these scenarios are not intended to represent any one region within the EU and may, therefore, not be reflective of the variabilities within the EU regions. Regional variations within EU waters suggest that these generic conditions could be less applicable for the authorisation of antifouling products on the National or Regional scale.

Several different critical parameters show high variability between EU regions and will affect the conclusions of any product-based risk assessment. A practical example of the relative importance of these parameters will be presented, demonstrating how the risk assessment may be amended to return more region-specific results.

Oral 22B

Efficiency and toxicity of antifouling sealer coats

João FERREIRA*[,1], Maria LAGERSTRÖM[1], Maria BIGHIU[1], Britta EKLUND[1] and Ann-Kristin WIKLUND[1]

[1] Department of Environmental Science and Analytical Chemistry (ACES), Ecotoxicology Unit (ACESx), Stockholm University, Stockholm, Sweden

* *joao.l.g.ferreira@gmail.com*

The development of marine biofouling on boat surfaces is a major problem for the shipping and leisure boat industry. Antifouling paints have significant economic importance within these industries, as application of such products is the most commonly used method to prevent the development of marine biofouling. Components of antifouling paints, such as copper, zinc, irgarol and TBT, can be highly toxic to the environment. The demand for such antifouling products, in European waters alone 6 million boats are used, means that leakage of toxic agents from antifouling paints on boat hulls is a source of biocide release into water bodies. The application of multiple layers of antifouling paints onto boat hulls is also a common practice among leisure boat owners. Such practice has led to the retention of banned paint components, such as TBT, on old paint layers of boat hulls over the years. The application of new layers of antifouling paints on boat hulls is normally preceded by the use of sealer coats, which are developed to prevent product incompatibilities by creating a barrier layer. Nowadays, with the increase usage of mechanical brushing devices for removal of biofouling from boat hulls the locking efficiency of such sealer coats gains even greater importance if leaching from older paint products to the environment is to be avoided.

Our study tested the performance of five sealer coats from leading paint producers. Experiments tested sealer coats toxicity to aquatic organisms, efficiency in locking underlying antifouling paints and resistance to brushing action. Testing of toxicity of sealer coats leachates, produced in 7‰ natural seawater, was done with the bacterium *Vibrio ficheri*, the alga *Ceramium tenuicorne*, the crustacean *Nitocra spinipes* and the gastropod *Theodoxus fluviatilis*. Results showed increased mortality, inhibition of growth or bioluminescence inhibition on at least one of the tested species for all the sealer coats tested. Furthermore, none of the sealer coats showed to be able to successfully lock biocide release from all the antifouling paints tested. Locking efficiency was dependent on the identity of the metal being released and the underlying layer of antifouling paint being tested, with brushing action leading to additional reduction of locking efficiency. Our conclusions therefore are that locking efficiency of such products should be improved to prevent release of toxic agents from underlying antifouling paints. The results also emphasise that brushing stress reduces sealer coats locking efficiency and therefore should be avoided. In order to safeguard environmental quality incorporation of biological tests in the regulatory process of such products is recommended.

Oral 23B

In situ studies of antifouling paint toxicity on snails

Maria BIGHIU[1]*, Britta EKLUND[1] and Ann-Kristin ERIKSSON WIKLUND[1]

[1] *Stockholm University, Stockholm, Sweden.*

* *maria.bighiu@aces.su.se*

Harbours (including marinas) are well recognized for accumulating pollutants due to the poor water exchange [1]. Due to their continuous release of biocides, antifouling paints are one of the main sources of pollution in harbours [2,3]. The fact that leisure boats coated with antifouling paints are stationary 90 % of the time [4] is a main contributor to increased levels of local contamination. Therefore it is important to evaluate the long-term effects of the mixtures of biocides and other contaminants, as they can be an early warning signal for a risk at population level. The aim of this study was to observe the physiological and biochemical effects of harbour water on a snail species commonly found in rivers throughout Europe, as well as in the Baltic Sea, *Theodoxus fluviatilis*. During two consecutive boating seasons we exposed caged snails in 2 or 3 marinas (2014 and 2015, respectively). The cages were placed at 1 m depth at all sites and were periodically brushed to ensure good water exchange. The exposure lasted 8 and 16 weeks in 2014 and 2015, respectively. The snail reproduction was assessed in terms of number of eggs laid in each cage after 2 or 4 weeks. During both years significantly less eggs were laid in all marinas compared to the reference sites (eg between 27- 99 % less eggs). The nutrients in the water were not limiting at any of the sites and therefore it is likely that the reduction in egg-laying in the marinas was due to other factors. The marina with the lowest snail reproduction in both years also had the highest mortality, i.e. 6 times higher than at a reference site. The chemical analysis of the water indicated the highest copper and zinc concentrations in the respective marina but further evidence is needed to confirm that these metals are the main cause of the observed toxic effects. Therefore, measurements of direct biological responses to metals such as copper and zinc by analysing the levels of metallothionein in snails are currently on-going. This integrated assessment of effects at different levels of biological organization could facilitate estimating the contribution of metals vs other organic contaminants to the overall toxicity observed. Moreover, we concluded that *in situ* exposure of snails is a good tool for evaluating the long-term effects of marinas on gastropods, which are a highly abundant and yet underrepresented group of organisms in toxicity testing.

[1] O. Foerl and G.J. Inglis, *Ecology* **2003**, 28:116-127
[2] Y. Sapozhnikova *et al. Marine Pollution Bulletin* **2013**, 69:189-194.
[3] W. Aly, I.D Williams and M.D Hudson, **2012.** Metal contamination in water, sediment and biota from a semi-enclosed coastal area. Environ Monit Assess.
[4] Swedish Transport Agency - Transportstyrelsen **2010**. “Båtlivsundersökningen, en undersökning om svenska fritidsbåtar och hur de används.”

Oral 24B

Evidencing the impact of trace metals release from antifouling paints into coastal Mediterranean environments: insights from Krka Estuary (Croatia) and Toulon Bay (France)

Cédric GARNIER*,[1], Ana-Marija CINDRIC[2], Duc Huy DANG[1,3], Gaël DURRIEU[1], Sébastien D'ONOFRIO[1], Dario OMANOVIC[2]

[1] Université de Toulon, PROTEE, EA 3819, 83957 La Garde, France.
[2] Ruđer Bošković Institute, Division for Marine and Environmental Research, Bijenička 54, Zagreb, Croatia
[3] Water Quality Center, Trent University, 1600 West Bank Drive, Peterborough, Ontario, Canada

** cgarnier@univ-tln.fr*

Trace metals such as Cu or Zn are widely used as biocide in antifouling paints, especially since the ban of TBT compounds. Their release from the paint, acting to prevent biofouling of the hull, can result in an overall increase of their concentration in environmental compartments such as water column and sediments from coastal environments, which could lead to adverse effect to sensitive species such as picophytoplancton, due to their potential toxicity. Coastal areas from Mediterranean Sea, due to its peculiar features (low tide, semi-enclosed Sea, high population density, touristic area, …), are particularly concerned by such threats. Consequently, we have investigated trace metals inputs, behavior and fate in two coastal areas, presenting contrasted characteristics: the Krka River estuary and the Toulon Bay. The Krka River (Croatia, Adriatic Sea) is a medium-size pristine Mediterranean river ending, after waterfalls (in the Krka National Park), in a 23-km long estuary which presents a permanently salinity-stratified water column. Due to its karstic watershed and low anthropogenic activities, Krka River and its estuary are oligotrophic with low levels of suspended particulate matter, nutrients and organic carbon, and ultratrace levels of heavy metals [1,2]. However, we evidenced that during the touristic period, the estuarine waters suffer from trace metals contamination linked to nautical activities, which strongly increases their overall levels in surface/brackish waters of the Šibenik Bay before being redistributed to the whole estuary through complex processes relatively similar to the ones encountered in open sea [2]. The Toulon Bay (North-Western Mediterranean Sea) is a semi-closed area of ~52 km^2 submitted to low tide, low freshwater inputs, medium-size coastal agglomeration (~0.5 M inhabitants), significant anthropogenic activities (1st French Navy harbor, nautical transport, aquaculture, tourism, …) and troubled history (scuttling of ~100 Navy boats in 1942, intense bombardments during 2nd World War, …). As a consequence, the Toulon Bay suffers a high multi-contamination of its sediments, distributed on the whole Bay. Indeed, based on a sound investigation on surface/deep sediment distribution of a large number of parameters and contaminants, a strong concentration gradient for numerous harmful substances was evidenced (examples of max/min factor observed in 0-5 cm surface sediments: 46× for Pb, 130× for Cu, 900× for Hg, 13500× for TBT) [3, 4]. Moreover, recent survey of dissolved metals concentration in surface water has demonstrated that even trace metal levels in the south part of the large Bay are at the level encountered offshore in the Mediterranean Sea, the inner parts strongly overpassed these values (e.g. factor of 55× for Cu, 160× for Pb), such contaminations being mostly related to past and present nautical activities [4].

[1] F. Elbaz-Poulichet, D.M. Guan, J.M. Martin, *Mar. Chem.* **1991**, 32, 211–224.
[2] A.-M. Cindrić, C. Garnier, B. Oursel, I. Pižeta, D. Omanović, *Mar. Poll. Bull.* **2015**, 94, 199-216.
[3] E. Tessier, C. Garnier, J.-U. Mullot , V. Lenoble, M. Arnaud, M. Raynaud, S. Mounier, *Mar. Poll. Bull.* **2011**, 62, 2075–2086.
[4] D.H. Dang, J. Schäfer, C. Brach-Papa, V. Lenoble, G. Durrieu, L. Dutruch, J.-F. Chiffoleau, J.-L. Gonzalez, G. Blanc, J.-U. Mullot, S. Mounier, C. Garnier, *Env. Sci. Techn.* **2015**, 49, 11438–11448.

Oral 25B

Antifouling innovation in a highly regulated environment: thinking outside the box or ticking boxes? *The here and now of EU-BPR*

Linda JONES*

Annex3 Consulting, Zandhuizen, The Netherlands

* *linda.jones@annex3.eu*

In the midst of other global regulatory schemes for biocides, the European Union system is one of the most comprehensive: its changes are followed and effects are felt worldwide. Other government competent authorities have studied Europe's advancements as an example, but also the global antifouling industry has closely watched the developments, with its product portfolio in mind.
Initially, the attention was focused mainly on the dossier evaluation of existing active substances, most of which have finally passed their regulatory review or are nearing the end of the review process. It is also hopeful to see that some new active substances for antifouling Product Type 21 have appeared on the scene which have actually made it through most of the regulatory hurdles. Considering also the 'mid-term' legislative changeover from the BPD (Biocidal Products *Directive* 98/8/EC) to the BPR (Biocidal Products *Regulation* (EU) No. 528/2012) this is a major achievement.
All-in-all, however, the regulatory process has thinned out the active substance arena with a reduced choice for paint formulators as the overall outcome. But what about new developments? Has the BPR stimulated innovation only outside the regulatory 'biocidal box', or can we still expect new additions to the list of approved substances? Whichever is the answer, it is certainly time to learn from the regulatory process until now, for new initiatives to have a better chance to succeed in the future.
It feels like we're only halfway there, with the procedures for authorisation of existing antifouling products still to follow. The focus on the active substances review caused postponement of many issues for the product authorisation stage. Various new pieces of regulatory guidance have recently appeared some specific to antifouling paints. What will happen with some major (political) issues is nonetheless left up to a little imagination. Still, paint companies are busy building dossiers and a number of them have already been submitted to the authorities.
This presentation looks at what can be learned from the regulatory process in terms of requirements, guidance and experiences, at active substance level as well as for antifouling paints. Some insight into the scope and application of the BPR is anticipated to be helpful for product developers working inside and outside the 'biocidal box', whether in universities, research centres or industry.

Oral 26B

Organotin speciation in historic layers of antifouling paint on leisure boat hulls

Maria LAGERSTRÖM[1*], Jakob STRAND[2], Erik YTREBERG[3] and Britta EKLUND[1]

[1] *Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, Sweden.*
[2] *Department of Bioscience, Aarhus University, Denmark.*
[3] *Department of Shipping and Marine Technology, Chalmers University of Technology.*

* *maria.lagerstrom@aces.su.se*

Antifouling paints containing organotin compounds, and tributyltin (TBT) in particular, were introduced in the early 1960's and quickly became widely used given their high efficiency [1]. However, due to their toxic effects, organotin compounds were banned in 1989 in the EU on boats <25m. This was followed by a global ban on all boats in 2008 by the International Maritime Organization [2]. Despite the over 25 year old prohibition of organotin paints, leisure boats still act as sources of TBT to the environment due to leaching from underlying historic paint layers on the hulls [3]. As TBT has been identified as a priority hazardous substance by the European Commission (Directive 2000/60/EC) and should therefore be eliminated from the environment as soon as possible, it is important to address these sources.
A new method for direct, non-destructive analysis by X-Ray Fluorescence (XRF) of tin on leisure boat hulls was recently published [4], allowing the identification of boats that likely have underlying coats of organotin paints. The XRF-method measures however only the total tin concentration and does not provide any speciation information, i.e. if the tin is in the form of harmful organotin compounds or harmless inorganic tin. The study presented here was carried out to investigate how much of the total tin is in the form of organotin compounds.
Paint samples from 23 leisure boats in 3 different countries around the Baltic Sea (Sweden, Finland and Germany) were collected and analyzed for their total tin and organotin content. For the determination of the organotin speciation, an extra extraction step involving a solvent mixture with a composition inspired by that of paint thinner was added to an existing accredited method for sediments. This was found to be necessary to fully extract all organotins from this matrix, indicating that the quantification of TBT and other organotins in sediments using existing methods may lead to an underestimation, if paint flakes are present in the sample. The speciation results show that most, if not all, of the total tin in the paints consists of organic tin compounds. Furthermore, many more species other than TBT such as dibutyltin (DBT) and monobutyltin (MBT) were present and, in many cases, TBT was not the main organotin compound in the paint. Some samples also contained high amounts of triphenyltin (TPhT), which has mainly been used as a fungicide but also, less commonly discussed, in antifouling paints [5].

[1] I. Omae, *Appl. Organomet. Chem.* **2003**, *17* (2), 81–105.
[2] IMO-MEPC 38 (1996) (v), "Terms of reference for a corresponding group on the reduction of harmful effects of the use of antifouling paints for ships", IMO-MEPC Paper MEPC 38/WP.6, **1996**.
[3] B. Eklund, M. Elfström, H. Borg, *Open Environ. Sci.* **2008**, *2* (1), 124–132.
[4] E. Ytreberg, L. Lundgren, M. A. Bighiu, B. Eklund, *Talanta* **2015**, *143*, 121–126.
[5] K. Fent, Antifouling Paint Biocides **2006**, Konstantinou, I. K. (Ed.), Springer Berlin Heidelberg, pp 71–100.

Oral 27B

New analytical method to measure release rates of copper under field conditions

Erik YTREBERG*[,1], John MOLÉN[1], Hampus INGVARSON[1]

[1] Department of Shipping and Marine Technology, Chalmers University of Technology, Gothenburg, Sweden

* *erik.ytreberg@chalmers.se*

Several methods exist to determine the biocidal release rates from anti-fouling paints. These methods are based on laboratory studies, field measurements or model calculations. Rotating cylinder methods, developed under the American Society for Testing Materials (ASTM) and International Organization for Standardization (ISO), have frequently been used in the laboratory to determine release rates of both organic biocides (e.g. TBT) and inorganic biocides (e.g. CuO). However, these methods were developed for experimentally screening purposes and do not to reflect field conditions. A few field methods have been developed to get more reliable and realistic release rate measurement. The most commonly used is the "Dome method" which was originally developed by the US Navy for measuring organotin and copper release rates *in situ* from a coated ship hull by using a closed re-circulating system [1]. Even though the method is recognized to be the most reliable indicator of environmental release rate it has not been used extensively since it is costly and involves divers. The aim of the current study was to bridge that gap by developing a cheap, fast and reliable release rate method based on X-ray fluorescence spectroscopy (XRF) that can be used to measure release rates under field conditions. The XRF method was used to determine release rates of copper from five different coatings applied on static panels submerged for 4 months in three different harbors located in Kattegat, the less saline Baltic Sea and in freshwater. The XRF antifouling paint application showed good relationship between increasing copper concentration and XRF Kα intensities (R^2 = 0.998). The results also showed release rates of copper to be governed by increasing salinity and that fouling, consisting of slime only, was similar on all copper based coatings.

[1] A. A. Finnie, *Biofouling* **2006,** *22*, (5), 279-291.

Oral 28B

A novel XRF application for boat inspection – Fast quantification of tin, copper and zinc

Britta EKLUND*[1], Maria BIGHIU[1], and Erik YTREBERG[2]

[1] *Department of Environmental Science and Analytical Chemistry (ACES), Stockholm, Sweden*
[2] *Department of Shipping and Marine Technology, Chalmers University of Technology, Gothenburg, Sweden.*

* *britta.eklund@aces.su.se*

TBT is still spread in the environment in spite of prohibition for use on leisure boats since 1989 and on ships from 2008 [1]. One important source of TBT is waste from old coatings on leisure boats [2,3]. A handheld X-ray Fluorescence (XRF) analyser calibrated for measurements of tin, copper and zinc in antifouling paints coated on leisure boats has been used on more than 1000 boats [4]. The main object was to investigate the occurrence of high values of tin, which indicate the presence of organotin compounds prioritized in the Water Framework to be phased out as fast as possible. The measurements have been performed in Finland, Sweden and Denmark. The results show that the majority of the boats did not contain much tin and the median values were 53, 34, 22, 17 and 13 µg Sn/cm^2 for boats at the West coast of Sweden, Helsingör at The Sound in Denmark, Helsinki in Finland, Freshwater in Sweden and brackish water in the Stockholm area in Sweden. However, high values of tin (i.e. > 400 µg /cm^2), which indicate the presence of organotin compounds were detected on between 10-20 % of the boats and this is considered to pose a risk to the environment. The variation among boats is high and maximum values up to 3000 µg Sn/cm^2 were found. The content of copper and zinc differs among the countries and the areas. The highest median concentrations of copper were found on boats at the West coast of Sweden (9500 µg/cm^2) > Helsingör at the Sound (8000 µg/cm^2) > Helsinki in the Finnish Bay (7500 µg/cm^2) > Stockholm area (2400 µg/cm^2) and lowest in freshwater (900 µg/cm^2). For comparison, one layer of 34 % copper-containing paint is approximately 4000 µg/cm^2. It is remarkable to find high copper values in freshwater since such paints have been prohibited for use on boats in freshwater in Sweden since 1993. The same order as for copper was observed for zinc with median zinc concentrations of 5600 at the West Coast of Sweden, 3700 in Helsingör at the Sound in Denmark, 3600 in Helsinki in the Finnish Bay, 1800 in the Stockholm area and 800 µg Zn/cm^2 in freshwater. This new application to the handheld X-ray analyser facilitates identification of boats with high contents of toxic metals. In particular boats with high tin concentrations, indicating organotin compounds, can then be recommended for removal of the old paint in accordance with the Water Framework Directive in the EU [5]. This would be a fast way to eliminate further discharges of these substances to the environment.

[1] Council Directive 89/677/EEC of 21 December 1989 amending for the eighth time Directive 76/769/EEC.
[2] B. Eklund, D. Eklund, *Environmental management*. **2014**, 53, 930-946.
[3] B. Eklund, L. Johansson, E. Ytreberg, *Journal of soil and sediments* **2014**, 14, 955-967.
[4] E. Ytreberg, M. A. Bighiu, L. Lundgren, B. Eklund, *In prep.*
[5] Water Frame Work Directive, 2000/60/EC

WEDNESDAY June 22, 2016

Plenary- 3 Innovative methods to approach microbial corrosion and its prevention

Pierangela CRISTIANI

Ricerca sul Sistema Energetico – RSE SpA, Milan, Italy.

Pierangela.cristiani@rse-web.it

The surfaces immersed in natural and non-sterile industrial water are rapidly colonized by microbial species rising to the complex micro-environment of biofilm. Almost any materials, including copper alloys and passivable metals, may be subjected to severe degradation or corrosion induced by the colonization of the microorganisms.
Biofilms are able to change the electrochemical characteristics of passivable metal surface, creating anodic and cathodic areas and inducing electroative effects, both in aerobic and/or anaerobic environment. The mechanisms of microbial corrosion has been widely studied but the process remain still largely underestimated and difficult to prevent, because the bacteria can modify in different biochemical, physico-chemical and electrochemical ways the metal/liquid interface. The release of enzymes by microrganisms into their external environment, as well chemical shuttles, provides the general bases for the interaction between cells and substrates.
Metabolomic profiling is one of the most promising, altough sophisticated, techniques attempting new insight on the enzymatic footprint of microbial corrosion cases.
The modern method of genomic component sequencing (such as Illumina and other pyrosequencing methods) allowed to document that a huge number of bacteria are generally involved in corrosion cases, mostly prokaryotes, and unculturable with the traditional microbiological techniques. Rarely, a single specie plays alone, except in lab experiments. Extremophilic microorganisms such as hypersaline and chemolytothrops involved in the Sulphur cycle (also culturable) usually have an important role, as they adapted to achieve energy in extreme environments for the life, poor of nutrients. They corrode metal when it is the only electron donors in their environment and they use salts such as sulphate (or nitrate) as final electron acceptors, in absence of oxygen. The energy that is available for microbial activity is highly dependent on the electrode potential, the electron transfer chain of the microorganism and its capability to deal with extreme environmental conditions.
The surface energy and its hydrophilic-hydrophobic propensity is of particular concern for the bacterial attachment. In fact, numerous research efforts have demonstrated that surface micro/nano-structure or surface energy have significant influence on fouling adhesion. During the past 30 years, polymer-based antifouling methods well exploited this concept, although the success of this techniques remain in macrofouling prevention and not to prevent biofilm. Recently, nanoparticles and nanofunctionalysed surfaces are investigating against bacteria attachment, also with nature-inspired approaches.
Electrochlorination is still largely used to prevent microbial corrosion in cooling circuits. The anodic polarization of surface has been also attempted, able to generate strong oxidants just close to the surface. Electrochemical probes can, finally, useful help to control on-line the treatment effectiveness and to monitor the early stage of biofilm growth [1].

[1] P. Cristiani. Risk assessment of biocorrosion in condensers, pipework and other cooling system components. Understanding biocorrosion: fundamentals and applications (EFC 66). Ed. Turid Liengen, Damien Féron, Régine Basséguy and Iwona Beech. Woodhead Publishing Limited. ISBN-13: 978-1782421207 ISBN-10: 1782421203.

Session 2 - Microbiologically induced corrosion-Biocorrosion - Room Colbert

Oral 29A

Halomonas titanicae- how corrosive is that microorganism actually compared to a sulfate reducer such as *Desulfovibrio indonesiensis*

Nanni NOËL*[1], Merlina KRANENBURG[1], and Job KLIJNSTRA[1]

[1] *Endures B.V., 1781 AT, Den Helder, The Netherlands*

* *nanni.noel@endures.nl*

Halomonas titanicae (*H. titanicae*) is a halophilic bacterium which was isolated 1991 from rusticle samples originating from the shipwreck of the RMS Titanic. It is a member of the group *Halomonadaceae* and it grows psychrotolerant under mesophilic conditions. However, this organism is also able to growth at 4 °C which made survival under deep sea on the metal surface of the shipwreck possible. *H. titanicae* is the first fully characterized microorganism which could be isolated from rusticles. Until now it is unclear if this microorganism was already present on the ship before its sinking or if its habitat is under deep sea [1, 2].

Interestingly, this microorganism is able to grow under a broad range of growth conditions which indicates an active metabolism under deep sea conditions but also under ambient conditions. Researchers found in the genome of the type strain of *H. titanicae* several genes related to metal corrosion [2]. But growth of this organism is possible without any iron source. So how corrosive is that microorganism actually and how does it behave under different growth or environmental conditions?

In several approaches we tested growth, biofilm formation and corrosiveness of H. titanicae including cold temperatures (down to 4°C), aerobic or anaerobic conditions and a pressure up to 100 bar. Methods such as total cell counts (TCC), epifluorescence microscopy (EFM), weight loss determination and pit analysis using an inverted microscope were used to investigate the behavior of *H. titanicae*. A high pressure vessel was designed to grow *H. titanicae* and *Desulfovibrio indonesiensis* (*D. indonesiensis*) under high pressure conditions and to compare corrosion behavior. Corrosion experiments under ambient conditions showed that *H. titanicae* is less corrosive as *D. indonesiensis*. So far no enhanced corrosion activity is shown for *H. titanicae* at 100bar whereas *D. indonesiensis* adapted to the high pressure conditions. Growth and biofilm experiments indicated that *H. titanicae* can grow under aerobic conditions on marine broth as well as anaerobically with nitrate. Biofilm formation was favored under anaerobic conditions.

[1] C. Sanchez-Porro, B. Kaur, H. Mann, A. Ventosa, *Int. J. Syst. Evol. Microbiol*. Vol 60, **2010**, p. 2768-2774.
[2] C. Sanchez-Porro, R. R. de la Haba, N. Cruz-Hernandez, J.M. Gonzalez, C. Reyes-Guirao, L. Navarro-Sampedro, M. Carballo, A. Ventosa, *genome A*, Vol 1, issue 2, **2013**, p. 1

Oral 30A

Influence of environmental seasonality on biocorrosion development over stainless steel AISI316L exposed to natural seawater

Leslie DAILLE[1.4],Maria Jose DE LA FUENTE[2,4], Diego FISCHER[2,4], Luis CARO[2,4] , Carlos GALARCE[2,4], Francisco ARMIJO[3,4], Magdalena WALCZAK[2,4], Gonzalo PIZARRO[2,4], Ignacio VARGAS[2,4], Rodrigo DE LA IGLESIA*[1,4].

[1] Biological Sciences, Pontificia Universidad Católica. Santiago, Chile.
[2]School of Engineering, Pontificia Universidad Católica, Santiago, Chile.
[3] School of Chemistry, Pontificia Universidad Católica. Santiago, Chile.
[4]Marine Energy Research & Innovation Center (MERIC).

** rdelaiglesia@bio.puc.cl.*

Corrosion is an electrochemical process that affect any surface exposed to aqueous or humid environment. It consists in a redox reaction which results in the dissolution of the material. One of the most common cases is the deterioration of metal surfaces. This reaction can be induced, facilitated or potentiated by the presence of microorganisms, phenomenon known as microbial induced corrosion (MIC or commonly known as biocorrosion). Microorganisms develop a complex biological matrix on the liquid-metal interface, known as biofilm. During biocorrosion, the biofilm generates microenvironments that locally change water chemistry (i.e. pH, ions concentration, redox potential) at the metal surface, inducing surface polarization and localized corrosion occurrence. Corrosion in marine environments is exacerbated because the metals are exposed to a fluid subjected to seasonal variations in both its physicochemical (temperature, salinity, nutrients) and biological (cell abundances)characteristics,which influence the electrochemical processes taking place.While previous analysis indicates that the microbial community colonizing the surface would be key to the development of a corrosive biofilm, it is not yet clear which environmental factors are critical for the development of the community and thus for biocorrosion.

The aim of this study was to understand how the development of marine biocorrosion over stainless steel is influenced by natural environmental seasonality. To accomplish this goal, an experimental model was developed, consisting in acrylic containers where stainless steel AISI 316L coupons were incubated in a running-seawater laboratory during 15 weeks. Two experiments were conducted, exposing the coupons to seawater during fall to winter and spring to summer seasons. Biocorrosion was evaluated over time at 1 week, 3 weeks, 5 weeks, 8 weeks, 12 weeks and 15 weeks after seawater exposure. A combination of electrochemistry and weight loss analysis were used to determine biocorrosion. Additionally, macroscopic inspections and analysis of the topology of the coupons through atomic force microscopy was performed to determinethe damage generated by the microbial community established on coupons surface.

After 15 weeks of seawater exposure, an increase in the corrosion current was observed in both seasons as well as increasing weigh loss.However, differences on the electrochemical behaviour of SS-316 was observed. The biofilm formed over the surface is macroscopically distinctive and generated ennoblement of the coupons exposed during fall/winter season, while spring/summer exposition caused a more active electrochemical behaviour. These results suggest that the composition of the biofilm established over the surface may varied according to seasonal variations and differentially affect the development of corrosion in the same location. These results could be useful to define construction strategies of coastal infrastructure.

Oral 31A

Marine electroactive biofilms responsible for stainless steel ennoblement - An EcoGenomic approach

Florian TRIGODET*,[1,2], Nicolas LARCHÉ[2], Dominique THIERRY[2], Loïs MAIGNIEN[1]

[1]Laboratory of Microbiology of Extreme Environments LM2E, UMR CNRS-IFREMER-UBO 6197, Institut Universitaire Européen de la Mer IUEM, Brest, France.
[2] French Corrosion Institute, Brest, France.

** trigodet.florian@gmail.com*

During ennoblement, marine microorganisms modify the open circuit potential of passive alloys towards positive values, thus increasing the risk of localised corrosion. Despite the practical importance of this, very little is known about the ecology of marine electro-active biofilms (MEABs), and the electron shuttling mechanisms at the alloy/biofilm interface. In this study, we used high-throughput DNA sequencing in order to better understand the EAB ecology and activity on stainless steel coupon surfaces immersed in recirculating mesocosms experiments. Multiple biological replicates exhibited similar microbial communities once the ennoblement has taken place, illustrating the deterministic processes shaping the EAB biofilm formation. Moreover, MEAB's exhibited a strong temperature-dependant composition and activity, with a sharp ennoblement activity loss above 38°C. This activity loss probably resulted from a change in MEAB composition as MEABs exhibited a strong temperature-dependent community structure. The assessment of microbial composition under those conditions is an exploratory step required for a deeper understanding of the microbial activity responsible for the ennoblement using EcoGenomic approaches.

Oral 32A

Microbial influenced corrosion in mixed microbial consortia from an equatorial environment

Prasanna JOGDEO[1], Martin SABALLUS[2], Christin KOCH[3], Diane McDOUGALD[1,4, 5], Dominique THIERRY, Scott A. RICE[1,4], and Enrico MARSILI[1*]

[1]Singapore Centre for Environmental Life Sciences Engineering, NTU, Singapore
[2]Technical University of Dresden, Dresden, Germany
[3]Helmholtz Centre for Environmental Research – UFZ, Leipzig, Germany
[4]School of Biological Sciences, NTU, Singapore
[5]iThree Institute, University of Technology Sydney, Australia

** emarsili@ntu.edu.sg*

Microbially influenced corrosion (MIC) describes the involvement of microorganisms in the deterioration of metallic and non-metallic materials [1]. Control of MIC is a significant cost for oil and naval industries, among others, and MIC has been a co-factor in large environmental disasters, such as oil spills. MIC is associated with complex microbial communities forming biofilms on surfaces. Environmental factors like nutrients, oxygen concentration, and convective fields affect the community composition and microstructure of biofilms, thus determining the corrosion rate of the material. Despite the understanding that MIC is the result of community level metabolic activity, most MIC studies have been performed using a single species or a very limited combination of species [2]. MIC of metal in the presence of a mixed microbial community can be entirely different from that of single species. In fact, biofilms formed on the metal surface can be a mixture of aerobic and anaerobic microorganisms, which can lead to different corrosion mechanisms.

The aim of this study is to combine electrochemistry, image analysis and –omics methods to assess MIC on stainless steel (SS) coupons exposed to mixed microbial consortia from equatorial coastal sediments. Initial experiments with SS immersed in coastal seawater show that the composition of mixed microbial biofilms depends on the composition of the SS used and is radically different from the composition of the planktonic community. A marine community was subsequently enriched using Marine Minimal Medium (3M) under laboratory conditions. Visualisation of metal surfaces and biofilms by confocal laser scanning microscopy (CLSM) and field emission scanning electron microscopy (FESEM) showed distinct changes in the topography of metal surfaces at the onset of MIC and reveal patterns of biofilm formation on the metal surface. Measurement of the corrosion potential (E_{corr}) and current (I_{corr}) complemented –omics and CLSM analyses. The effect of several environmental parameters (e.g., stirring, nutrient concentration, surface polishing and oxygen concentration) on MIC rate were investigated in a systematic manner. The carbon source determines the composition of the microbial community, thus the corrosion rate. Surface polishing affects the topography of the metal surface, which in turn changes the localisation of biofilms on the surface as compared to unpolished coupons. Biofilm thickness determines diffusional limitations, thus increasing MIC rate.

Our result show that the community composition and biofilm assembly on the metal surfaces are among the main determinants of MIC in mixed microbial consortia.

[1] B. Little, J.S. Lee, *Int. Mater. Rev.* **2014**, 59, 384-393.
[2] P. Zhang, D. Xu, Y. Li, K. Yang, T. Gu, *Bioelectrochem.* **2015**, 101, 14-21.

Oral 33A

Effect of *bacillus sp.* biofilm on corrosion of Al thermal sprayed coatings and cathodic protection of SS 316L in marine environment

Leila ABDOLI, and Hua LI*

Key Laboratory of Marine Materials and Related Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China.

** lihua@nimte.ac.cn*

Corrosion in the marine environment is the most remarkable issue influencing environment and economy. Thermal sprayed aluminum coatings have been extensively used as protective layers in the marine environment. The corrosion behaviors of the coatings with colonization of microorganisms on their surfaces yet remain elusive. In this study, the corrosion behavior of thermal sprayed Al coatings deposited on SS316L in artificial seawater (ASW) in the presence of *Bacillus sp.* bacteria was investigated. The analytical techniques including electrochemical impedance spectroscopy (EIS), cyclic polarization measurements, and scanning electron microscopy (SEM) were employed for the investigation. It was surprisingly noted that presence of the bacteria-pertained biofilm enhanced the corrosion resistance of the Al coatings at initial stage of exposure and then corrosion resistance decreased after 3 months immersion, but still in inoculated solution, Al coatings showed higher corrosion resistance in compared to sterile solution. It could be because of the compact biofilm and corrosion products deposited in the defects of Al coating during corrosion process. Biofilm cannot only form a protective film on the coating surface, but also close micro pores to cut off the passage of corrosion medium quickly. This so-called “self-sealing behavior” [1] occurred during the whole corrosion test period. As results showed pitting corrosion happened for SS 316L in presence of *bacillus sp*. Thermal sprayed Al coating not only can act as a protective layer against aggressive environments, but also protect the steel as sacrificial anode which can improve performance and extend the working life.

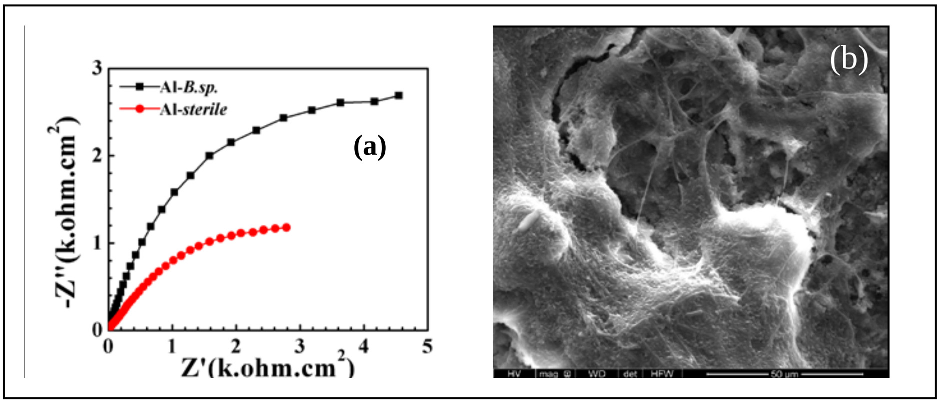


Fig. 1: Electrochemical impedance results for the Al coatings in the ASW without/with the bacteria after 90 days (a), and SEM image of Al coating surface after 90 days immersion in bacteria-containing solution (b).

[1] Y-X. Chen, B-S. Xu, Y. Liu, X-B. Liang, Y. Xu, *Trans. Nonferrous Met. Soc. China,* **2008**, 18, 603-609.

Oral 34A

Self-assembled and dip-coated nanolayers as anti-biofouling protective coatings on copper, copper alloys, and stainless steel

Loránd ROMÁNSZKI*[,1], Iaryna DATSENKO[2], Zoltán MAY[3], Judit TELEGDI[1,4], Lajos NYIKOS[1] and Wolfgang SAND[2]

[1] Functional Interfaces Research Group, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Budapest, Hungary.
[2] Aquatic Biotechnology, Biofilm Centre, Faculty of Chemistry, University of Duisburg–Essen, Essen, Germany.
[3] Plasma Chemistry Research Group, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Budapest, Hungary.
[4] Institute of Media Technology and Light Industry, Faculty of Light Industry and Environmental Engineering, Óbuda University, Budapest, Hungary.

** romanszki.lorand@ttk.mta.hu*

Bacterial attachment, biofilm formation and the consequent biofouling and biocorrosion cause severe damage worldwide. Since biocorrosion usually starts up under a developed biofilm, the strategies to control it are strongly related to the inhibition of microbial adhesion. Two different approaches are in application: 1) use of dissolved inhibitors and biocides; and 2) modification of surfaces by coatings.
Here we demonstrate a possible dual practical application of self-assembled monolayers of hydroxamic and phosphonic acids, and dip-coated polystyrene nanolayers against electrochemical and microbiologically influenced corrosion. Dip-coated polystyrene layers of sub-micrometre thickness (85–500 nm) have been applied on copper and copper alloys (aluminium brass, copper-nickel 70/30), as well as on stainless steel 304, and produced an effective barrier against corrosion and adhesion of corrosion-relevant microorganisms. According to the dynamic wettability measurements, the coatings exhibited high advancing (103°), receding (79°) and equilibrium (87°) contact angles, low contact angle hysteresis (6°) and surface free energy (31 mJ/m^2). The corrosion rate of copper-nickel 70/30 alloy samples in 3.5% NaCl was as low as 3.2 µm/a (44% of that of the uncoated samples), and in artificial seawater was only 0.9 µm/a (29% of that of the uncoated samples). Cell adhesion was studied by fluorescence microscopy, using monoculture of *Desulfovibrio alaskensis*. The coatings not only decreased the corrosion rate but markedly reduced the number of bacterial cells adhered to the coated surfaces. The PS-coating on copper gave the best result, 2×10^3 $cells/cm^2$ (1% of that of the uncoated control). The studied nanolayers hamper the attachment of microorganisms and the biofilm formation, as proven in AFM and epifluorescence microscope experiments conducted not only with *Desulfovibrio alaskensis* monoculture, but also with mixed microorganism population of industrial cooling water.

Session 15 – Climate changes, invasive species and biofouling- Room Bonaparte

Keynote 5B

Increased defenses against fouling in non-native populations of an invasive seaweed

Shasha WANG[1], Mark LENZ[1], Gaoge WANG[2], Dapeng BIAN[3], Florian WEINBERGER[*,1]

[1]*Marine Ecology Division, Helmholtz-Zentrum für Ozeanforschung (GEOMAR), Kiel, Germany*
[2]*College of Marine Life Sciences, Ocean University of China, Qingdao, China*
[3]*Xunshan Group Co., Ltd, Rongcheng, China*

* *fweinberger@geomar.de*

Defenses against foulers were compared among eight populations of the red macroalga *Gracilaria vermiculophylla* in the native range (2 in China, 2 in Japan) and the non-native range (2 in Germany, 2 in France). Foulers investigated were (a) two strains of the diatom *Stauroneis constricta,* isolated from China and from Germany, and (b) two filamentous macroalgae, *Ceramium tenerrimum,* collected in China, and *C. virgatum*, collected in Germany. Fouling assays with a fully crossed design were realized in both ranges in different seasons, using living individuals of *Gracilaria* and artificial substrates impregnated with *Gracilaria* surface extracts. Both groups of foulers and native and non-native epibionts alike attached significantly less to living algae (reduction by 45 to 52 %) and to substrata covered with extracts that came from non-native *G. vermiculophylla* populations (reduction by 9 to 17 %). Diatoms settled least on surfaces impregnated with hexane extract, while *Ceramium* settled least on surfaces coated with dichloromethane extract, suggesting that multiple chemical defense compounds may be involved.
Our study provides first evidence of resistance to fouling pressure determining the invasion success of marine organisms: In *G. vermiculophylla* multiple fouling resistance traits were selected during an invasion history of few decades.

Oral 29B

LC-MS based metabolomics in integrated field and laboratory approaches towards unravelling the impact of metal contamination on marine biofilms

Laurie FAVRE*[,1], Annick ORTALO-MAGNE[1], Clément Coclet[1,2], Jean-François BRIAND[1], Benjamin MISSON[2], Cédric GARNIER[2], and Gérald CULIOLI*[,1]

[1] *Université de Toulon, MAPIEM, EA 4323, La Garde, France.*
[2] *Université de Toulon, PROTEE, EA 3819, La Garde, France.*

* *Corresponding authors (favre@univ-tln.fr, culioli@univ-tln.fr)*

The Toulon bay gathers the main port of the French Navy, a commercial harbor and several marinas. Consequently, this marine area is historically contaminated with heavy metals such as copper, lead or zinc [1].

This present study aims to better understand the relationships between chemical, biochemical, and biological components of marine biofilms and metal contamination. For this purpose, natural biofilms were first harvested from artificial surfaces immersed during a one month field experiment at five locations along an anthropization gradient in the Toulon bay with contrasted pollution levels. A LC-MS based metabolic profiling of these samples was then conducted along with microbial communities characterization (abundance, diversity) and analysis of exopolymeric substances (EPS). A comparative study between these data and associated geochemical parameters (temperature, salinity, pH, dissolved organic carbon, nutrients, heavy metal …) was also carried out.

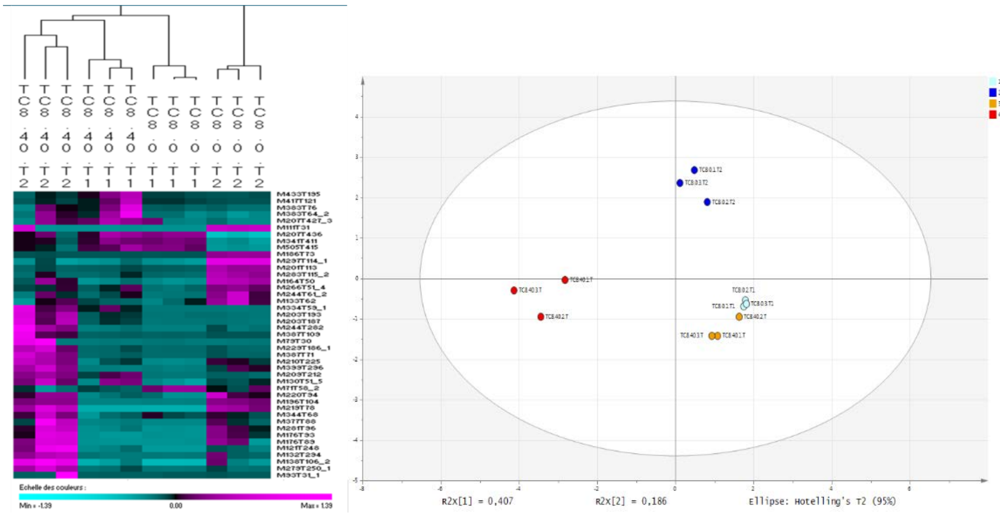


Fig. 1. Effect of copper on the metabolome of Pseudomonas lipolytica *TC8: (left) Heat map reflecting metabolite changes and (right) PLS-DA comparison of metabolomic profiles of bacterial cells cultured with or without copper*

In a second phase, *in vitro* experiments were realized in order to determine how copper pollution would affect bacterial metabolic pathways. Laboratory cultures were conducted with several biofilm-forming marine bacteria isolated in the Toulon bay or in the Morbihan gulf. The analysis of the bacterial metabolic profiles led to the identification of biomarkers (Fig. 1) whose production is induced by the presence of copper, suggesting an adaptation of their metabolisms following the exposure to this metal.

[1] E. Tessier, C. Garnier, J.-U. Mullot, V. Lenoble, M. Arnaud, M. Raynaud & S. Mounier *Mar. Pollut. Bull.* **2011**, 62, 2075–2086.

Oral 30B

The transport of marine biofilms through freshwater via the Okeechobee Waterway ('Florida's Panama Canal') and their effects on subsequent macrofouling recruitment

L. Holly SWEAT*[1], Geoffrey W. SWAIN[1,2], and Kevin B. JOHNSON[1]

[1]*Dept. of Marine and Environmental Systems, Florida Institute of Technology, Melbourne, FL, USA*
[2]*Center for Corrosion and Biofouling Control, Florida Institute of Technology, Melbourne, FL, USA*

* *hsweat2007@my.fit.edu*

Marine biofilms form on submerged surfaces and commonly influence the settlement of macrofoulers. Biofilms adhering to ship hulls may be carried thousands of miles, and their effects on macrofoulers, therefore, have implications for bioinvasions. Passage through freshwater shipping routes is less effective than previously thought at killing marine macrofoulers. However, no studies have examined how freshwater transport affects the mortality of biofilm organisms such as diatoms. Persistence and survival of diatoms were investigated in biofilms developed on three modern ship hull coatings: a copper antifouling paint, a silicone fouling-release coating and an inert epoxy basecoat. Biofilms cultivated on opposite coasts of Florida were reciprocally transplanted through 165 km of freshwater in Florida's Okeechobee Waterway. Using a specially designed test vessel, panels were transported on the hull and in recirculating and flow-through containers. Transport method affected diatom community composition, resulting in new biofilms. Recruitment and growth of several macrofouling species were altered by the disparate biofilms that developed under different transport conditions and coating types. Responding macrofoulers included polychaetes, hydroids, bryozoans, and macroalgae. These results provide a fresh perspective on the role of shipping in the spread of invasive species.

Oral 31B

Barnacle adhesion and biomineralization in a changing ocean: assessing the effects of seawater salinity and pH

Gary H. DICKINSON*[1], Jessica A. NARDONE[1], Conall G. MCNICHOLL[1], Kyle R. SIEGEL[1], Dana TEDESCO[1], Beatriz ORIHUELA[2], and Daniel RITTSCHOF[2]

[1] *The College of New Jersey, Department of Biology, Ewing, NJ, USA*
[2] *Duke University Marine Laboratory, Beaufort, NC, USA*

** dickinga@tcnj.edu*

Barnacles are common and dominant members of marine biofouling communities throughout much of the world's oceans. They tenaciously adhere to nearly any inert surface in the marine environment, including ship hulls, aquaculture facilities, and other marine structures, resulting in a tremendous cost and performance burden for maritime industries. Barnacles adhere using a secreted proteinaceous cement, which forms adhesive bonds with surfaces and cures. Although we are beginning to understand the biochemical mechanisms involved in barnacle adhesion, relatively little is know about how the environment affects barnacle adhesion and mineralization. Here, we assess the impact of variations in salinity and pH on adhesion and biomineralization in the barnacle *Amphibalanus (= Balanus) amphitrite*.

In two separate experiments, barnacle larvae were cultured from adults collected from the Beaufort Inlet, NC, USA. In the first experiment, juvenile barnacles were acclimated to eight target levels of salinity, ranging from 10 – 45 psu in steps of 5, while keeping pH and temperature as consistent as possible and exposed to target salinities for 16 weeks. At the conclusion of the exposure period, barnacle adhesion strength was quantified in shear following ATSM standards. Salinity significantly impacted adhesion strength. Adhesion strength was significantly higher in barnacles held at 15 psu as compared to those at 35 and 45 psu. Effects of salinity on biomineralization, however, appeared minimal. Salinity did not exert a significant effect on area of the base plate, thickness of the base plate, shell mass, or microhardness of the shell plates (a measure of resistance to deformation).

In a second experiment, juvenile barnacles were exposed to three levels of pH (8.1, 7.8 & 7.5) while temperature and salinity were held constant. These pH levels correspond to pCO_2 of approximately 400 µatm (current ambient), 800 µatm (predicted within the next 100 years) and 1750 µatm (predicted within the next 300 years). Barnacles were exposed for 13 weeks to these conditions and adhesion strength (in shear) was quantified after the exposure period. In this case, the effect of pH on adhesion strength was not significant, but pH level did affect biomineralization. Area of the base plate was significantly greater when barnacles were grown at reduced pH (7.8 or 7.5). Total alkalinity of exposure seawater was consistently and significantly higher at pH 7.5, suggesting that despite increased base plate area in barnacles held at 7.5, dissolution of shell plates occurred.

In summary, changes in ocean chemistry have the potential to affect the adhesion and biomineralization process in the barnacle *Amphibalanus amphitrite*. The adhesion process, which could include secretion of the glue and/or the glue assembly process, is sensitive to salinity but not pH. Biomineralization, in contrast, is sensitive to pH but not salinity. This work was supported by US Office of Naval Research.

Oral 32B

New life, new challenge: antifouling defence patterns of native and non-native populations of an invasive seaweed suggest a potential for rapid defence adaptation to new microbial foulers

Mahasweta SAHA[1]*, Jutta WIESE[1], Florian WEINBERGER[1], and Martin WAHL[1]

[1] *Helmholtz center for Ocean research, Kiel, Germany.*

**sahamahasweta@gmail.com*

Seaweeds are important secondary substratum for colonisation by micro and macrofoulers and are also known to be extremely successful biological invaders in marine environments - offering potential models for unravelling the mechanisms favoring such invasions. Rapid adaptation to novel biotic and abiotic factors can be critical to invasion success, an aspect which is still at its infant stage of investigation. Among biotic factors, foulers have the potential to determine invasion success or failure of invasive seaweeds. However, this perspective has been ignored so far. We tested whether the impressive invasion success of the red seaweed *Gracilaria vermiculophylla* may be enhanced by a rapid adaptation of anti-fouling defense against potentially facultative new target microfoulers in the invaded range. Native and invasive *Gracilaria* populations were equally well defended against presently co-occuring bacterial foulers. However, native populations were weakly defended against microfoulers from the invaded range, while invasive populations were weakly defended against microfoulers from the native range. Thus, the invasive populations exhibited an adaptation of their antifouling defense capacity to cope with the new foes, but have lost capacity to fend off old foes. These results provide the first evidence that confrontation by new foulers can trigger a rapid defence adaptation of seaweeds, which could be necessary for invasiveness.

Oral 33B

Project Helm: big data and multivariate modeling for fouling risk mitigation

Richard RAMSDEN[1]*, Jeremy THOMASON[2], Peter LELLIOT[3], Paul DAY[3], Duncan VAN ROERMUND[4]

[1] *AkzoNobel Coatings, Gateshead, UK.*
[2] *Ecoteknica, Newcastle, UK*
[2] *South Coast GIS, Arundel, UK*
[2] *Tessella, Abingdon,UK*

* *Richard.ramsden@akzonobel.com*

The settlement and growth of fouling on the hull of a marine vessel is governed by multiple complex interconnected ecosystems. Biofouling can be affected by factors as diverse as environmental conditions, vessel operational characteristics and fouling control coating.
Partially funded by Innovate UK, the Helm project has pulled together multiple disparate data sources to create a Big Data resource of potential factors. This database was developed which contains:

- Latitude/Longitude data on nearly 25,000 vessels, every 15 minutes for 5 years,
- 8 environmental parameters associated with each vessel location,
- Coating performance data on all vessels,
- Static and dynamic vessel characteristics data,
- Over 3.6 Billion data records,
- 2.75 TB of data.

The visualisation and exploration of this data allowed complex multivariate models to be derived from over 1400 variables, which represent the state-of-the-art in biofouling risk analysis, as well as a rich resource for the development of further modelling applications and risk assessments. These biofouling challenge and risk mitigation models have numerous applications, in coating specification, technical development of new fouling control strategies as well as the translocation of invasive species.

THURSDAY June 23, 2016

Plenary- 4 Bio-inspired anti-fouling compounds

Peter PROKSCH[1,*]

[1]*Heinrich-Heine University, Institute of Pharmaceutical Biology and Biotechnology, D-40225 Duesseldorf, Germany*

* *proksch@uni-duesseldorf.de*

The world-wide ban of synthetically derived anti-fouling compounds such as TBT has spurred the search for new ecologically friendly alternatives that feature a high target-specificity but a low toxicity. Marine invertebrates such as sponges are famous for their structurally diverse bioactive compounds, many of which are unprecedented among terrestrial organisms. Sponges usually feature a clean surface and hence must have strategies to avoid attachment of fouling organisms and blocking of pores that would be disastrous to filter-feeding organisms. Our search for bio-inspired anti-fouling leads therefore focuses on sponges and bioactive compounds from these organisms. In a broader search that involved a small library of structurally diverse natural products isolated by our group from different sponges bastadin derivatives showed promising activities involving barnacle larvae as test organisms. Synthetically prepared congeners of sponge-derived bastadin derivatives such as 5,5′-dibromohemibastadin-1 (DBHB) that suppress the settling of barnacle larvae are also strong inhibitors of blue mussel phenoloxidase (PO), which is a key enzyme involved in the firm attachment of this invertebrate to substrates and, thus, a promising molecular target for anti-fouling research. The IC_{50} value of DBHB as the most active enzyme inhibitor amounts to 0.8 μM. Inhibition of phenoloxidase by DBHB is likely due to complexation of copper(II) ions from the catalytic centre of the enzyme by the α-oxo-oxime moiety of the compound as shown by X-ray structure determination of a copper(II) complex of DBHB. Based on the pharmacophoric properties of DBHB a SAR study using synthetically prepared DBHB analogues was conducted. Several congeners, which feature structural variations of the DBHB core structure, were prepared. These structural modifications include, e.g., different halogen substituents present at the aromatic rings, different amine moieties linked to the (*E*)-2-(hydroxyimino)-3-(4-hydroxyphenyl)propionic acid, the presence of free *vs.* substituted aromatic hydroxyl groups and a free *vs.* methylated oxime group. All compounds were tested for their inhibitory activity towards the target enzyme *in vitro*, and IC_{50} values were calculated. Derivatives, which structurally closely resemble sponge-derived hemibastadins, revealed superior enzyme inhibitory properties *vs.* congeners featuring structural moieties that are absent in the respective natural products. This study suggests that natural selection has yielded structurally-optimized antifouling compounds.

Session 10 – Impact & Applications of marine fouling and corrosion research and technologies - Room Colbert

Keynote 5A

Global ocean industry collaboration to address the economic and environmental impacts of marine fouling

Christine VALENTIN*

World Ocean Council

**christine.valentin@oceancouncil.org*

The introduction of invasive species via biofouling is a global, cross-sectoral issue that requires an international, mutli-industry approach to the research, development and testing of solutions that are practical, effective and can be implemented by industry. A collaborative, cross-sectoral, global effort on biofouling (and other operational marine environmental challenges shared by many ocean industries) creates opportunities for synergies, economies of scale and public/private partnerships.

The World Ocean Council (WOC) has identified biofouling as a priority work area. The WOC is the international ocean business leadership alliance that brings together companies to develop collaboration in ocean sustainable development, science and stewardship. WOC Member companies include shipping, oil/gas, fishing, aquaculture, offshore renewable energy, seabed mining, marine science and technology, and other sectors - as well as “affiliated organization” members from research and scientific institutions.

The WOC is working to create an international, multi-industry “platform” to address biofouling. The platform will: bring together key stakeholders (industry, science, government, environment NGOs): catalyze collaboration among ocean industries on biofouling; coordinate development of a shared industry, science and research agenda; and develop practical, cost-effective solutions and practices to address biofouling based on good science and risk assessment.

The collaborative international WOC “platform” on biofouling is spurring the interest and involvement of a growing number of ocean industry operators to participate in a collective approach to tackling the issue of biofouling as a vector for invasive species.

Oral 35A

Antifouling coatings for marine energy applications: criteria, challenges, and analysis

George BONHEYO*,[1,2], Jiyeon PARK[1], Andrew AVILA[1], Robert JETERS[1], Eric WINDER[1], Curtis LARIMER[3], Beradette HERNANDEZ-SANCHEZ[4], Michele DENTON[4], Michael HIBBS[4], Paul SAVAGE[5], and Shane STAFSLIEN[6]

[1] Pacific Northwest National Laboratory-Marine Science Laboratory, Sequim, WA, United States.
[2] Washington State University, Pullman, WA, United States
[3] Pacific Northwest National Laboratory, Richland, WA, United States.
[4] Sandia National Laboratory, Albuquerque, NM, United States
[5]Brigham Young University, Provo, UT, United States
[6]North Dakota State University, Fargo, United States

** George.Bonheyo@pnnl.gov*

The United States Department of Energy Office of Energy Efficiency and Renewable Energy (EERE) supports the development, deployment, and commercialization of technologies to extract energy from wind and water resources. Recognizing a need for effective antifouling technologies to maximize energy capture and reduce operations and maintenance costs, EERE's Wind and Water Power Technologies Office (*WWPTO*) supported an analysis of specific needs and requirements for both marine hydrokinetic (MHK) and wave energy conversion (WEC) systems as well as offshore wind energy farms. The WWPTO also supported the development of novel coatings and a comparison of these novel coatings with examples of existing antifouling coatings.

Performance analysis was carried out at the Pacific Northwest National Laboratory's Marine Science Laboratory located in Sequim, WA. Tank testing was conducted to allow control of water velocity so that coating performance could be evaluated under near static and simulated high velocity tidal currents (≤5knots, 2.6 m/s) found at typical MHK, WEC, and offshore wind energy locations. To replicate the natural environment, seawater was continuously pumped from Sequim Bay, located on the Strait of Juan de Fuca in the Salish Sea. Continuous pumping introduced organisms throughout all tidal and diurnal cycles into the test tanks and began 3 months before coatings testing began to establish a natural community of organisms, as evidenced by the diversity of species colonizing the fiberglass walls of the tanks.

Seventeen different coatings were painted onto aluminum coupons and exposed for 30, 60, and 90 days, with 6 replicates of each coating provided for each velocity and timepoint. In total, 596 coupons were analyzed by measuring changes in wet and dry mass, the accumulation of nonpurgeable total organic carbon, visual inspection, and a new method that combines biological staining and digital image processing.[1] The results found that all of the commercial and novel coatings exhibited fouling within 30 days. Some of the novel PEG-based coatings delaminated in both the static and velocity tanks. By 60 days, a number of coupons displayed heavy fouling that included the growth of macrobiotic species such as barnacles, mussels, tubeworms, and bladed algae. Coatings employing a fouling release strategy were the best performers despite exposure to velocities well below their recommended performance thresholds. Longer-term studies are needed along with detailed analysis to determine the impact different degrees of fouling might have on device performance.

[1] C. Larimer, E. Winder, R. Jeters, M. Prowant, I. Nettleship, R.S. Addleman, and G. Bonheyo, *Anal Bioanal Chem*. **2016**, 408(3), 999-1008. DOI 10.1007/s00216-015-9195-z.

Oral 36A

Corrosion and biofouling of offshore wind monopile foundations

Claire CANNING*[1, 2], Tariq DAWOOD[2], Elizabeth J. COOK[3], Julia RACE[4], Asif TAHIR[5]

[1]*Industrial Doctoral Centre for Offshore Renewable Energy, Edinburgh, UK*

[2]*EDF Energy R&D UK Centre, London, UK*

[3]*Scottish Association for Marine Science (SAMS), Oban, UK*

[4]*Department of Naval Architecture, Ocean and Marine Engineering, University of Strathclyde, Glasgow, UK*

[5]*Environment and Sustainability Institute, University of Exeter, Penryn, UK*

* *c.canning@ed.ac.uk*

The impacts of corrosion and biofouling on offshore wind turbine foundations is considered to be a key issue in terms of operation and maintenance (O&M) which must be better addressed. The majority of offshore wind farms currently use monopile foundations to support the turbines. Early design assumptions for monopiles determined that no corrosion protection was required for the internal surfaces since they should be completely sealed and water tight, and therefore corrosion would cease quickly once oxygen was consumed in the confined space. However, it is becoming increasingly apparent that this air/water-tight design is difficult to achieve in practice; with many foundations experiencing significant internal leakages through failing export cable seals, and oxygen ingress during ventilation. The primary concern is that this situation replenishes corrosive species within the monopile and may accelerate corrosion of the internal surfaces.

Degradation of the monopile steel due to biofouling growth on the external surfaces is another concern faced by operators. Biofouling can create chemical environments on metallic surfaces that accelerate corrosion. Furthermore, the accumulation of biofouling on can influence the hydrodynamic properties of a structure leading to increases in the drag and inertia coefficients. Fouling represents an additional non-structural mass which may decrease the natural frequency of a foundation towards that of the loading frequency and therefore increasing the probability of resonance. In addition to structural concerns, offshore wind structures have been described as “stepping stones” in the spread of non-native and potentially invasive biofouling species.

This paper presents a case study of the internal corrosion and external biofouling issues experienced at Teesside Offshore Wind Farm (OWF); a 62MW wind farm in the UK owned and operated by EDF Energy. The various methodologies implemented to obtain corrosion and biofouling data from the wind farm are described and the preliminary results are discussed.

Acknolgements: The Industrial Doctoral Centre for Offshore Renewable Energy is funded by the Energy Technologies Institute and the RCUK Energy Programme, grant number (EP/J500847/1).

Oral 37A

13 years experience with fouling release coating on a RNLN frigate

Job KLIJNSTRA*[1], Mark BAKKER[1], Jans BAAS[2] & Natasja BOUMAN[3]

[1] Endures BV, Den Helder, The Netherlands
[2] Royal Netherlands Navy, Den Helder, The Netherlands
[3] Netherlands Defence Materiel Organisation, Den Haag, The Netherlands

** Job.Klijnstra@Endures.nl*

Since 2001 the Royal Netherlands Navy (RNLN) has stimulated research on properties and applied aspects of fouling release coatings (FRC) on (large) navy ships. Laboratory work first concentrated on long term activity in static raft tests and vulnerability of FRC's for mechanical damage. In parallel more practical experience was gathered from FRC test patches on various ships.

Following this preliminary work and supported by literature information the RNLN decided to start with a full scale ship test of a fouling release coating on an M-class frigate. In 2004 a so-called first generation FRC was applied on the entire underwater hull except the propellers and the boot top area. The latter was provided with an SPC. An experimental protocol was set up for regular diver inspections to monitor hull fouling and coating condition. After 4 years sailing in both temperate and tropical water mainly slime and algal fouling was found and except for some local damages, the coating was largely intact. As long as the ship remained active limited (soft) fouling had developed with little influence on ship capabilities. At idle times of 6 – 8 weeks, however, fouling could reach a critical level on this product.

Ship test was continued in 2008 with recoat of hull with next generation FRC onto cleaned, existing tiecoat and topcoat. Also boot top area was recoated with SPC. Diver and dry dock inspections again revealed mainly slime and soft fouling on the FRC whereas the boot top area was fouled with many barnacles. No reports were made on ship capability problems due to hull fouling.

At next dry docking in 2013 the FRC was in good condition, again only local damages were present and no adhesion problems onto previous coats could be detected. Large number of small tubeworms was found on the skeg, this had developed only during the last year before dry docking. Results observed in 2013 stimulated the RNLN to continue the test with this ship for another docking period. This time a third generation product from same supplier was applied on top of the previous coating. Results with this product after 3 years sailing will be presented.

Both the experience thus far and the potential of fouling release coatings to achieve reduction in fuel consumption (costs) and greenhouse gas emission, have stimulated ideas for implementation of a "Fuel Saving Hull Maintenance Strategy" by the Royal Netherlands Navy. Application of fouling release coatings on all four vessels of the M-class frigates and an intended 8 years docking interval for hull maintenance are important components therein. Experience will also be used to underpin a business case for other vessels of the fleet.

Oral 38A

Effects of biofouling on performance, as measured during a series of ship trials conducted on the high- speed, jet-powered catamaran USNS Choctaw County (EPF 2)

Dominic CUSANELLI[1,*], Michael LACNY[1], Eric HOLM[1]

[1] *Naval Surface Warfare Center, Carderock Division (NSWCCD), West Bethesda, Maryland USA*

* *dominic.cusanelli@navy.mil*

Biofouling, the accumulation and growth of waterborne organisms on a vessel's hull(s) and propulsor(s), severely degrades ship operating performance and results in a loss of speed as well as increased power and fuel consumption. Very little data currently exists on how biofouling affects the powering of vessels featuring alternative hull designs or propulsion systems. This presentation will outline the mechanics used for obtaining powering data under varying biofouling conditions for a high-speed, water-jet powered twin-hull catamaran.
USNS Choctaw County (EPF 2) provided a unique opportunity to evaluate biofouling effects on ship performance, over a reduced time period, as her hulls and propulsors were not well protected from accumulation of organisms. Thus she displayed a rate of biofouling accumulation much higher than comparable ships. The trial series was conducted as four individual underway phases, and during each equivalent powering events were executed. Trial phases were interspersed with waiting periods to allow for the accumulation and growth of biofouling, and with comprehensive hull and propulsor inspections and cleanings.
Inspections of the hulls for biofouling were carried out using a remotely-operated vehicle (ROV), while inspections of the propulsors were conducted by commercial divers. In order to obtain an improved understanding of spatial variation in biofouling as it may affect vessel performance, the ROV was used to record biofouling condition at 70 locations, 35 on each hull. To ensure accuracy of the powering measurements and comparisons between phases, trial events were executed while keeping ship engineering and environmental variables, and operating conditions, as equivalent as possible, with the exception of the hull and propulsor biofouling. The ship was fully instrumented to measure all required powering parameters, ship and environmental variables, and operating conditions. Reciprocal powering runs were conducted throughout the operational propulsion plant range from engine idle through full power with all water-jets powered and fully opened. Measured data were used to determine the characteristic relationships of ship speed, shaft RPM, shaft torque, delivered power, and propulsion engine fuel burn rates for each biofouling condition. Results were compared to evaluate the effects of the hull and propulsor biofouling on the ship's performance. Annual and quarterly power, fuel, and cost impacts for the biofouling levels were estimated using the Class annual speed-time profile.
Results of the evaluations indicated that moderate biofouling (biofilm 45%, grass 50%, shell 5%) caused a 4.3 knot reduction in maximum ship speed and a 19.2% increase in fuel consumption. Substantial bio fouling (biofilm 25%, grass 5%, shell 70%) effected a 11.4 knot speed reduction and 75.5% increase in fuel consumption. Most surprisingly, the contribution of moderately biofouled propulsors (biofilm 98%, shell 2%) was only a speed loss of less than 0.2 knots and a 2.5% increase in fuel consumption. Additionally, it was determined that generally biofouling does not have a greater impact in increasing drag at slower speeds than higher speeds for this alternative hull design and propulsion system.

Oral 39A

Propeller roughness condition and its impact on vessel fuel efficiency – A case study on US Navy CG- and DDG-class vessels

Crystal LUTKENHOUSE[1], Brian BRADY[2], Jamaal DELBRIDGE[1], Elizabeth HASLBECK[1,*], Eric HOLM[1], Dana LYNN[3], Thad MICHAEL[1], Angela ROSS[1], David STAMPER[1], Carol TSENG[1], and Anthony WEBB[2]

[1] Naval Surface Warfare Center, Carderock Division (NSWCCD), West Bethesda, Maryland USA
[2]Naval Ship Systems Engineering Station (NSSES), Philadelphia, Pennsylvania USA
[3] Retired from NSWCCD, Severna Park, Maryland USA

** elizabeth.haslbeck@navy.mil*

Fouling roughness on a ship's propeller(s) increases frictional resistance requiring vessels to use more power and therefore fuel in order to reach a given speed. US Navy ship propellers are generally unprotected from two forms of fouling – cathodic chalk (also referred to as mineral deposits) and biological fouling (hard and soft forms). This paper outlines methods we developed for assessing the fouling or roughness condition of in-service propellers, calculating the effect of this roughness on propeller performance, and estimating ship fuel penalties associated with the roughness.

We conducted a comprehensive survey of propellers US Navy vessels in order to quantify the baseline roughness (or fouling) condition of propellers across the fleet. We developed methods for assessing the fouling or roughness condition of in-service propellers, calculating the effect of this roughness on propeller performance, and estimating ship fuel penalties associated with the roughness. Our method accounted for roughness location on the blade (9 regions per face), hard fouling height and distribution, and severity and coverage of cathodic chalk. Drag coefficients were developed from existing methods (cathodic chalk) and from recent experimental data (hard biofouling) and were incorporated into a powering analysis that accounted for vessel operational tempo, plant alignment, fuel not used for propulsion, and engine specific fuel consumption to compute the roughness impact on propeller performance and calculate the associated baseline fuel penalty. The revised modeling process represents a significant improvement over approaches previously used by the Navy insofar as it accounts for the type, degree and distribution of fouling on propeller blade faces, the propeller fouling penalty over a wide range of speeds, and the operational profile and plant alignment of the ships.

Based on data from 57 inspections of 40 different ships at 5 US Navy bases during 2012-2013 we determined the annual propeller fouling penalty incurred by active DDG and CG class vessels to be 2.5% of propulsion fuel use. A relationship was established between the length of time spent pierside between propeller cleaning and ship operations. For ships going on deployment (ship departing its home port for at least four months and travelling to foreign ports), up to 50% of all pre-activity cleanings are conducted too far in advance of activity and by that hard biofouling develops and at least a subset is retained on the blade surfaces. Though our understanding is less clear for ship leaving port for shorter operations, at the time these ships go to sea data suggest propellers may be more heavily fouled than propellers of ships going on deployment. Results indicate where technology changes can be made in order to save fuel and enhance fleet operational efficacy and provide baseline metrics from which to estimate potential fuel savings and reduce propeller fouling impact on fleet operations. Modifications to the timing and frequency of cleanings and/or the use of propeller coatings are likely to have the most benefit.

Oral 40A

Influence of hydrodynamic stress on frictional drag and fouling community structure

J Travis HUNSUCKER*,[1,2], Kelli HUNSUCKER[1], Harrison GARDNER[1], and Geoffrey SWAIN[1]

[1] *Center for Corrosion and Biofouling Control, Florida Institute of Technology Melbourne, FL, USA*
[2] *SHIPWRIGHT LLC, Port Everglades, FL, USA*

* *jhunsucker2008@my.fit.edu*

Biofouling communities have been shown to vary in abundance, size and community structure along a ship hull and in static vs dynamic coating testing [1,2]. It is unknown what role the hydrodynamic stress plays in these differences and if they are manifested in the resulting frictional drag penalty. A study was conducted to examine the role of the hydrodynamic stresses on the development of the fouling community structure and resulting frictional drag. Three replicates of a 10 x 20 cm test panel coated with a commercial fouling release coating were exposed to three different hydrodynamic stresses that corresponded to a linear velocity of 0, 5, and 10 kts. The dynamic treatments were conducted on a 120 cm diameter disk with a duty cycle consisting of five days of rotation followed by two days of static immersion. Biofilm samples and frictional drag measurements were made immediately following the five day dynamic period. These measurements show the evolution of the community structure and resulting frictional drag for the three different speeds over a period of five weeks. During the static period, fouling was assessed to include total % fouling cover, diatom abundance and community composition. The frictional drag data were normalized by the fouling area and community composition to determine if there was a relationship between the normalized frictional drag and the hydrodynamic treatment.

[1] Hunsucker, Kelli Zargiel, et al. *Biofouling* **2014**, 30, 1133-1140.
[2] Zargiel, Kelli A., and G. W. Swain. *Biofouling* **2014**, 30, 115-129.

Session 13 – New antifouling responsive and textured surfaces - Room Bonaparte

Keynote 6B

Bio-inspired marine antifouling strategies for improved deployment performance

Fiona REGAN*

[1] *School of Chemical Sciences, Dublin City University, DCU Water Institute, Glasnevin, Dublin 9, Ireland*

** Fiona.regan@dcu.ie*

Biofouling on deployed in-situ sensors without regular removal or cleaning can disrupt sensor data collected. To date, this occurrence has been prevented by the application of biocidal coatings, many of which are harmful to the aquatic environment and which have now been legislatively controlled [1,2]. The current replacement antifouling materials under development are largely unsuited to sensor technologies as they have been developed with large scale applications in mind, such as those required by the shipping industry. Therefore, a strategy for the development of novel, sustainable, antifouling materials for sensor applications is required. Bio-inspiration refers to adapting strategies already developed in the natural world to problems encountered in modern science and technology [1]. Often the solution to a particular problem or a means of improving an existing solution can be seen if the natural solutions to a similar problem are studied in detail. Tuning material properties to inhibit or prevent settlement and attachment of microorganisms is of interest. Here, optimization of nano- and microscale structures on immersed surfaces can be utilized to improve cell removal while reducing adhesion strength and the likelihood of initial cellular attachment. Engineered surfaces capable of controlling cellular behaviour under natural conditions are challenging to design due to the diversity of attaching cell types in environments such as marine waters, where many variations in cell shape, size and adhesion strategy exist [3]. Nevertheless, understanding interactions between a cell and a potential substrate for adhesion, including topographically driven settlement cues, offers a route to designing surfaces capable of controlling cell settlement. Biomimetic design of artificial surfaces, based upon microscale features from natural surfaces, can be utilized as model surfaces to understand cell-surface interactions. The microscale surface features of the carapace from the crustacean Cancer pagurus for example has been previously found to influence the rate of attachment of particular organisms when compared to smooth controls [4]. In this study it was hypothesised that an AF effect could be induced through the replication of a synthetic surface where both the combination of surface features and chemistry would enhance the AF ability of these replicated surfaces. In this paper, the potential of biomimetic antifouling materials for application to environmental sensors is discussed. We outline a number of strategies for the identification and production of novel biomimetic antifouling approaches and discuss the pitfalls of developing antifouling materials based on biomimetic design.

[1] J. Chapman and F. Regan, Advanced Engineering Materials 01/**2012**; 14(4):B175-B184.
[2] J. Chapman, C. Hellio, T. Sullivan and F. Regan, *International Biodeterioration & Biodegradation*, Part A, **2014**, 86, 6-13.
[3] J. Chapman, T. Sullivan, E. Kitteringham, F. Regan, *Journal of Materials Chemistry B.* **2013**, 1, 6194-6200.
[4] T. Sullivan, K. Mcguinness, N. O Connor, F. Regan, *Bioinspiration & Biomimetics* **2014**, 9.

Oral 34B

Electroactive polymers based on ferrocenyl methacrylates for antifouling applications

Ronald NGUEMA EDZANG[1], The Hy DUONG[1], Marlène LEJARS*[1], Jean-François BRIAND[1], Jean-Manuel RAIMUNDO[2], Christine BRESSY[1], Hugues BRISSET[1]

[1] Université de Toulon, Laboratoire MAtériaux Polymères-Interfaces-Environnement Marin (EA 4323 MAPIEM),SeaTech-Ecole d'Ingénieurs, Toulon, France
[2] Université d'Aix-Marseille, CINaM, UMR 7325, case 913, 163 Ave de Luminy, 13288 Marseille, cedex 09, France

** Marlene.lejars@univ-tln.fr*

Because of the reversible redox properties of ferrocene and its anti-bacterial activity [1], ferrocenyl-based polymers are interesting to synthesize as new anti-adhesive binders for marine antifouling coatings [2].
We present here the homopolymerizations of different ferrocenyl-based methacrylic monomers by the RAFT process using 2,2-azobis(isobutyronitrile) (AIBN) as the initiator and 2-cyanoprop-2-yl dithiobenzoate (CPDB) as the transfer agent at 70°C, in toluene (Fig). [3]

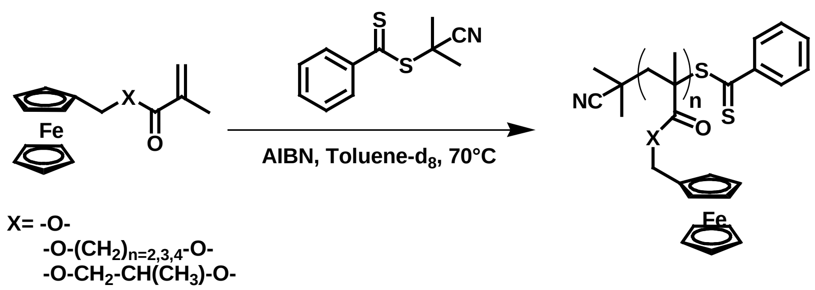


Fig. Synthesis of ferrocenyl methacrylic homopolymers by the RAFT process

Physico-chemical properties (monomer conversion, number-average molar masses (M_n), dispersity values,…) will be described. Electrochemical properties of homopolymers will also be discussed and their anti-adhesive properties toward marine bacteria will be presented.

[1] M. Okochi, T. Matsunaga, *Electrochimica Acta*, **1997**, 42, 3247-3250.
[2] M. Lejars, A. Margaillan, C. Bressy, *Chem. Rev.* **2012**, 112, 4347-4390.
[3] R. W Nguema Edzang, M. Lejars, H. Brisset, J.-M. Raimundo, C. Bressy, *RSC Advances*, **2015**, 5, 77019-77026.

Oral 35B

TRAP - Triggered Antifouling Protection

Mattias BERGLIN*[1], Anna JANSSON[1], Anna-Lisa WRANGE[1], Arne HALLGREN[2], Per JONSSON[3] and Emiliano PINORI[1]

[1]Department of Chemistry, Materials and Surfaces, SP Technical Research Institute of Sweden, Box 857, SE-501 15 Borås, Sweden
[2] INOVYN Sverige AB, SE-444 83 Stenungsund, Sweden
3 Dept of Marine Sciences, University of Gothenburg, SE-452 96 Strömstad, Sweden

** Mattias.berglin@sp.se*

Present biocide-based antifouling strategies are based on a continuous release of biocides into the environment if the antifouling efficacy is to be maintained. Both from an environmental and life cycle assessment such biocide-release solutions could not be regarded as sustainable. Sessile marine species are susceptible to colonization by epibionts and many of them produce bioactive secondary metabolites to remain fouling free. To minimize the usage of resources some of these organisms have employed the strategy of immobilizing the secondary metabolite at the surface/water interface. First upon surface exploration the epibiont comes into contact with the substance. We have biomimicked this strategy for development of low emission antifouling [1, 2]. The paradigm shift from "release" to "no-release" opens up new possibilities as there is no need for eroding coating systems for long-term antifouling efficacy and common bulk polymers could be transformed into antifouling systems.

In this presentation the theoretical background, i.e. requirements for antifouling substances and polymer matrix, will be discussed. Initial results of transforming a common polymeric film (wrap) made of polyvinyl chloride (PVC) into maintaining long-term barnacle protection will be used as an example. In short, the PVC film was loaded at 0.1% with a natural substance (abamectin), which is produced by the bacteria *Streptomyces avermitilis*. The PVC hardness was controlled by varying concentrations of plasticizer, and the effect on release and antifouling efficacy was investigated. The surface properties of the PVC films were thoroughly characterized both prior and after immersion in artificial seawater (ASW) by SEM, ToF-SIMS and water contact-angle measurements. The PVC films were evaluated in a field study in Sweden and the one year follow up data will be presented.

[1] E. Pinori, H. Elwing, M. Berglin, *Biofouling*, **2013**, 29, 763-773.
[2] E. Pinori, M. Berglin, LM. Brive, M. Hulander, M. Dahlström, H. Elwing, *Biofouling* **2011**, 27,941-953.

Oral 36B

Polymers supported electroactive species for antifouling applications

The Hy DUONG[1], Djibril FAYE[2], Frédéric GOHIER*[2], Hugues BRISSET[1], Pierre FRERE[2], Jean-François BRIND[2], Philippe LERICHE[2], Christine BRESSY[1]

[1] Université de Toulon, Laboratoire MAtériaux Polymères-Interfaces-Environnement Marin (EA 4323 MAPIEM), SeaTech -Ecole d'Ingénieurs, Toulon, France
[2] Université d'Angers, MOLTECH-Anjou, UMR CNRS 6200, groupe SCL, UFR Sciences, 2 bd Lavoisier, Angers, France

** frederic.gohier@univ-angers.fr*

In the scope of developing microstructured redox addressable polymers for antifouling applications,[1] one important step consists in designing oligomeric or polymeric species with suitable redox properties, reasonable processability and controlled size. With this objective, we have chosen a strategy which implies in a first main step the preliminary synthesis of a non conjugated polyacrylic polymer with controlled molar masses **A**. Electroactive pendent groups can then, by chemical or electrochemical oxidation, lead to various non-soluble electroactive species targeted **B**. Moreover, the strategy chosen allows the geneses of co-polymers propitious for microstructuration [2].

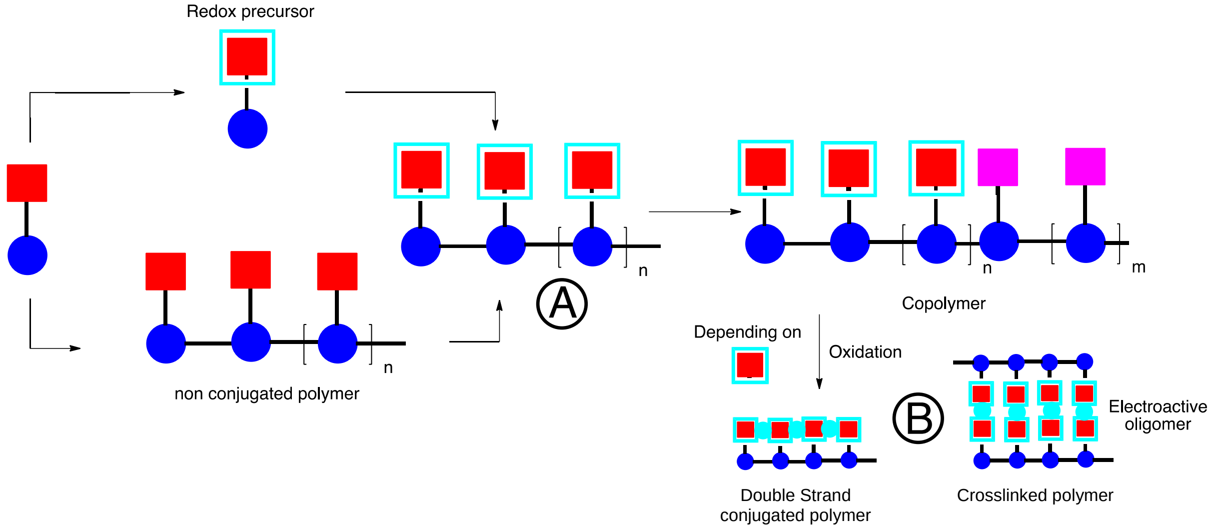


Fig. Explored strategies towards targeted electroactive microstructured polymers

We present here the different approaches developed for obtaining targeted polymers, their limitations, advantages and potentialities. Electrochemical and spectroscopic characterizations of polymers are also discussed. Noteworthy, biological tests are under investigation to determine the efficacy of the electro-active polymers against marine bacteria and will be presented in details elsewhere.

[1] ANR Astrid, AF-electrocoatings, http://af-electrocoatings.univ-tln.fr/project-af-electrocoatings/
[2] T.H. Duong, J-F. Briand, A. Margaillan, C. Bressy, *Appl. Mater. Interfaces* **2015**, 7(28), 15578–86.

Oral 37B

Patterned photo-crosslinking of thermo-responsive hydrogels for dynamic surface structures.

Sander KOMMEREN[1]*, Tim SULLIVAN[1], Josie DONGMO[2], Cees BASTIAANSEN[1,3]

[1]*Eindhoven University of Technology, Dept. of Chemical Engineering and Chemistry, Functional Organic Materials & Devices, Eindhoven, The Netherlands*
[2]*Johannes Gutenberg-University Mainz, Institute for Organic Chemistry, Mainz, Germany*
[3]*Queen Mary University of London, School of Engineering and Material Science, London, United Kingdom*

* *s.kommeren@tue.nl.*

The development of smart surfaces that have dynamic properties have been actively pursued in recent years.[1] For example thermoresponsive hydrogel surfaces have been used for the investigation of cell behavior and even as potential antifouling coatings.[2-4] The dynamic properties of such coatings are thought to actively help prevent and/or detach micro- and macro-fouling organisms. Here, we report a novel approach for creating thermoresponsive hydrogel coatings with a switchable surface topography on a single substrate. The hydrogel coatings are based on the thermal responsive poly(N-isopropylacrylamide) (PNIPAm) utilizing a solubility change at the lower critical solution temperature (LCST) at around 32 °C. The addition of a photo-crosslinking monomer to the PNIPAm polymer provides the ability to cross-link the polymer after polymerization. The use of a polymer makes it possible to make coatings on a single substrate by, for example, spray-coating. The polymer coating is cross-linked by multiple UV mask illumination steps resulting in a cross-link density pattern in the coating. This results in a predesigned surface topography when swollen. Due to the thermoresponsive properties of the polymer, the hydrogel can be switched to a smooth state when the temperature is increased and back to a structured state with a decrease in temperature. A smart dynamic coating that changes its surface properties with temperature has been created with potential as an active antifouling coating.

[1] P.M. Mendes, *Chem Soc Rev* **2008**, 37, 11, 2361-2580.
[2] L.K. Ista, G.P. López, *Journal of Indust. Microbiol. & Biotechnol.* **1998**, 20, 121-125.
[3] M.A. Molina, C.R. Rivarola, M.F Broglia, D.F. Acevedo, C.A. Barbero, *Soft Matter.* **2012**, 8, 307.
[4] Q. Yu, L.K. Ista, P. López, *Nanoscale*, **2014**, 6, 4750.

Oral 38B

Progress in Philips RunWell UV-based anti-fouling technology

Bart SALTERS[1*], Roelant HIETBRINK[2],

[1] *Philips Research, Eindhoven, The Netherlands.*
[2] *Philips IP&S, Eindhoven, The Netherlands*

* *Bart.Salters@philips.com*

At ICMCF 2014, we presented the novel concept of using UV light for anti-fouling purposes. [1] By emitting UV light of a specific wavelength and intensity, outwards of the submerged surface, this surface can be kept clean. At that moment in time, we had obtained a ‘proof of principle’, though of course at that early stage, lots of questions were still open. Since, a lot of progress has been made, as we focused our work on the most crucial areas. In this presentation, we will give an update on the progress in several of these areas.
First of all, we will give an update on the effectivity of UV-based anti-fouling. We have tested the performance in various places in the world, in various conditions; and results will be shown. We have established power and intensity requirements, and have tested several optical concepts that deliver those power levels to the active surface. These numbers translate into total power requirements for an entire hull solution
One of the main challenges is the mechanical strength of such a solution, and the associated lifetime of the envisioned product. Results of these tests will be discussed, as well as the conclusions and subsequent improvements.
Based on these advances in our technology, an updated outlook on the business case will be shared, and progress in the product development will be discussed. Finally, results from experiments in some additional application areas, such as heat exchangers and niche areas will be shown.

Fig. 1: ~30x30cm sample, virtually spotless after 3 month immersion at sea in high fouling conditions. The test surface outside of the active area is completely covered in barnacles.

[1] B. Salters, R. Hietbrink, ICMCF **2014**

Oral 39B

Development of an inexpensive nontoxic biomimetic composite antifouling coating

R. Shane ADDLEMAN[1]*, Curtis LARIMER[1], Chris BARRETT[1], Jonathan D. SUTER[1], Xiye XIONG[2], Chuck SMALLWOOD[1], Eric WINDER[3], Robert JETERS[3], Jiyeon PARK[3], and George T. BONHEYO[3]

[1] *Pacific Northwest National Laboratory, Richland, USA.*
[2] *University of Pittsburgh, Pittsburgh, USA.*
[3] *Marine Science Laboratory—Pacific Northwest National Laboratory, Sequim, USA.*

**Raymond.Addleman@pnnl.gov*

We will present research efforts into the development of a novel polymer nanomaterial composite coating that has demonstrated excellent antifouling properties. The coating combines two biomimetic approaches: a lotus leaf like texture with the slippery surface of a pitcher plant. The result is a low surface energy, foul-resistant, self-healing surface. The coating is a blend of inexpensive, nontoxic biocompatible components. When sprayed or painted on a surface and cured, the coating is superhydrophobic. Then a low-energy lubricant is infused throughout the structure, resulting in a stable slippery liquid interface. Nanoporous material in the coating aids in retention of the lubricant, extending useful lifetime of the slippery liquid surface. Nanoporous material also creates a reservoir for slippery liquid that allows the coating to have self-healing properties. Marine, medical, environmental and sensor applications will be discussed.

Fig. 1: A biomimetic composite coating that emulates both the superhydrophobic lotus leaf and the slippery pitcher plant repels water from the area surrounding the ICMCF lettering. This low cost sprayable coating has low surface energy and a self-healing surface.

Session 10 – Impact & Applications of marine fouling and corrosion research and technologies - Room Colbert

Oral 41A

Design of pressure drop section to measure frictional drag of fouling control surfaces

Serkan TURKMEN*[,1], Irma YEGINBAYEVA[1,] and Atlar MEHMET[1]

[1] *Newcastle University School of Marine Science and Technology, Newcastle upon Tyne, United Kingdom.*

* *serkan.turkmen@ncl.ac.uk*

The development of test methodologies for the evaluation of the hydrodynamic performance of fouling control surface including the effect of coatings and biofilms is particularly complex as the turbulent flow regime experienced on the surface of a ship needs to be simulated in experimental facilities. Using coated flat test panels in narrow flow channels (i.e. flow cells) is less complex, more robust and attractive to investigate the skin friction characteristics of these panels in fully developed turbulent flows.

Within the framework of the EU-FP7 project SEAFRONT [1], Newcastle University's School of Marine Science and Technology (UNEW-MST) enhanced their existing flow cell measuring section, which is used for classical biofouling adhesion strength tests, with a sophisticated pressure drop measurement section to evaluate the skin friction characteristics of flat test panels.

This new section provides effective measurements of the skin friction characteristics of standard UNEW test panels (218mmx600mm) in clean and biofilmed conditions in seawater. The new section also allows to fit an enhanced adaptor, which can accommodate number of micro slides, to conduct classical biofilm adhesion strength tests as well as the pressure drop measurements for skin friction analysis.

In this study the design and numerical optimization of the new pressure drop section as well as its calibration process are presented. The physics of the flow were simulated by solving the Reynolds Averaged Navier Stokes (RANS) equations. An LDA window was introduced in the test section to calibrate the system by measuring the flow profile.

The experiments convincingly show that the new pressure drop section can simulate typical boundary layer flow regime around a commercial ship and can be thus successfully used to measure the drag performance of clean and biofilmed (mainly slime) coatings in seawater or fresh water. The measured data shows a good agreement between the numerical predictions.

[1] Seafront "Synergistic Fouling Control Technologies ", 2013, Annex-I Description of Work, EU-FP7 Collaborative project, Grant agreement no: 614034

Oral 42A

Validation of computational model for predicting frictionalresistance by using typical profile data for fouled surfaces

Bercelay NIEBLES ATENCIO*[1], Jan WIELANT[2], Meisam FARZANEH[1], Valery CHERNORAY[1]

2OCAS NV, Zelzate, Belgium

**meisam@chalmers.*se

Fouling is the major contributor to the surface roughness and waviness of a ship hull. Foulingincreases frictional resistance and consequently, fuel consumptions. Therefore, it is essential to get adeep understanding of influence of fouling on the ship drag force. In the present work, we propose anumerical technique to simulate fluid flows over fouled surfaces using Computational Fluid Dynamics (CFD). To study the growth of fouling a number of panels are exposed in the sea site and scanned atregular time intervals. 3D surface profiles are measured by means of laser scanningin dry and wetstate and after removal of the loose fouling fraction. The scanned geometries are imported into a CFDsoftware and flow simulations are performed. To accurately capture the microscale features of fouling, sufficiently fine computational mesh is generated and suitable computational models are selected.Roughness wall function, representing the influence of roughness on flow boundary layer, is developed and drag force is calculated. The effects of fouling size and characteristics on the boundary layer growth and flow resistance are investigated. To examine the effects of fluid velocity, computational simulations are performed for several flow Reynolds Numbers.

Acknoledgements: This research is supported by the EU FP7 Project “Low-toxic cost-efficient environment friendly antifouling materials” (BYEFOULING) under Grant Agreement no. 612717.

Oral 43A

A new approach to predicting the impact of fouling control coatings on ship efficiency

Barry KIDD *, Haoliang CHEN, Alistair FINNIE, Jack HAYDEN, Richard RAMSDEN

International Paint Ltd., Stoneygate Lane, Felling, Gateshead, NE10 0JY, UK

* barry.kidd@akzonobel.com

A new approach to provide ship owners and operators with more reliable and transparent predictions of the relative powering requirements and potential fuel and CO_2 savings for ships coated with different fouling control coating options will be discussed. The presentation will provide an overview of the key challenges for marine coatings suppliers, the market drivers that led to the development of this new predictive tool, and the predictive models that underpin it.

This new approach has led to a number of refinements and improvements over previous models that can be broken down into two main parts. Firstly the prediction of the total roughness change over a drydock cycle based on a number of aspects including a new total roughness model incorporating hull and coating micro, macro and fouling roughness, a new model linking substrate preparation and coating application choices to macro roughness, new coating-specific fouling roughness models, and an enhanced understanding of the impact of vessel operational profile including hull cleaning events on coating performance. Secondly the correlation of total roughness, total ship resistance and powering requirements, based on new Computational Fluid Dynamics (CFD) resistance and wake field flow models for different representative hullforms, incorporation of these CFD models in optimised ship powering requirement calculations, derivation of speed / power curves as a function of total roughness, and an enhanced understanding of how ship powering requirements is influenced by the total roughness.

The development of these new predictive models is both challenging and complex and the presentation will focus on the development of fouling control coating performance and vessel powering requirement models. In particular the connection between fouling control coating performance and vessel operational profiles will be discussed in conjunction with the benefits that arise from the adoption of more transparent models of future performance. Finally, the presentation will review approaches to compare and validate ship performance prediction models with data collected from vessels in service.

Oral 44A

A practical approach for predicting fouling impact on ship resistance

Yigit Kemal DEMIREL*, Paula KELLETT, Osman TURAN, Atilla INCECIK

University of Strathclyde, Glasgow, United Kingdom

* *yigit.demirel@strath.ac.uk*

The efficiency of ships is a key concern for the marine industry however the prediction of this efficiency in realistic conditions can still prove problematic. For this reason, a practical approach to the prediction of the impact of biofouling on ship resistance is proposed.
Firstly, the total resistance values of an in service coastal tanker model were obtained at a ship speed of 11 knots and validated with the experimental data generated in the AQUO Project [1]. Following this, a new roughness function model was developed within the scope of the FOUL-X-SPEL Project [2], based on existing literature and employed in the wall-function of a CFD solver. Full-scale unsteady 3D RANS simulations were then carried out to predict the effect of different biofouling conditions on the resistance of the ship model, and the percentage increases in drag coefficients were predicted.
The resulting increases in the drag coefficients were then compared with those obtained using the similarity law procedure of Granville [3]. Very good agreement was observed between the two sets of results. This suggests that the present CFD approach can predict the roughness effects of biofouling on the resistance of a 3D full-scale ship. In other words, the applicability of the wall-function approach to simulate the surface roughness on ship hulls, rather than on flat plates, was shown.
The main advantage of using CFD is that it makes it possible to combine roughness effects with nonlinear effects such as spatial distribution of fouling, as different wall functions can be applied on different surfaces or different parts of a surface, to more accurately represent observed fouling on real ships. In addition, simulations such as ship motions in waves, self-propulsion and manouevring can be conducted with realistic hull surface conditions. These would not be possible using the similarity law scaling procedure as this procedure can only predict the roughness effects on the frictional resistance of flat plates representing ships. Without a doubt, these conditions and the roughness functions used in this study may not necessarily represent all types of fouling conditions, since the assumptions made are based on the observations made in the literature. Future pieces of work may be the investigation of the roughness function behaviours of heterogeneous fouling accumulation, as seen on hulls, and an investigation into the range of applicability of the selected roughness length scale for the present conditions.
It is important to note that the application of the proposed wall-functions within CFD does not cause any additional run-time for a typical towing test simulation. For this reason, this method is not expected to cause any additional run-time for a typical self-propulsion or seakeeping simulations. Therefore, this approach stands as a practical prediction method for both academia and industry.

[1] AQUO (2012-2015). AQUO: Achieve QUieter Oceans by shipping noise footprint reduction [Online]. http://www.aquo.eu/
[2] FOUL-X-SPEL. (2011-2014). FOUL-X-SPEL: Environmentally friendly antifouling technology to optimise the energy efficiency of ships [Online]. http://www.foulxspel-antifouling.com/
[3] P. S. Granville, *Journal of ship research* **1958**, 2, 52-74.

Session 7 – Adhesion, signaling & biofilm formation - Room Colbert

Keynote 6A

Quorum sensing, biofilms and biofouling: a complex relationship

Ana OTERO[*,1], Andrea MURAS[1], Celia MAYER[1] and Manuel ROMERO[1,2]

[1]*Departamento de Microbiología y Parasitología, Facultad de Biología, Edificio CIBUS; Universidade de Santiago de Compostela*
[2] *School of Life Sciences, Centre for Biomolecular Sciences, University Park, University of Nottingham, Nottingham. UK.*

* *anamaria.otero@usc.es*

Extracellular chemical communication systems, generally known as Quorum sensing (QS), are used by bacteria to coordinate the expression of genes involved in many key physiological processes, mainly related to adaptation to the environment and pathogenesis, including biofilm formation and/or dispersion. The discovery in the late 1990’s by Givskov et al. [1] that the red seaweed *Delisea pulchra* produced specific compounds –the halogenated furanones- to block the Gram-negative bacteria QS systems and avoid surface colonization by bacteria, ignited the search of novel anti-biofilm compounds targeting the bacterial QS systems. Since then, our knowledge on biofilm structure and physiology has greatly advanced and the potential of QS inhibition as anti-biofilm strategy has been confirmed in several systems. Control of bacterial biofouling was successfully achieved in membrane bioreactors for wastewater treatment by using Quorum Quenching (QQ) enzymes in a pilot-plant scale [2]. A similar strategy has proved effective for the control of pathogenic bacteria attachment on medical surfaces [3]. In our laboratory we have been studying the effect of QQ enzymes on dental plaque formation. Although the production of acyl-homoserine lactones (AHLs), the signals used by Gram-negative bacteria, has not been described in cultivable oral pathogens the addition of AHL-degrading enzymes greatly reduced dental plaque formation *in vitro*. This result suggests that further research on the mechanisms of action of QS inhibitors and enzymes in complex natural biofilms is required.

In the marine environment, the production of QS signals by bacteria has been described to serve as a cue for eukaryotic organisms for settlement [4] and therefore the interference with QS mechanisms has been proposed as a novel anti-fouling strategy. On the view of the very high QQ activity found in marine samples [5], we have been evaluating marine bacteria as source QS inhibitors with anti-biofilm activity in the framework of the EU Project Byefouling. One of the main problems encountered is the selection for suitable marine bacteria to be used as models for anti-biofilm research since, as found for dental plaque, the lack of activity of a compound in single-species biofilm does not exclude the presence of activity against mixed natural populations, and/or an effect on eukaryotic colonization.

Acknowledgements: This work has been partially supported by the EU Project Byefouling (Seventh Framework Programme for research, grant agreement nº 612717).

[1] M. Givskov, R. de Nys, M. Manefield, L. Gram, R. Maximillien, L. Eberl, S. Molin, P.D. Steinberg, S. Kjellegerg, *J. Bacteriol.* **1996**, 178, 6618-6622.
[2] S. Lee, S-K. Park, H. Kwon, S.H. Lee, K. Lee, C.H. Nahm, S.J. JO, H-S. Oh, P-K Park, K-H. Choo, C-H. Lee, T. Yi, *Environ. Sci Technol*. **2016***,* 50, 1788-1795.
[3] K. Ivanova, M. M. Fernandes, A. Francesko, E. Mendoza, J. Guezguez, M. Burnet, T. Tzanov. ACS *Appl. Mater. Interfaces* **2015**, 7, 27066–27077.
[4] S. Dobretsov, M. Teplitski, V. Paul, *Biofouling* **2009**, 25, 413-427.
[5] M. Romero, A.B. Martín-Cuadrado, A. Otero, *Appl. Environ. Microbiol.* **2012,** 78, 6345-6348.

Oral 45A

Inhibition of violacein production in marine bacteria *Pseudoalteromonas ulvae* TC14 by quorum sensing inhibitors

Armande Mireille AYE[1], Sofyane ANDJOUH[1] Olivier BOTTZECK[1], Annie PRAUD-TABARIES[1], David DAUDE[2], Éric CHABRIERE[2], Yves BLACHE[1] and Maëlle MOLMERET*[1]

[1] Laboratoire Matériaux Polymères Interfaces Environnement Marin (MAPIEM) Université de Toulon, CS 60584, 83041 Toulon Cedex 9 France.
[2] Unité de Recherche sur les Maladies Infectieuses et Tropicales Emergentes France UMR CNRS-IRD 6236, IFR48, Aix-Marseille Université, Marseille, France

** maelle.molmeret@univ-tln.fr*

Biofouling control on immersed inert surfaces or in moist atmosphere is a necessity in the marine sector for both economic and environmental reasons. Microbial biofilm formation, the initial step of biofouling development, can be intrinsically linked to the communication system "quorum sensing" (QS). Several Gram negative bacteria use quorum sensing mechanism to express many phenotypical behaviors including the production of virulence factors, pigment production, luminescence and biofilm formation [1]. Thus, the inhibition of quorum sensing mechanism in these bacteria may lead to slow biofilm formation down and subsequently biofouling settlement [2]. In order to screen QS inhibitors in marine conditions, the marine bacterium *Pseudoalteromonas ulvae* called TC14 has been proposed as potential marine biosensor [3].
QS Inhibition assays using TC14 were performed with commercial compounds [4, 5], synthetic analogues [6, 7] and natural lactonases SsoPox [8]. The commercial 3-oxo-C_6-HSL was able to inhibit violacein production, mobility, adhesion and biofilm formation at a non-toxic concentration. Esculetin and *p*-benzoquinone, known to interfere with bacterial QS were also involved in inhibition of violacein and biofilm formation. Some inhibitors such as esculetin seems compete with the AHLs molecules which agonize the production of violacein in TC14 [3].
Overall, this study show that the marine strain *P. ulvae* TC14 is responsive to QS inhibitors and suggests that it may be used as a tool for the detection of anti-QS molecules in conditions closed to the marine environment. The long term objective is to find a way to limit biofilm formation, using various non-toxic molecules targeting a large spectrum of marine bacteria.

[1] M. B. Miller, B. L. Bassler, *Annu. Rev. Microbiol.* **2001**, 55, 165-199.
[2] S. Dobretsov, M. Teplitski, V. Paul, *Biofouling*, **2009**, 25, 413-427.
[3] A. M. Ayé, M. Bonnin-Jusserand, F. Brian-Jaisson, A. Ortalo-Magné, G. Culioli, R. Koffi Nevry, N. Rabah, Y. Blache, M. Molmeret, *Microbiology*, **2015**, 161, 2039-2051.
[4] G. Brackman, U. Hillaert, S. Van Calenbergh, H. J. Nelis, T. Coenye, *Res. Microbiol.* **2009**, 160, 144-151.
[5] S. Dobretsov, M. Teplitski, M. Bayer, S. Gunasekera, P. Proksch, V. J. Paul, *Biofouling*, **2011**, 27, 893-905
[6] S. Andjouh, Y. Blache, *Bioorg. Med. Chem. Lett*. **2015**. 25, 5762-5766.
[7] D. Linares, O. Bottzeck, O Pereira, A. Praud-Tabariès, Y. Blache, *Bioorg. Med. Chem. Lett*. **2011**, 21, 6751-6755.
[8] S. Hraeich, J. Hiblot, J. Lafleur, H. Lepidi, L. Papazian, J.-M. Rolain, D. Raoult, M. Elias, M. W. Silby, J. Bzdrenga, F. Bregeon, E. Chabriere, *PLos ONE* **2014**. 9**,** e107125.

Oral 46A

Adsorption of alginate and albumin affects colonization behaviors of bacteria and diatoms in artificial seawater

Xiaoyan HE and Hua LI*

Key Laboratory of Marine Materials and Related Technologies, Key Laboratory of Marine Materials and Protective Technologies of Zhejiang Province, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China.

** lihua@nimte.ac.cn.*

Alginate is a typical linear polysaccharide widely existed in some brown algae and bacteria that actively take part in fouling and biofouling. Alginate-related biofouling relies on its ability to form bonds by binding divalent cations. Albumin is also known for its influence on biofouling. Here, alginate and albumin were chosen as the typical biomacromolecules to build a simplified conditioning layer model to investigate their influence on adhesion of typical bacteria and diatoms. Negative-staining electron microscopy was employed to characterize the conformations of the molecules after their interactions with important divalent cations present in artificial seawater. It is speculated that the conformational changes would play significant roles in regulating the adhesion of microorganisms. Single-stranded alginate with varied length of 50-385 nm depending on matrix materials was realized. After recruitment of divalent calcium ions to form calcium alginate, unusual tangling of the alginate chains is clearly seen, giving rise to formation of spiral conformation of exaggerated egg-box assembly. The assembly consists of four repeating units, each of which comprises three Ca^{2+}-linked G-block pairs and one M-block pair. Preferable linking of calcium ions with alginate followed by quick adsorption on substratum creates a conditioning layer, showing marked capability of regulating formation of biofilm required for occurring of biofouling through promoting effectively colonization of *Bacillus sp.* and attachment of *Phaeodactylum tricornutum*. Moreover, adsorption of albumin showed positive effect on colonization of *Bacillus sp.* and attachment of *Phaeodactylum tricornutum*. Apart from their involvement in conditioning layer, adsorption of alginate and albumin also affects EPS formation, protein expression, and polysaccharide synthesis, which enhance adhesion of the microorganisms. The approach we proposed in this research is effective in visualizing conformations of polysaccharides/proteins after interactions with divalent cations, in turn facilitating biofouling research.

Oral 47A

A sticky situation: understanding the mechanism of diatom adhesion

Nicole POULSEN*[1], Nils KRÖGER[1,2], Matthias T. BUHMANN[1], Martina LACHNIT[1], Jennifer KLEMM[1]

[1]ZIK B CUBE, Technische Universität Dresden, Dresden, Germany;
[2]Department of Chemistry and Food Chemistry, Technische Universität Dresden, Dresden, Germany;

** poulsen@bcube-dresden.de*

Diatoms are unicellular algae that have the impressive capability of colonizing any natural and man-made submersed surfaces, including many of the commercially available antifouling surfaces. Surface adhesion of raphid pennate diatoms is achieved through the secretion of adhesive mucilage strands through a dedicated slit in their silica cell wall, which is termed the raphe. Adherent cells can then move by gliding across the surface, depositing trails of the adhesive material. In order to combat the tenacious fouling ability of diatoms on man-made structures a deeper understanding of the chemical composition of their adhesive biomolecules is required. Previously we have developed a method to purify the diatom adhesive trails and demonstrated that they contain a complex mixture of carbohydrates and proteins [1]. Unlike the well characterized adhesion mechanism of marine mussels, diatom adhesion does not appear to be mediated by proteins containing dihydroxyphenylalanine (Dopa). To gain a deeper understanding into the role of proteins in diatom adhesion we have performed a proteomics analysis of the adhesive trails isolated from the problematic fouling diatom, *Amphora coffeaeformis*. Among the proteins identified in this analysis are a set of 13 proteins which exhibit rather diverse sequences in their N-terminal regions but share a conserved C-terminal domain, which includes the tetrapeptide motif GDPH. Interestingly, the GDPH motif has previously been observed in a small number of other proteins (i.e. sea star foot protein [2], mucins [3], sperm zonadhesin [4]) where it undergoes autocatalytic proteolysis between the aspartic acid and proline residues triggered by a decrease in pH. Antibodies raised against some of the diatom GDPH proteins have confirmed their presence in the adhesive trails.

Acknowledgments: This work was supported by the U. S. Air Force Office of Scientific Research [grant number FA9550-12-1-0093] to NP and NK

[1] Poulsen et al. *Biofouling* **2014** 30, 513-523.
[2] Hennebert et al *PNAS* **2011** 111: 6317-6322.
[3] Lidell et al *J Biol Chem* **2003** 278:13944–13951.
[4] Bi et al *Biochem J* **2003** 375:477–488

Oral 48A

Analysis of marine adhesives of diatoms with X-Ray nanoprobe fluorescence

Susan STUHR[1,*], Tobias SENKBEIL[1], Peter CLOETENS[2], Yang YANG[2], and Axel ROSENHAHN[1]

[1] Analytical Chemistry – Biointerfaces, Ruhr-University Bochum, Bochum, Germany
[2] ESRF, Grenoble, Cedex, France

* *susan.stuhr@ruhr-uni-bochum.de*

Fouling release technologies aim on weakening adhesion to keep surfaces clean. Understanding the mechanism of adhesion allows to develop new techniques to interfere with adhesives and to foster adhesive failure. We try to understand which inorganic and organic components are present in the underwater adhesive. Diatoms secrete an underwater adhesive that is capable to stick to surfaces with a surprisingly large range of physicochemical properties. Especially their prevalence on modern fouling release coatings causes a severe problem for marine coating industry. The adhesive of diatoms contains a complex mixture of substances including majorly polymers such as polysaccharides or glycoproteins. While the organic matrix can be studied by analytical techniques including gel electrophoresis, HPLC and mass spectrometry, the inorganic components in the material are difficult to access due to their small quantities. To analyze presence and activity of metals and halogens in diatoms, synchrotron based nanofocus X-ray fluorescence (XRF) has been applied. The diatom species for the experiment is *Navicula perminuta*. The algae could be completely removed from the surface with a water flosser and the adhesive traces could be visualized by staining. SEM-EDX measurements at unstained samples showed the presence of Cl in the adhesive but could not be used for the evidence for the heavier metals due to the low excitation. Data from XRF experiments carried out at PETRA III (P06) and the ESRF (ID16A-NI) showed the elemental composition of the algae shell and could be also used to determine elements present in the secreted EPS.

Oral 49A

The effect of surface chemistry on diatom movement and aggregation

John FINLAY*, Nick ALDRED, Sofia FRANCO, Anthony CLARE

School of Marine Science and Technology, Newcastle University, UK

* *John.Finlay@newcastle.ac.uk*

Diatom slimes are a persistent problem on silicone-based elastomeric fouling-release coatings. Diatoms generally attach strongly to these low energy surfaces and, although the biofilms are relatively thin, cause drag on the hulls of ships resulting in substantial economic losses. Diatoms that constitute these biofilms are capable of gliding motion that facilitates movement to regions that offer better conditions for survival and multiplication. The motile cells produce polymers which have dual functionality, serving as both motility polymers and also as adhesives attaching the cells to the surface. Differences in the movement and dispersion of diatom cells across surfaces is related to surface properties and may be indicative of biofilm development and adhesion.
Analysis of diatom motility was accomplished using a combination of approaches. The mean number of motile cells was determined for a range of surface chemistries and compared to the results of hydrodynamic removal studies. Time-lapse recordings at 1 fps were made over a 20-minute period on the same range of surfaces and the resulting frames were compiled into movies from which data relating to the mean speed and direction of motile cells were collected. Longer duration experiments monitored the movement of diatoms on different surfaces using a phase contrast inverted microscope with a motorised programmable stage, in order to observe surface-specific differences in the distribution of cells on the surfaces over time. The movement of diatoms on surfaces can lead to cell aggregations that may influence the structure of more mature biofilms. Analysis of this process can provide information that will assist the understanding of cell-surface interactions critical to effective antifouling and fouling-release performance of marine coatings.

Oral 50A

Evaluation of quorum quenching and anti-biofilm activity in temperature resistant marine bacteria isolated from marine macroalgae

Andrea MURAS[1*], Celia MAYER[1], Sarah IKEDIASHI[1] and Ana OTERO[1]

[1] *Universidade de Santiago de Compostela, Santiago de Compostela, Spain.*

* *andrea.muras@usc.es*

The formation of bacterial biofilm is the first step in the development of the biofouling process and is often dependent on a cell-to-cell chemical communication process known as Quorum Sensing (QS). The Gram-negative marine bacteria involved in this process frequently use acyl-homoserine-lactones (AHLs) as the main quorum signal. Therefore, the identification of molecules and/or enzymes interfering with AHL-mediated QS signal systems, a process known as Quorum Quenching (QQ), has been proposed as a novel anti-fouling strategy.
Due to the interest in spore-producing bacterial species for biotechnological applications, a collection of 155 thermo-resistant marine bacteria isolated from the surface of macroalgae from Atlantic Ocean were screened for QQ activity using *Chromobacterium violaceum* biosensors. Three types of extracts (aqueous and methanolic extracts from biomass and dichlorometane from culture media) of the strains presenting QQ activity were tested for anti-biofilm activity against the marine, biofilm-forming bacteria *Vibrio aestuarianus*, *V. tubiashii, Pseudoalteromonas flavipulchra* and *P. maricaloris* using the crystal violet staining assay. The anti-biofilm activity of the most promising candidates was confirmed using the xCELLigence System RTCA SP (ACEA, Biosciences Inc.).
Seven out of the 155 strains tested presented wide-spectrum QQ activity. All of them were identified as members of the genus *Bacillus*. The crystal violet screening method allowed identifying 15 extracts with anti-biofilm activity, of which only four presented QQ activity. The extracts obtained from the most promising anti-biofilm candidates were tested in the xCELLigence system against *P. flavipulchra* and *P. maricaloris*. The experiments using the xCELLigence technology allowed the identification of 2 extracts that were able to reduce the biofilm formation in *P. flavipulchra* or *P. maricaloris* by 40-50%, but none of them was able to intercept the QS signals in the biosensors.
Results indicate that the anti-biofilm activity found in the marine *Bacillus* strains against mono-specific marine biofilms is not related to the presence of QQ activity against AHLs. However, the efficiency of QQ strategies as anti-fouling approach in the multi-species biofilms present in the environment cannot be excluded.

Acknowledgements: This work has been supported from the European project BYEFOULING "Low-toxic cost efficient environment-friendly antifouling materials" (FP7-OCEAN-2013 612717).

Session 11 – Novel environmentally friendly antifoulants
Room Bonaparte

Keynote 7B

Evaluation of novel natural and synthetic antifoulants derived from Arctic terrestrial and marine sources

Johan SVENSON*,[1] Lindon W.K.MOODIE[2], Gunnar CERVIN[3], Rozenn TREPOS[4], Henrik PAVIA[3], and Claire HELLIO[5]

[1]Department of Chemistry, Materials and Surfaces SP Technical Research Institute of Sweden, Box 857, SE-501 15 Borås, Sweden
[2]Department of Chemistry, University of Umeå, SE-901 87, Umeå, Sweden
[3] Department of Biological and Environmental Sciences - Tjärnö, University of Gothenburg, SE-452 96 Strömstad, Sweden
[4]School of Biological Sciences, University of Portsmouth, Portsmouth PO1 2DY, UK
[5]Université de Bretagne Occidentale, LEMAR UMR 6539, IUEM - Technopole Brest-Iroise rue Dumont d'Urville, 29280 Plouzané, France

**Johan.svenson@sp.se*

The diverse array of organisms inhabiting the marine world offers access to new and exciting chemical scaffolds, which hold potential for the development of nature inspired antifouling solutions. Several sessile marine species produce bioactive secondary metabolites to remain fouling free despite their stationary way of life. Several different plants adopt a similar strategy to prevent the growth of competing species by producing allelopathic compounds inhibiting growth and germination of other plants.
The current presentation summarizes the search for, and optimization of, Arctic marine antifoulants from the sponges *Stryphnus fortis*, *Geodia barretti* and the colonial ascidian *Synoicum pulmonaria*[1,2]. The circumboreal shrub *Empetrum nigrum* is known for producing an array of simple dibenzylic allelopathic compounds which also have been tested for their antifouling potential along with a library of synthetic analogs[3].
In addition, the current presentation reports the first study of the powerful effects of simplified cationic peptidic compounds, initially derived from the innate immune system, on marine biofouling and on organisms in a marine setting[4].
Several of the investigated natural compounds and their synthetic mimics display antifouling activities towards the growth and adhesion of both marine microalgae and bacteria at concentrations down to 10 ng/mL. Selected compounds also inhibit the settlement of *Balanus improvisus* barnacles cyprids at submicromolar concentrations in a non-toxic manner.

[1] K.Ø. Hanssen, G. Cervin, R. Trepos, J. Petitbois, T. Haug, E. Hansen, J.H. Andersen, H. Pavia. C. Hellio, J. Svenson, *Mar. Biotechnol*. **2014**, 16, 684-694.
[2] R. Trepos, G. Cervin, C. Hellio, H. Pavia, W. Stensen, K. Stensvåg, J.S. Svendsen, T. Haug, J. Svenson, *J. Nat. Prod*. **2014**, 77, 2105-2113.
[3] Manuscript in preparation.
[4] R. Trepos, G. Cervin, C. Pile, H. Pavia, C. Hellio, J. Svenson, *Biofouling* **2015**, 31, 393-403.

Oral 40B

From marine natural products (MNPs) to synthetic leads: a new wave of green antifouling solutions?

Sofyane ANDJOUH*[1] and Yves BLACHE[1]

[1] *Université de Toulon, Laboratoire MAPIEM, EA 4323, Avenue de l'Université, BP 20132, F-83957 La Garde Cedex, France*

* *sofyane.andjouh@univ-tln.fr*

Biofouling is natural process initiated by biofilm development on artificial or natural surfaces through an exopolymeric matrix, followed by settlement of macrofoulers (macroalgae, inverterbrates...) [1]. The prevention of biofouling development and the reduction of surface contamination is a very important issue in shipping [1], aquaculture [2], offshore petroleum industry [3]. Employment of metal-based paints has been the widely strategies used to control and eradicate biofouling processes. These coatings are found to adversely affect the environment due to the collateral damage inflicted on the marine ecosystem and non-target species [4].
An interesting and promising line of research is inspired by biomimetic solutions. Indeed, most marine organisms are prone to biofouling, and colonisation of their surfaces. Despite this, several of them have developed various defense systems to maintain unfouled and clean exterior surfaces [5]. Recently, the demand of eco-friendly antifouling materials increases greatly and non-toxic strategies including the incorporation of natural antifouling compounds (MNPs) from marine organisms into coatings has been extensively investigated currently as effective alternatives to toxic antifoulants [6]. However, field assays and paints formulation require large quantities of MNPs and the difficulties of mass production becomes a serious constraint. These factors led to consider the synthesis of analogues maintaining the natural framework in order to keep biological activity. Such biomimetic approaches, involving synthesis of analogues of natural products on large-scale for industrial purposes, represent durable green antifouling solutions.
In this context, we have developed an efficient strategy to optimize structure of natural antifouling compounds based on structure-activity relationships studies (SAR). Herein, we optimized the structure of antifouling marine natural products using "click chemistry" methodologies as interesting high through processes (Figure 1). This methodology led to obtain some potent anti-biofilm leads exhibiting low toxicity when compared to standard biocides such as TBTO or ZINEB, or standard antibiotic ampicillin.

Keywords: MNPs, 1,2,3-triazole, biofilm, structure-activity relationships, click chemistry.

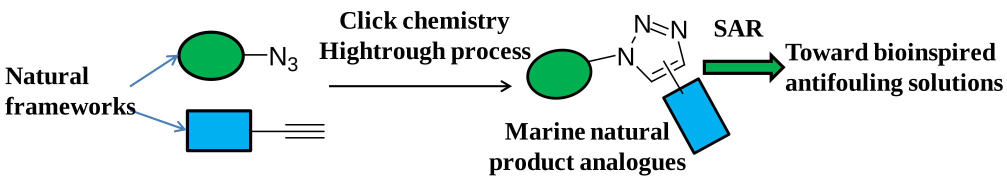


Fig 1: Design of marine natural product analogues.

[1] D. M. Yebra, S. Kiil and K. Dam-Johansen, *Prog. Org. Coat.* **2004**, 50, 75.
[2] I. Fitridge, T. Dempster, J. Guenther and R. de Nys, *Biofouling* **2012**, 28, 649.
[3] T. Yan and W. X. Yan, *Biofouling* **2003**, 19, 133.
[4] Y. Kotake, *Biol. Pharm. Bull.* **2012**, 35, 1876.
[5] P. J. Krug, in *Antifouling Compounds*, eds. N. Fusetani and A. Clare, Springer Berlin Heidelberg, **2006**, vol. 42, ch. 1, pp. 1.
[6] M. S. Acevedo, C. Puentes, K. Carreño, J. G. León, M. Stupak, M. García, M. Pérez and G. Blustein, *Int. Biodeterior. Biodegradation* **2013**, 83, 97.

Oral 41B

Camptothecin as an antifouling compound: laboratory tests and field applications

Danqing FENG, Yanqing SHENG, Hui LIU, Pei SU, and Caihuan KE*

College of Ocean & Earth Sciences, Xiamen University, Xiamen, PR China.

** chke@xmu.edu.cn*

Terrestrial plants are a rich source of natural bioactive products, some of which may have potential in green antifouling technology. Eighteen alkaloid compounds from terrestrial plants were here examined for anti-settlement activities against the barnacle *Balanus albicostatus* larvae, the bryozoan *Bugula neritina*, and the marine bacterium *Pseudomonas* sp. TB4. The results of the bioassays showed various antifouling activities in sixteen alkaloids. Five alkaloid compounds, evodiamine, camptothecin, sinomenine, stephanine, and strychnine, with pronounced antifouling activity in bioassays and sufficient availability to provide the quantities needed for field trials with panels, were chosen to be incorporated into paints with 20% w/w and exposed in the sea. Capsaicine, the natural alkaloid compound previously proved to be an active antifoulant [1], pyrithionc zinc and cuprous oxide served as positive controls. In the field, camptothecin showed the most potent antifouling performance among the five tested compounds. Camptothecin exhibited significantly less fouling coverage than the positive controls and the negative control (coating without any antifoulant) after one year in the sea, suggesting that camptothecin has great potential as an antifoulant. To examine the toxicity of camptothecin to non-target organisms, its effect on survival of the brine shrimp *Artemia saline* larvae was tested. The 24 h LC_{50} value was 7.23 μg ml^{-1} for camptothecin, while for tributyltin 4.14×10^{-5} μg ml^{-1} [2], and copper 0.28 μg ml^{-1} [3]. Antifouling coating containing camptothecin, which may be usable as a green antifoulant, was then applied to fishing nets in the field (Fig. 1). Camptothecin exhibited significant antifouling efficiency on fishing nets in the sea. In summary, this investigation indicated that camptothecin is a potential environmentally friendly antifouling agent.

Control (A) Treatment Control Treatment (B)

Fig. 1 Field application of camptothecin on fishing nets submerged in Lingshui Bay, Hainan, China. (A) Submerged for 12 months; (B) Submerged for 1.5 months. Control: coating without any antifoulant; treatment: coating containing 20% camptothecin.

[1] Q.W. Xu, C.A. Barrios, T. Cutright, B.M.Z. Newby, *Environ. Toxicol.* **2005**, 20, 467-474.
[2] B. Panagoula, M. Panayiota, J. liopoulou-Georgudaki, *Int. J. Toxicol.* **2002,** 21, 231-233.
[3] S.Z. Zulkifli, F.Z.A. Aziz, S.Z.M. Ajis, A, Ismail, Nauplii of brine shrimp (*Artemia salina*) as a potential toxicity testing organism for heavy metals contamination **2014**, A.Z. Aris, et al. (Eds.), Springer Verlag, Singapore, p. 233-237.

Oral 42B

A new material with low surface energy yielded by reaction of peptide and stainless steel

Pan CAO[1], Ying YANG[2], Xiuqin BAI[1], and Chengqing YUAN*[,1]

[1] SchoolofEnergyandPowerEngineering,WuhanUniversityofTechnology,Wuhan,P.R.China.
[2] SchoolofMedicine,KeeleUniversity,Staffordshire,United Kingdom.

* ycq@whut.edu.cn

Attachment of marine fouling organisms causes ship hull fouling and corrosion. The adhesion of destructive organisms can be reduced by low surface energy material used in manufacturing the hull. In this study, a new bioorganic metallic material was obtained through the reaction between polypeptide and 304 stainless steel which was named Bs. FTIR of the new material surface indicate some functional groups which belong to peptide. Sulfur and nitrogen are negligible in 304 stainless steel. However, they were detected by SEM-EDS on surface of the new material. XPS of Bs surface exhibits the change of electron states of iron, sulfur, nitrogen and carbon. All of the above evidences proved that a new material was yielded by chemical reaction. The material possesses a higher contact angle than before, which indicated that it is an environmentally friendly material with low surface energy. Reactions between different concentrations of peptide solution and stainless steel have been studied. The analysis of content of nitrogen and sulfur, contact angle and hardness indicates that the samples treated with peptide will have higher hardness and contact angle with the concentration of 10 μg/ml. This study provides a new method for antifouling research of ships.

[1] P. Cao, C-Q Yuan, Ma C Y, Y.Yang,X-Q.Bai, X-J.Wang,X-Y.Ren,H.Xie, X.P.Yan, *RSC Advance,* **2015,** 5,78030-78037.
[2] E-M Davis, D-Y Li, R-T Irvin, *Biomaterials* **2011,** 32, 5311-5319.
[3] J-D Adkins, A-E Mera, M A Roe-Short, G-T Pawlikowski, R-F Brady. *Progress in Organic Coatings*, **1996**, 29, 1-5.

Oral 43B

Impact of a hemibastadin derivative on microfouling settlement

Tiffany Le NORCY[1*], Hendrik NIEMANN[2], Peter PROKSCH[2], Claire HELLIO[3], Isabelle LINOSSIER[1], Karine REHEL[1], Fabienne FAY[1]

[1] Laboratoire de Biotechnologie et Chimie Marine, Institut Universitaire Européen de la Mer, Université de Bretagne-Sud, 56100 Lorient, France
[2] Institute of pharmaceutical biology and biotechnology, Heinrich-Heine-University Düsseldorf, 40225 Düsseldorf, Germany
[3] Laboratoire des sciences de l'Environnement MARin, Institut Universitaire Européen de la Mer, Université de Bretagne Occidentale, 29280 Plouzané, France

** tiffany.le-norcy@univ-ubs.fr*

First bastadins isolated from the marine sponge *Ianthella basta* have attracted wide attention because of their biological activities. Indeed bastadins are known for their antifouling, antimicrobial and anti-inflammatory properties. From these natural compounds, chemists have developed many bastadins or hemibastadins derivatives.
After identifying the minimal inhibitory concentration of a derivative hemibastadin against four bacteria strains (*Paracoccus* 4M6, *Pseudoalteromonas* 5M6, *Vibrio* D66 and *Pseudomonas aeruginosa* PAO1), the anti-adhesion or anti-biofilm activities were evaluated in flowcell system by observations in laser scanning confocal microscopy. The experiments showed that the molecule induced an inhibition of biofilm formation without any effect on the adhesion. The compound DBHB was also integrated in varnishes based on a polyester binder. This matrice is a biodegradable polymer which has been synthetized in the laboratory with no antifouling properties. The microfouling colonization on varnishes with the molecule was studied in natural conditions and in controlled conditions.
For the natural condition, samples were immerged in the Kernével harbor of Lorient during May to June 2015. And for the controlled condition, varnishes were immerged in a photobioreactor (medium: ASW 30g/L and peptone 1g/L, pH 7.5, temperature 20.0°C, light 12H:12H 250 µmol.m^{-2}.s^{-1}). To create a marine environment, three bacteria strains (*Paracoccus* 4M6, *Pseudolateromonas* 5M6 and *Bacillus* 4J6) and microalgae (*Cylindrotheca closterium* AC 170) were grown in the photobioreactor. Results obtained after immersion in natural condition and in controlled condition were showed an inhibition of microfouling settlement on varnishes with the derivative hemibastadin.

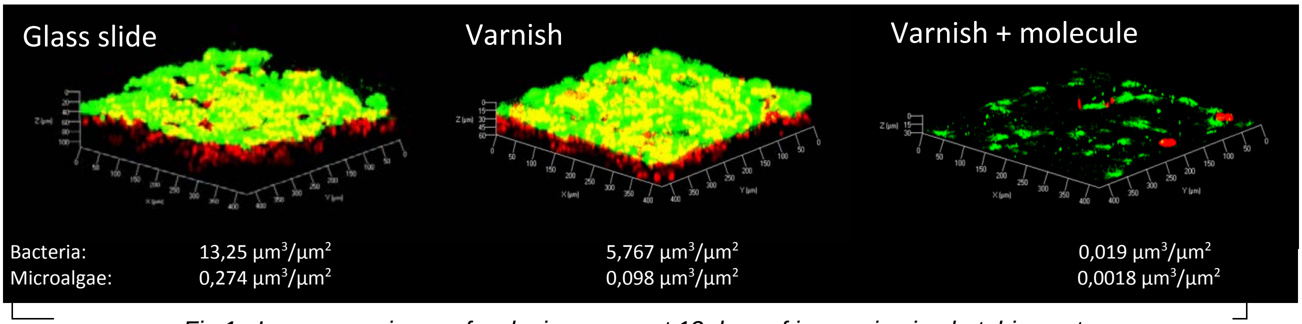


Fig 1 : Laser scanning confocal microscopy at 13 days of immersion in photobioreactor

Oral 44B

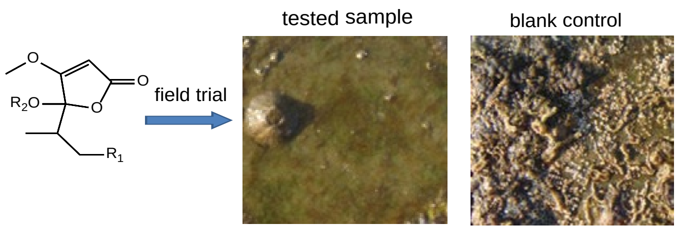
Progress in antifouling compounds from marine-derived fungi

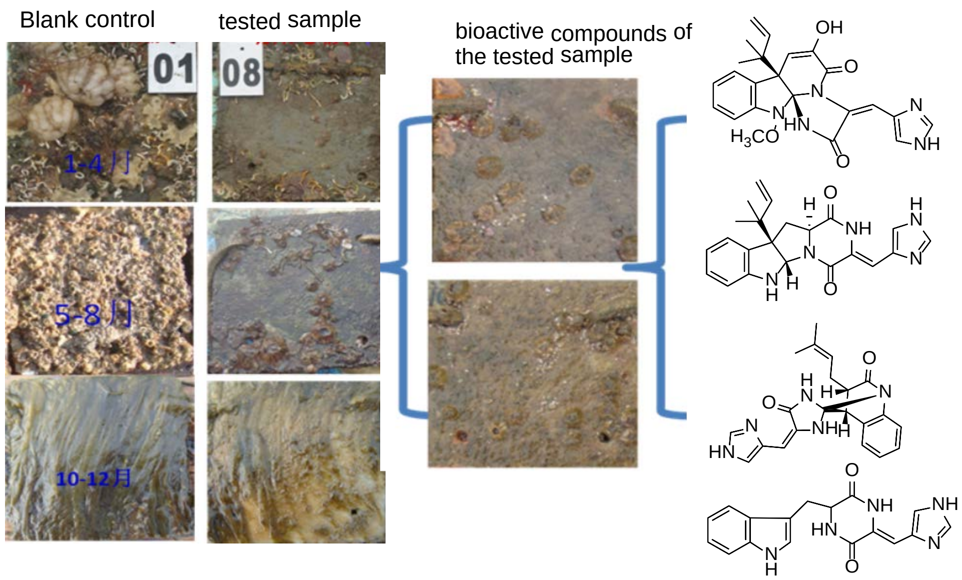
Shu-Hua QI*, Xiao-Yong ZHANG, Xu-Hua NONG, Jie WANG

Key Laboratory of Tropical Marine Bio-resources and Ecology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, 164 West Xingang Road, Guangzhou 510301, China

** shuhuaqi@scsio.ac.cn*

Marine derived microbial secondary metabolites are promising potential sources of nontoxic antifouling agents. Over the past seven years, we have obtained over forty antifouling compounds from marine-derived fungi. These compounds mainly included alkaloids, butyrolactones, polyketides, and fatty acids. The antifouling activity was primarily evaluated by antibacterial activity against larval settlement inducing bacteria, and antilarval activity against larval settlement of bryozoan Bugula neritina and Balanus Amphitrite, and then tested in field trial. The potentials of these antifouling compounds as natural no-toxic antifouling agents are under further evaluation.





Acknowledgments: The work presented in this study has been funded by the Natural Science Foundation of China (41376160) and Regional Innovation Demonstration Project of Guangdong Province Marine Economic Development (GD2012-D01-002).

Oral 45B

Strategic advantages of functionalized POSS derivatives applied to anti-fouling concepts

Monika PILZ*[1], Nicolas RIVAL[1], and Eirin LANGSETH[1]

[1]*SINTEF Materials and Chemistry, Materials and Nanotechnology Department, Nano and Hybrid Materials Group, Oslo, Norway.*

* *monika.pilz@sintef.no*

The general principle of most of antifouling paint systems is based on slow release of biocide compounds with time. Copper(I) oxide (Cu_2O) is mostly used as their primary active ingredient and directly added to formulations usually also followed by selected organo-metallic co-biocides like Cu- or Zn-pyrithiones. The control over release during service life is depending on different coating technologies in use. Novel antifouling concepts are aiming on encapsulation of active species with “smart” nanocontainers which provides triggered release by external stimuli like mechanical damage, presence of aggressive species, pH changes.

Several approaches with nanosized structures are under development and functionalized derivatives based on polyhedral oligomeric silsesquioxanes (POSS) are among the promising ones contributing to enhance anti-fouling performance. Those hyper-branched hybrid nanostructures ($[O_{3/2}Si(CH_2)_3NX_2]_{n,\ n=8,10,12}$ derive from a cost-efficient two-step production (www.funzionano.com), including a sol-gel process followed by functionalization. This synthesis route has the strategic advantage to yield in a variety of chemical surface functionalities appropriate to tune response efficiency to prevent micro- and macro-fouling (Fig. 1).

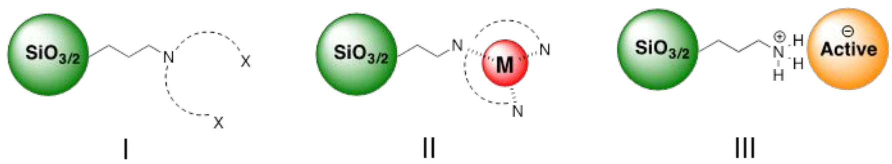


Fig. 1: Scheme of promising units for strategic anti-fouling concepts based on POSS nanostructure.

Different structural features of POSS derivatives (I, II, and III) as carriers for active species have been synthesized at SINTEF Materials and Chemistry and their anti-fouling activity screened. The release of active compounds from POSS complexes by environmental stimuli (e.g. artificial seawater) has been investigated in the laboratory.

Field exposure of modified self-polishing coatings has started to assess their resistance to bio-fouling in marine environment.

Acknowledgements: This research is supported by the EU FP7 Programme / THEME [OCEAN 2013.3] within the collaborative project “BYEFOULING - Low-toxic cost-efficient environment-friendly antifouling materials” (www.byefouling-eu.com) under Grant Agreement no. 612717, coordinated by Christian SIMON, SINTEF Materials and Chemistry.

Oral 46B

Photocatalytic zinc oxide nanocoatings: a green alternative to biocidal antifouling coatings

Priyanka SATHE*,[1, 2], Jutta RICHTER[2], Myo tay zar MYINT[1], Sergey DOBRETSOV[2] and Joydeep DUTTA[1, 3]

[1] Chair in Nanotechnology, Water Research Centre, Sultan Qaboos University, Muscat, Oman.
[2] Department of Marine Science & Fisheries, College of Agriculture & Marine Sciences, Sultan Qaboos University, Muscat, Oman.
[3] Functional Materials Division, Materials and Nano Physics Department, ICT School, KTH The Royal Institute of Technology, Stockholm, Sweden

* *priyankasat@gmail.com*

Biofouling is a major problem in marine installations and accounts for heavy economic burden on shipping industries, desalination plants and in aquaculture. Due to the toxicity associated with current antifouling paints, numerous efforts are being made to develop novel, less toxic but effective antifouling technologies. In the present work, a novel antifouling coatings of zinc oxide (ZnO) nanorod was investigated in an outdoor static mesocosm experiment using seawater collected from the Sea of Oman under natural day and light cycle (light) and in the dark (mimicking the night). The total bacterial density and viability monitored over a week was found to reduce 6-fold in the presence of nanocoatings and sunlight. Comparative evaluation of toxicity from fabricated nanocoatings and commercial biocidal paints were evaluated using marine fish. MiSeq Illumina sequencing of 16 rRNA genes of bacterial biofilms developed on substrata revealed the presence of 16 different bacterial classes with the most common ones including *Alphaproteobacteria*, *Gammaproteobacteria, Flavobacteria* and *Sphingobacteriia*. Different microbial communities were formed under light or dark conditions in the presence of nanorod coatings or without them (control). The observed antifouling activity of the ZnO nanocoatings is attributed to the formation of reactive oxygen species (ROS) through photocatalysis of seawater in the presence of sunlight. Our experiments demonstrate that ZnO-based nanorod coatings can successfully mitigate biofouling under static conditions and can be used as a low toxic green alternative to biocidal antifouling coatings.

Oral 47B

Antifouling strategy compounds from Red Sea organisms

Julie PETITBOIS*[1], Sultan S. AL-LIHAIBI[2], Ahmed ABDEL-LATEFF[2], Walied M. ALARIF[2], Erina YOSHIMURA[3], Yasuyuki NOGATA[4], Tatsufumi OKINO[1]

[1]Hokkaido University, Sapporo, Japan.
[2]King Abdulaziz University, Jeddah, Saudi Arabia.
[3]CERES Inc., Tokyo, Japan.
[4]Central Research Institute of Electric Power Industry, Abiko, Japan.

* *juliepetitbois@ees.hokudai.ac.jp*

Biofouling is responsible for many economical and ecological problems such as the increasing of cost maintenance in the naval field, diseases in aquaculture and the introduction of potentially harmful organisms in ecosystems. To fight against this deleterious phenomenon, chemical, physical and biological strategies exist but some have side-effects on non-targeted organisms. Since several years, research focuses on eco-friendly natural molecules from marine organisms, mainly sessile, to mimic their defenses against fouling.
Red Sea is a unique ecosystem as it is partially isolated from the open ocean and is the most saline sea in the world because of the combination of the lack of precipitation and high heat which facilitates high levels of evaporation. As a result, Red Sea organisms are more likely to produce unique compounds to adapt these conditions and compete against each other to keep their ecological place. Crude extracts and pure compounds from the Saudi Red Sea organisms are studied and tested toward *Balanus amphitrite* larvae, a typical marine fouling invertebrate which is wildly distributed. Seventy nine extracts were tested on barnacle larvae at different concentrations (100, 10 and for some of them 1 µg/mL) to evaluate their degree of activities: five percent of them were very active (exhibiting at least 70% of inhibition at 1 µg/mL), 32% were moderately active (exhibiting at least 70% of inhibition at 10 µg/mL) and 9% were slightly active (exhibiting at least 70% of inhibition at 10 µg/mL). Extracts of the two soft corals, *Sarcophyton glaucum* and *Sarcophyton* sp., and the sponge, *Hyrtios* sp., were sources of in total seven new active compounds: two cembranoids, a sesquiterpene, a sterol, a highly apolar compound and two not yet identified compounds. All these compounds inhibit the settlement of barnacle larvae without showing any toxic effect. Therefore, there are good candidates for being part of new eco-friendly antifouling paints.
Up to now, mainly terpenoid-related compounds were isolated from the Red Sea organisms, which is one of the chemical family offering promising results. Research is ongoing to characterize the not-yet identified compounds and to isolate new kind of compounds with anti-settlement activities on barnacle larvae.

Oral 48B

Low voltage UV-light emitting miniature LEDs for marine biofouling control: laboratory and field testing

Richard PIOLA*[,1], Bart SALTERS[2], Clare GRANDISON[1], Mark CIACIC[1] and Roelant HIETBRINK[2]

[1] Environmental Signature Control Group, Defence Science and Technology Group, Melbourne, AUSTRALIA.
[2] Philips Research Laboratories, Eindhoven, The Netherlands

** richard.piola@dsto.defence.gov.au*

The accumulation of biofouling on marine vessels and structures is an ongoing issue for managers and operators. Traditional marine antifouling solutions are typically in the form of underwater coatings. These coatings work by creating a surface environment that is not desirable for the settlement and growth of living organisms – typically through the use of chemical biocides. Over time chemicals can become depleted in the coating (rendering it less effective) and are released into the surrounding water, resulting in potentially adverse effects on the environment. We present on a different approach for biofouling prevention, in which a UV light emitting layer is applied on exposed underwater surfaces for the inhibition of settling organisms. The introduction of miniature UV LEDs as a light source enables them to be embedded into thin, flexible, coating-like structures, in which the UV light dissipates evenly within the surface. Optical design elements ensure the light escapes more or less uniformly all over the coating layer. In this presentation, we discuss novel advancements in the design and fabrication process for this technology, including initial predictions of large area antifouling protection based on computer simulations and laboratory measurements of UV diffusion. We also discuss the findings of field investigations examining the efficacy of UV LEDs for the prevention of marine biofouling under real-world conditions, testing several design iterations of UV LED arrays across a range of exposure environments and scenarios. Field results are compared against initial theoretical simulations and measurements of the UV light intensity to validate baseline assumptions.

Oral 49B

Bursting the iodine vapor bubble: iodine infused aeration for biofouling prevention

Natasha C. DICKENSON[1*], Michael JAMES[1], Jason KRUMHOLZ[2], Kelli HUNSUCKER[3], and Michael RADICONE[4]

[1] Naval Undersea Warfare Center Division Newport, Rhode Island, USA
[2] McLaughlin Research Corporation, Middletown, Rhode Island, USA
[3] Center for Corrosion and Biofouling Control Florida Institute of Technology, Melbourne, Florida, USA
[4] I2 Air Fluid Innovation, Inc., Huntington Station, New York, USA

* natasha.dickenson@navy.mil

Aeration, a directed continuous stream of air bubbles applied to a submerged surface, is one environmentally-friendly and relatively inexpensive method for deterring the settlement of fouling organisms. The inclusion of iodine vapor (I_2) within air bubbles may provide additional fouling prevention by reducing microbial counts and biofilms. A series of field experiments using small-scale aeration system prototypes were conducted in Newport, Rhode Island and Port Canaveral, Florida in 2015 to assess the use of standard aeration and I_2-infused aeration as methods for biofouling prevention. Submerged panel surfaces were monitored for the establishment of biofilms and macroscopic fouling which were quantified to obtain estimates of percent cover. The I_2-infused aeration treatments exhibited the lowest mean percent cover of hard fouling throughout the study period, and significantly less hard fouling coverage than the control in both locations, but was less effective in the prevention of soft fouling species such as algae and tunicates. Percent coverage of soft biofouling organisms was similar between the standard aeration and I_2-infused aeration treatments. The I_2-infused aeration treatment displayed slightly lower mean percent cover of hard fouling compared to standard aeration, however differences in percent cover of hard fouling between standard and I_2-infused aeration were not large enough to be statistically significant. Follow-on testing in 2016 in Port Canaveral examined the efficacy of a full-scale aeration system deployed on a small vessel with sections coated with a foul-release coating (Intersleek®1100), an ablative copper coating (Interspeed®BRA-640), and an epoxy barrier coat coating to demonstrate if I_2-infused aeration is more effective as complementary method to foul release coatings or other biocides. Preliminary results show that after two months of immersion, minimal to no hard fouling accumulated on the Intersleek®1100, Interspeed®BRA-640, and epoxy coated panels exposed to I_2-infused aeration, while controls for these treatments accumulated significantly more fouling consisting of both soft and hard fouling. Biofilm composed the majority of the fouling observed on panels coated with Intersleek®1100 and Interspeed®BRA-640 treated with I_2-infused aeration. Variation in the amount of fouling cover from the top to the bottom portions of the panels and between sun exposed and shaded treatments along the hull was evident for all coatings and treatments. Successful testing of standard and I_2-infused aeration methods would determine whether I_2-infused aeration yields sufficient additional benefit relative to standard aeration in preventing fouling to justify any logistical and financial complexities of large scale implementation, paving the way for future efforts to transition from a prototype to a full demonstration scale-up on a vessel.

Acknowledgments: Funding and support for this work has been received from the Naval Undersea Warfare Center Division Newport Strategic Investment Program

FRIDAY June 24, 2016

Plenary- 5 Assessing the ship hull fouling penalty – Current knowledge & outstanding questions

Michael SCHULTZ[1*]

[1] *U.S. Naval Academy, Annapolis, MD USA*

* *mschultz@usna.edu*

Nearly since mariners first took to the seas, they have understood that biofouling accumulation on their hulls adversely affects vessel performance. This paper will review the sizable body of research that has focused on quantifying the hydrodynamic impact of biofouling on ships. Based on this review, the present state of knowledge in this area will be summarized. Next, questions that remain unresolved will be noted and discussed.
Finally, future directions for research to shed light on the outstanding issues will be considered.

Acknowledgements: This research was funded by the U.S. Office of Naval Research (ONR)

Session 4 – Biosecurity, risk management & Prediction in marine protection - Room Colbert

Keynote 7A

The importance of adopting pragmatic vessel biofouling management measures for mitigating the dispersal of aquatic invasive species – An Australian perspective

Ashley COUTTS*[,1], Nick GUST[1], Rene REINFRANK[1], Pat LEWIS[1], and Jeremy LANE[1]

[1] *Biofouling Solutions Pty Ltd, Kingston, Tasmania, Australia.*

* *acoutts@biofoulingsolutions.com.au*

By 2020, the Convention on Biological Diversity Aichi Biodiversity Target 9 calls for invasive alien species and pathways to be identified and prioritized, priority species to be controlled or eradicated and measures be implemented to manage pathways to prevent further introduction and establishment. Shipping is widely acknowledged as one of the key vectors for the accidental spread of Aquatic Invasive Species (AIS) worldwide. Initially, ballast water discharge was thought to be the major shipping mechanism for the dispersal of AIS, hence the creation (and imminent ratification) of the International Convention for the Control and Management of Ships' Ballast Water and Sediments (BWM). However, numerous studies in many locations around the world have indicated that vessel biofouling has been responsible for the introduction of more AIS than ballast water. To achieve Aichi Biodiversity Target 9 by 2020, effective and pragmatic management of vessel biofouling is now required. The International Maritime Organization (IMO) has developed voluntary Guidelines for the Control and Management of Ships' Biofouling to Minimize the Transfer of Invasive Aquatic Species. These Guidelines will be instrumental for assisting countries develop their own biofouling measures. For example, New Zealand will be the first country to develop mandatory biofouling measures which are due for implementation in 2018. Such measures require vessels arriving with "clean hulls" with permissible thresholds based on the size and/or percentage cover of biofouling within specified hull locations. However, these permissible thresholds could be argued to be expensive, impractical and too difficult to verify and enforce. An alternative biofouling management approach is to prohibit the entry of specific AIS which have been risk assessed as potentially having a "high likelihood" of establishing and causing significant economic, environmental, social/cultural, and/or human health consequences. For the past seven years, the Western Australian Department of Fisheries has been actively managing the unwanted arrival of 78 "noxious fish" species into Western Australian waters, albeit amongst oil and gas related vessels and infrastructure. While such measures have been extremely successful, they have also been expensive to comply with, enforce, and there have been challenges with positively identifying certain "noxious fish" species. Nevertheless, such an approach has provided industry with greater flexibility than enforcing a "clean hull" standard. One oil and gas project in Western Australia adopted a "clean hull" standard for all vessels visiting their project. While this standard was extremely expensive for vessels to achieve, it was a relatively easy standard to enforce. Biofouling Solutions Pty Ltd. has conducted over 300 vessel inspections amongst 52 different vessel types in accordance with both biofouling management standards (i.e. "clean hull" and targeted "noxious fish" species). This presentation will share some of the lessons learnt from the enforcement of these two standards in the hope that these lessons will be considered when developing future cost-effective, pragmatic biofouling management requirements.

Oral 51A

Minimising marine biosecurity risks of vessels' biofouling in Australia

Sonia GORGULA* [1], Peter STOUTJESDIJK[1], Helen WALKER[1] and Emily LAWSON[1]

[1] *Australian Government Department of Agriculture and Water Resources, Canberra, Australia.*

* *sonia.gorgula@agriculture.gov.au*

Biofouling is one of the oldest mechanisms of human-mediated transport of marine species and variously considered a leading contributor of non-indigenous marine species (NIMS) introductions in multiple global locations (Hewitt et al 2011). In Australia, more NIMS have life history characteristics associated with biofouling than any other vector (Hewitt and Campbell 2010), some of which may be harmful to Australia's unique environment, economy, human health and way of life.

The Australian Government Department of Agriculture and Water Resources has been working on an approach to vessel biofouling management since the mid 2000s. In late 2015, a national review of marine pest biosecurity arrangements in Australia was completed, highlighting vessel biofouling management as a significant biosecurity gap and recommending a way forward.

As a result, the department is developing new biosecurity arrangements for internationally arriving vessels to reduce the risk of NIMS introductions associated with biofouling. Research has been completed to establish the role of vessels' biofouling in historical marine invasions in Australia and on the diversity of operational profiles of vessels trading in Australian ports.

The proposed regulatory framework for vessels' biofouling in Australia will be based on reducing risk and closely aligned with international guidelines. The aim is to reduce the likelihood of future marine pest introductions in Australia by encouraging the adoption of best practice maintenance through biofouling management plans and record books. This includes the application of appropriate antifouling coatings, operation of marine growth prevention systems on sea-chests and in-water inspections with biofouling removal as required. The proposed arrangements will provide consistency with the direction set by the International Maritime Organization and governments concurrently progressing biofouling requirements, including New Zealand and the states of Western Australia, Hawaii and California.

Oral 52A

Biofouling management: Flash info de Nouvelle-Zélande!

Eugene GEORGIADES*, Abraham GROWCOTT and Daniel KLUZA

Ministry for Primary Industries, Wellington, New Zealand.

* *Eugene.Georgiades@mpi.govt.nz*

Biofouling on ships had been demonstrated to be a significant pathway for the unintentional introduction and establishment of non-indigenous species into new environments.
New Zealand is at the forefront of managing vessel biofouling and is the first country in the world to issue a border standard regulating biofouling on incoming international vessels. The vessel biofouling Craft Risk Management Standard (CRMS) comes into force in May 2018 to allow industry time to adapt their biofouling management plans. Vital to the success of the CRMS is the conduct of robust science to underpin decision-making and policy.
New Zealand's Ministry for Primary Industries (MPI) has been active in commissioning scientific research to inform the implementation of biofouling regulations and on-going management of vessels and infrastructure.
MPI have been active in promoting and aligning biofouling management science with other jurisdictions to establish a global community of practice.

Biofouling Management
New Zealand is involved in both international and domestic efforts to improve ship hull maintenance to minimise biosecurity risks, but recognises that there is a lack of robust, independent information on the effectiveness of preventive tools and techniques to minimise ships' biofouling, particularly for niche areas. MPI initiated a project to identify effective hull maintenance practices to inform shipping and regulatory authorities of activities that could constitute best practice.

In-water Cleaning
The International Maritime Organization (IMO) recently adopted guidelines that encourage ship owners and operators to implement biofouling management practices. These include the use of effective anti-fouling systems and routine in-water cleaning to reduce the development of biofouling. MPI has commissioned projects to inform standard testing requirements for in-water cleaning systems for external and internal surfaces of vessels. Such standards are needed to ensure that the cleaning method effectively removes or treats the biofouling whilst the preventing release of non-indigenous organisms into New Zealand's marine environment.

Biosecurity in Aquaculture
The production infrastructure for aquaculture and, in the case of shellfish production the organisms themselves, provide a habitat for the settlement of biofouling organisms. Substantial economic costs to industry are associated with biofouling control, illustrating the need for effective preventive technologies and mitigation methods. The Biosecurity in Aquaculture project provides farmers with relevant technical information, biosecurity objectives and best practice options to enable informed decisions to be made regarding their on-farm biosecurity and biofouling management.

Oral 53A

Ship biofouling management to minimise species translocation: What works best?

John A LEWIS[1]*, and Eugene GEORGIADES[2]

[1] *ES Link Services Pty Ltd, Castlemaine, Australia.*
[2] *Ministry for Primary Industries, Wellington, New Zealand*

* *jlewis@eslinkservices.com.au*

Biofouling impacts on ship performance by both increasing hull friction and therefore fuel consumption, and by impeding the function and efficiency of propulsion, steering and internal cooling and other seawater systems. Ship biofouling has also been demonstrated to be a significant pathway for the translocation of marine species resulting in the unintentional introduction of non-indigenous species into new environments. Biofouling control is best achieved by good biofouling management practice, which primarily requires the installation, operation and maintenance of appropriate antifouling systems.

New Zealand is actively involved in international and domestic efforts to improve ship hull maintenance to minimise biosecurity risk and has recognised the need for more robust, independent information on the effectiveness of preventative tools and techniques to minimize ships' biofouling, particularly for niche areas. To address this, New Zealand's initiated a project on the effectiveness of biofouling maintenance practices to inform both shipping and regulatory authorities of the best management practices. The aim was to obtain detailed information from vessels world-wide on the condition and attributes of ship biofouling management systems on their arrival in dry-dock. Collating and analysing information from many ships of different sizes and type, operating in different regions, would enable a robust assessment of system efficacy. One focus of the project was to assess the efficacy of different marine growth prevention systems (MGPS) or other methods for minimising marine growth inside sea chests.

Information and data were gathered by personal attendance at dockings or from docking reports prepared by technical personnel. Vessel types covered included offshore tugs and supply vessels, cruise ships, passenger ferries, car carriers, ro-ro cargo ships, tankers and dredging vessels. MGPS types observed included copper anodic, ultrasonic, and drip dosing systems, and effects of the use of different, or multiple coating systems on hulls and niches also documented. This talk will provide a brief overview of the more interesting findings.

Oral 54A

Testing for effective prevention and removal of biofouling from ships – lessons learnt from testing of ballast water management and the fouling removal chain

Cato C. TEN HALLERS-TJABBES,*

MEA-nl, The Netherlands

*cato@catomarine.eu

Both biofouling and ballast water from ships are vectors in the transfer non-indigenous and often invasive aquatic species and pathogens to the detriment of the environment, human health and amenities. Ballast water is considered to contribute about one-third to the transfer of non-indigenous aquatic organisms world-wide. Hull fouling composes a comparable risk. Both environmental risks are regulated by the International Maritime Organization (IMO, the UN agency for shipping), albeit to a different extent. The (mandatory) Ballast Water Management Convention has been in place since 2004 (IMO, 2004), while the (voluntary) Guidelines for the control and management of ship's biofouling only emerged in 2011 (IMO, 2011). As a result a wealth of ballast water management systems (BWMS) and of expertise in verification testing of such systems has been developed. For preventing and treating biofouling such expertise has predominantly been developed in view of developing policies for antifouling prior to the pending mandatory regulations to ban all organotins from ships and in the wake of the Anti-fouling Convention (IMO, 2001). Existing and developing methods for prevention and removal of biofouling will have to be tested for efficacy and effectiveness in fouling removal and for environmental acceptability, in order to be certified. The need for in-water hull cleaning is increasing along with the demand for fuel economics for ship owners and charterers. Hull cleaning increases the risk of spreading non-indigenous and possibly harmful organisms; removed hull fouling should be rendered harmless by proven technologies. Testing of such technologies, although they are intended for another biosecurity problem associated with shipping, will have much in common with the testing of BWMS. The challenges will equally be a need to demonstrate adequate efficacy and compliance by reducing the residual amount of organisms to a level low enough to minimize the risk of transfer of non-indigenous aquatic organisms. The challenge lies predominantly in showing that such low levels can be achieved, without having an adverse effect on the aquatic environment by the methods applied. MEA-nl has a long-standing expertise (since 2002) in the development and performance of testing BWM systems for certification and has explored and adapted a wide range of detection methods for its research on BWM testing. The expertise can, mutatis mutandis, be applied to explore optimal testing of strategies for removal of biofouling. Moreover, MEA-nl has a sound understanding in working within regulatory frameworks for water management in view of waste water management, safe removal chains and permits. Similar challenges are expected to be faced when systems for removal of biofouling need to be tested. In view of biofouling, MEA-nl has the capacity to be involved in tests and sampling procedures such as:

- Long-term testing of exposed materials in ambient water of different salinities in a permanent configuration, a different approach from testing in artificially prepared test water.
- Testing of materials with or without exposure to visible light and UV irradiation; such tests may assist in the treatment of fouling problems in cooling water installations of major industrial settlements.
- Simulation of different flow regimes according to the needs of the client.
- Ship-board testing for efficacy of cleaning methods for ships' hulls.

IMO, 2011. MEPC.207(62), the 2011 Guidelines for the control and management of ships' biofouling to minimize the transfer of invasive aquatic species, IMO. 2001. Adoption of the Final Act of the Conference and any Instrument, Recommendations and Resolutions resulting from the work of the Conference. International Conference on the Control of Harmful Anti-fouling Systems October, IMO, London, 5 October (2001). IMO, 2004. International Convention for the Control and Management of Ships' Ballast Water and Sediments. International Maritime Organization.

Oral 55A

A mathematical model to predict wild life population affected by chemicals released from AF/AC paint

Kiyoshi SHIBATA[1]

[1] *Chiba Institute of Technology, Narashino, Japan.*

* *shibata.kiyoshi@p.chibakoudai.jp*

The aquatic ecological risk assessment is generally made by evaluating the ratio of Predicted Environmental Concentration to the Predicted Non-Effect Concentration, introducing an assessment factor. Sometimes, the value of the assessment factor is very large to cope with uncertainty in scientific knowledge and natural phenomena itself. It makes development or commercialization of new chemicals very conservative. In addition, the uncertainty in the aquatic ecological system is very significant, because of complexity and fluctuation of the ecological processes, and difficulties in the quantitative observation. The adaptive risk management has been developed in forestry or fishery to cope with such uncertainties.

The adaptive management is a systematic process to reduce uncertainties and maintain the ecological soundness, by repetition process of monitoring key indicator and implementation. It is essential to compare the monitoring results to predict based on theoretical or empirical model, and to modify the implication based on reduction of the uncertainty in the ecosystem.

In this work, a mathematical model has been developed to identify the key indicator in ecological system affected by antifouling agent and examine its sensitivity.

The model is designed to predict the occurrence of extermination of a certain species in a ecosystem by calculating population fluctuation, which is affected by concentration of the chemical, dose-response relationship, as well as the population density. The fluctuations in the population, dose-response, and concentration are expressed by random numbers. Three parameters are controlling their fluctuation rage. In every trial calculation, different fluctuating change in the population is obtained, and the occurrence of the extermination is evaluated by large number of the trial calculation.

The sensitivities of the parameters in the prediction of extermination were examined to identify key controlling element of the model. And the significant elements in monitoring the system will be discussed.

Oral 56A

How conservative is the regulatory human health risk assessment? Comparisons between calculated and analytical data using Selektope® as an example

Lena LINDBLAD[1*] and Mika SCHEININ[2],

[1]I-Tech AB, AZ BioVenture Hub, Mölndal, Sweden.
[2]University of Turku, Turku, Finland

** Lena.Lindblad@i-tech.se*

Selektope® is a new antifouling biocide that was approved according to the Biocidal Product Regulation (BPR) in 2015. According to the European guidelines, a human health risk assessment shall be done and the risk shall be judged acceptable before approval. The risk assessment is based on a number of assumptions regarding the active substance's systemic uptake through dermal and inhalation exposure. The exposure models differ between professional and amateur users, and are supposed to represent realistic worst case scenarios.
Since the risk assessment relies mostly on assumptions on systemic bioavailability and comparisons with data from animal (rat) toxicology studies, safety factors are added to the risk evaluation. The safety factors are to cover unknown parameters and inter- and intra-species differences. Together with assumptions, toxicology data and safety factors, the risk assessment shall cover a worst case scenario. But how realistic is the worst case scenario?
Two Selektope® exposure investigations initiated by I-Tech have been performed, bioavailability after dermal exposure and evaluation of acceptable total systemic exposure. The investigations were performed as two clinical trials in healthy volunteer subjects, according to Good Clinical Practice (GCP) and after appropriate ethical approval. By using a modification of Fick's law of diffusion together with measured plasma levels of medetomidine, the active ingredient of Selektope®, it was possible to determine dermal exposure bioavailability to 0.06% based on 4 dm^2 skin coverage and 1% incorporation of Selektope® in an antifouling formulation. This is to be compared to a default level in dermal uptake of 10%, an overestimation of 166-fold for systemic uptake from dermal exposure.
The No Observed Effect Level regarding systemic exposure to Selektope® has been set at a plasma concentration of 0.1 ng/ml for dexmedetomidine, the pharmacologically active enantiomer of medetomidine. To investigate the total dose of Selektope® that can be entering the circulation during 6 hours without exceeding the NOEL, a constant rate drug infusion was given to six men and six women. The total dose of racemic medetomidine (as the veterinary drug product Domitor Vet® 1 mg/ml) that was given during the six hours to a 60 kg person was 77 µg. This is to be compared with the acceptable dose according to the exposure model for professional spraying application Tier 2d, which will allow for intake of 7.7 µg.
With Selektope® as an example, the present regulatory human exposure risk assessment calculation results in a ten times lower dose compared with actual experimental evidence. If then adding a safety factor of 10 covering unknowns in pharmacodynamics and pharmacokinetics, it adds up to a factor of 100. If the risk assessment is based on animal toxicity data, another factor of 10 will be added. A discussion is needed whether the present risk assessments regarding human exposure represent realistic worst case scenarios or whether they are over-conservative. A more realistic worst case evaluation would allow for a friendlier innovation climate within the area of active antifouling substances.

Session 1 – Marine corrosion: Materials & Coatings
Room Bonaparte

Keynote 8B

Active protective multi-functional coatings on basis of "smart" nanocontainers

Mikhail ZHELUDKEVICH*[,1,2], Joao TEDIM[2], and Mario FERREIRA[2]

[1] *Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Max-Plank-Str. 1, 21502 Geesthacht, Germany*
[2] *Department of Materials and Ceramic Engineering, CICECO – Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal*

* *mikhail.zheludkevich@hzg.de*

The destructive effect of environment and the corrosion induced degradation are the important problems which determine the service life of many metallic components including those exploited in marine environments. The application of organic coatings is the most common and cost effective method of improving protection and durability of metallic structures. However the degradation processes develop faster after disruption of the protective barrier. Therefore an active protection based on “self-healing” of defects in coatings is necessary to provide long-term effect. The active corrosion protection of metallic substrates can be achieved by the addition of corrosion inhibiting compounds to the protective coatings. However, direct mixing of an inhibitor with coating formulations can lead to important drawbacks decreasing barrier properties of the coating and diminishing activity of the inhibitor. Moreover the complexity of the corrosion mechanisms and variety of the conditions where metallic structures can be used calls for the combination of different inhibitors in the same corrosion protection system. This is very problematic in the case of direct addition of different inhibitors due to cross-talk between them.
The present paper overviews our recent progress in development of novel protective coatings with self-healing ability on the basis of nanocontainers that release entrapped corrosion inhibitor in response to presence of corrosive species. The new nanocontainers for organic and inorganic corrosion inhibitors were developed in this work employing nanocarriers including polyelectrolyte layer by layer assembled structures [1], mesoporous nanoparticles [2], halloysite nanotubes [3] and different nanoclays [4,5]. The combination of different nanocontainers in the same coating system was demonstrated to provide an important cooperative effect especially when active coatings for hybrid assemblies are considered [6,7].

[1] M.L. Zheludkevich, D.G. Shchukin, K.A. Yasakau, H. Möhwald, M.G.S. Ferreira, *Chemistry of Materials*, **2007**, 19, 402.
[2] F. Maia, J. Tedim, A.D. Lisenkov, A.N. Salak, M.L. Zheludkevich and M.G.S. Ferreira, *Nanoscale*, **2012**, 4, 1287-1298.
[3] D.G. Shchukin, S.V. Lamaka, K.A. Yasakau, M.L. Zheludkevich, H. Möhwald, M.G.S. Ferreira, *Journal of Physical Chemistry C*, **2008**, 112, 958-964.
[4] M.L. Zheludkevich, S.K. Poznyak, L.M. Rodrigues, D. Raps, T. Hack, L.F. Dick, T. Nunes, M.G.S. Ferreira, *Corrosion Science*, **2010**, 52, 602-611.
[5] M.L. Zheludkevich, J. Tedim, C.S.R. Freire, S.C.M. Fernandes, S. Kallip, A. Lisenkov, A. Gandini, M.G.S. Ferreira, *Journal of Materials Chemistry*, **2011**, 21, 4805-4812.
[6] M.L. Zheludkevich, J. Tedim, and M.G.S. Ferreira, *Electrochimica Acta*, **2012**, 82, 314-323.
[7] 17. M. Serdechnova, S. Kallip, M. G.S. Ferreira, M. L. Zheludkevich, *Electrochemistry Communications*, **2014**, 41, 51-54.

Oral 50B

Corrosion study of copper-based antifouling coatings on 5083 aluminum

Kevin CHASSE*, [1], Andrew SCARDINO[1, 2], and Geoffrey SWAIN[3]

[1] *Naval Surface Warfare Center Carderock Division, W. Bethesda, MD, USA*
[2] *Defence Science and Technology Group, Melbourne, Australia*
[3] *Florida Institute of Technology, Melbourne, FL, USA*

**kevin.chasse@navy.mil*

Traditional self-polishing, copper-based (cuprous oxide) antifouling systems (CuAF) are effective at controlling biofouling and have long been widely adopted by ship operators globally on steel hulls [1]. American Bureau of Shipping Rules prohibits the use of CuAF on aluminum vessels, owing to a concern of galvanic or other forms of corrosion [2]. Aluminum is more anodic, i.e. electronegative, in the electrochemical series than copper and when the two metals are in contact in seawater, the aluminum will undergo galvanic corrosion. Other copper-free antifouling coating systems, which use zinc oxide or ECONEA™, in lieu of cuprous oxide, are used as antifouling coatings for aluminum vessels. Given that modern hull coating systems comprise an epoxy anticorrosive layer and a topcoat containing cuprous oxide (not metallic copper), and are subject to cathodic protection, there is a paucity of data to support an informed risk assessment of when and how the corrosion can occur if CuAF are used on an aluminum vessel. This project used a combination of electrochemical techniques to understand the influence of cathodic protection on several commercial CuAF and copper-free coating systems in a series of laboratory experiments and two field studies. Coated 5083 aluminum specimens with a round flaw were held potentiostatically for 30 days and electrochemical impedance spectroscopy (EIS) was used to study the film properties from the open-circuit potential (OCP) to -1200 mV versus silver-silver chloride (Ag/AgCl) reference in ASTM D1141 ocean water. The flawed surfaces were characterized with microcopy to evaluate the extent of copper deposition and localized corrosion over this potential range. In the two field studies, panels with a linear flaw were exposed to natural seawater, with and without cathodic protection, at Cape Canaveral, FL and Fort Lauderdale, FL for 3 months. Results imply that there is a complex relationship among copper deposition, calcareous deposit formation, and corrosion of 5083 aluminum. Formation of calcareous deposits reduced the extent of corrosion at the most cathodic potential. Current monitoring alone during the potentiostatic holds was not a reliable measurement of corrosion behavior; however, EIS measurements in combination with post-test characterization showed the general trends in behavior. Results from the field studies supported the findings in the laboratory for the potential range that was examined. Copper from the CuAF coatings may deposit on the aluminum surface in the absence of calcareous deposits to facilitate corrosion if 1) the anticorrosive epoxy is compromised and 2) the cathodic protection system is not properly controlled. Longer term studies of these AF coating systems under field conditions is required to inform the risk over a vessel's full docking cycle.

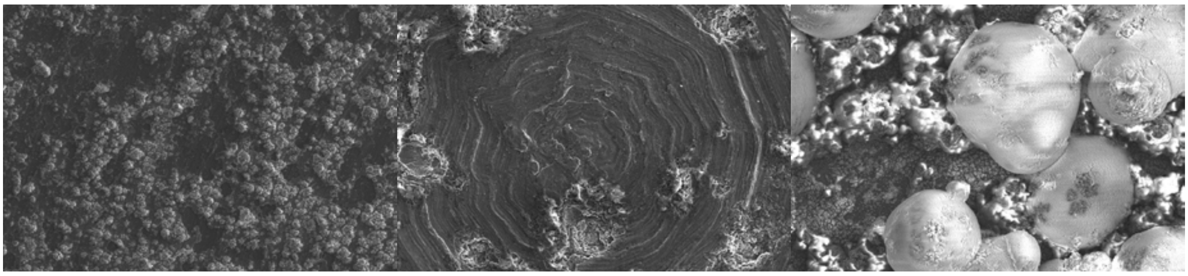


Fig. 1: CuAF laboratory coupons after 30 days of immersion depicting: (a) OCP with copper nodules, (b) -1000 mV vs. Ag/AgCl with evidence of pitting, and (c) -1200 mV vs. Ag/AgCl with calcareous deposits.

[1] J.D. Ferry and D.E. Carritt, *Ind. and Eng. Chem.* ***1946***, 38, 612-617.
[2] ABS - American Bureau of Shipbuilding Rules Section 26, dated 2015.

Oral 51B

A comparison between corrosion protection properties of polyaniline nanofibers and polyaniline nanotubes prepared via self-organization

François-Xavier PERRIN*[1], Cynthia OUEINY[1], Sophie BERLIOZ[1]

[1] *Laboratoire MAPIEM EA 4323, Université de Toulon BP 20132, 83957 La Garde Cedex.*

* *perrin@univ-tln.fr.*

The widely used Cr compounds have been banned in Europe since 2007 and soon worldwide due to their highly carcinogenic effect. Driven by regulations, researchers have focused on the development of green alternative coatings. In the last three decades, polyaniline (PANI) has received much attention as an anticorrosive pigment because of its easy preparation, low cost, good environmental stability and unique electronic properties. There is still much debate regarding the exact mechanism of protection of PANI. The mechanism that operates depends on many experimental factors: coating type, emeraldine form (conductive, ES or non-conductive, EB), corrosive environment, etc. Common mechanisms of corrosion protection are interpreted as physical barrier, adsorption, anodic protection and shift of electrochemical interface. Nanostructuration of PANI is expected to increase the interactions with metal substrate which increases the efficiency of electron transfer between metal and PANI. We will report here the formation of high quality PANI nanotubes and PANI nanofibers by interfacial polymerization using organophosphonic acid in the aqueous phase. The crucial template role of in situ formed and precipitated oligoanilines in the formation of PANI nanotubes by falling-pH self-assembly method will be highlighted. In our case, PANI nanotubes are more efficient pigments than nanofibrillar PANI. We will show that the higher efficiency of PANI-DPA nanotubes is not related to the different morphology (nanotube vs nanofiber) but to the inhibitive properties of the organophosphonic acid dopant of PANI nanotubes.

Acknowledgments: The authors gratefully acknowledge the Ministère de l'Education et de la Recherche for his financial support.

Oral 52B

Implementation of advanced technologies for application of protective coatings in Russian shipbuilding

Valeriy M. LEVSHAKOV, Olga F. FEDOROVA*, Aleksey A. VASILYEV, Nelli P. MASLOVA[1],

[1] *JSC Shipbuilding and Shiprepair Technology Center, Saint-Petersburg, Russia.*

**info@sstc.spb.ru*

Cleaning and application of protective coatings (painting and electroplating) are one of key operations in shipbuilding and shiprepair, their quality and productivity give direct effect to durability and operational reliability of ships and marine facilities, as well as to terms and cost of their construction and repair. Due to adoption in recent years of a number of international shipping acts, requirements to painting of ships, separate structures, tanks and outer plating became more strict and turned to be directly supervised by classification societies.

In Russian shipbuilding practice, painting works make up to 10% of total labor input in ship construction. At the same time, painting and electroplating are considered one of the least attractive activities, due to large amount of manual work (48%), and numerous operations with toxic and explosive materials.

Durability of protective coatings is by 50-60% depends on quality of surface preparation, by 20% on application quality and only by 20% on quality of paint itself. Obtaining quality coatings with guaranteed 10-15 years of service life is only possible when the work is performed in special cleaning and painting chambers, up-to-date electroplating lines, where all procedural conditions are observed, such as microclimate, drying modes, etc.

JSC SSTC, as a leading Russian research center for development and implementation of advanced shipbuilding technologies, has designed series of cleaning and painting chambers, setting chamber size depending on size of processed units, principal design of painting chambers for leading Russian shipyards, principal technologies for cleaning and coating of hull structures, and for electroplating. The company has a pilot electroplating bay for mastering of advanced galvanic techniques.

Basic principles for organization of painting and electroplating activities in JSC SSTC projects are:

- Performance of up to 70% of painting before shifting the hull to the building berth;
- Installation of cleaning and painting chambers with highly efficient equipment;
- Mechanization of painting operations at the building berth;
- Automation of small-size items painting’
- Designing and setting-up modern inter-regional electroplating shops, equipped with automated production lines, effective filtering and ventilation systems, system for re-circulation and disposal of solutions, and meeting current requirements to environmental and industrial safety.

Oral 53B

Electrochemical studies and numerical modelling of laser alloyed Al-Sn-Ti coating in saline environment.

Olawale FATOBA[1*]; Abimbola POPOOLA[1]; Sisa PITYANA[2]

[1]Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Faculty of Engineering and the Built Environment, P.M.B X680, Pretoria, South Africa.0001
[2]Centre for Scientific and Industrial Research-National Laser Centre, BLD 46F, Pretoria, South Africa.0001

** fatobaolawale@yahoo.com; FatobaOS@tut.ac.za*

The conventional surface modifications and coatings cannot fulfil the performance of material surface under corrosion and wear and environments. Therefore, an alternative technique for enhanced surface properties is needed by different industrial sector. The investigation of Al-Sn-Ti coatings on UNS G10150 steel by laser alloying technique is aimed at enhancing the surface properties of Al-Sn-Ti coatings on UNS G10150 steel. Laser power of 750 and 900W, scanning speed of 0.6 and 0.8m/min, and alloy composition of 20Al-20Sn-60Ti, and 25Al-25Sn-50Ti were used in the research. A 3 kW continuous wave ytterbium laser system (YLS) attached to a KUKA robot which controls the movement of the alloying process was utilized for the fabrication of the coatings. The steel alloyed surfaces were investigated for its hardness and corrosion behaviour at different laser processing conditions. The steel samples were cut to corrosion coupons, and immersed into 3.65 % NaCl solution at 30^{o}C using electrochemical technique. The microstructures of the developed coatings and uncoated samples were characterized by optical (OM) and scanning electron microscope (SEM/EDS). Moreover, X-ray diffractometer (XRD) was used to identify the phases present. The results showed improved properties by increasing the Ti content from 50 to 60%. The optimum properties were obtained at 20Al-20Sn-60Ti alloy at laser power of 750W and speed of 0.8 m/min. The corrosion rate of the optimum composition gave significant protection in 3.65 % NaCl solution and 2-times the hardness of the substrate was achieved. The enhanced hardness and corrosion resistance performance was attributed to the intermetallics and corrosion products such as titanium-tin (Ti_6Sn_5), aluminium-tin-titanium ($AlSn_2Ti_5$), titanium-aluminium (Ti_3Al), titanium-aluminium (TiAl), tin-aluminium-chloride ($Ti(AlCl_4)_2$), halite syn (NaCl). Response surface model (RSM) used in this research corresponds with the experimental results.

Keywords: Corrosion, Hardness, Morphology, RSM, and Al-Sn-Ti coating

Oral 54B

Electrochemical assessment of ammonium benzoate as corrosion Inhibitor of mild steel in 0.5M HCl solution: solanum tuberosum extract as surfactant

Olaitan AKANJI[1*], Cleophas LOTO[2], Abimbola POPOOLA[1] and Andrei KOLESNIKOV[1]

[1] *Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa.*
[2] *Department of Mechanical Engineering, Covenant University, Ota, Nigeria*.

* *laitan436us@yahoo.com*

Surface deterioration by corrosion is one of the complications associated with ageing facilities and components especially under some service environments. Studies involving performance of corrosion inhibitors had been identified as one of the critical research needs for improving the durability of mild steel used in various industrial applications. This paper investigates the inhibiting effect of Ammonium benzoate against thecorrosion ofmild steel in 0.5M HCl solution. The steel samples were cut to corrosion coupons, and immersed into 0.5M HClmedium at 30˚C using gravimetric and electrochemical techniques. The microstructures of the developed thin films and uncoated samples were characterized by optical (OM) and scanning electron microscope (SEM/EDS). Moreover, X-ray diffractometer (XRD) was used to identify the phases present. Results obtained reveal that the compound (Ammonium benzoate) performed effectively giving a maximum inhibition efficiency of 79% of 2% v/v concentration from weight loss analysis and 80.9% at 2%v/v concentration from polarization test.Moreover, the results obtained from potentiodynamics polarization had good correlation with those of the gravimetric method. The adsorption of the inhibitor on the mild steel surface from the acid was found to obey Temkin's adsorption isotherm. Scanning electron microscopy (SEM/EDX) observation confirmed the existence of an absorbed protective film on the metal surface.In addendum, combination of ammonium benzoate and solanum tuberosum extract greatly reduced the corrosion rate with ~ 90% efficiency compared to ordinary ammonium benzoate.

Keywords: Corrosion, Ammonium benzoate, Hydrochloric Acid, Mild Steel, and Solanum tuberosum.

Poster session

PT S1-1

Lanthanum and yttrium rare earth based conversion to improve the 6061 & 2024 aluminum alloys protection.

BEKHITI DJILLALI*[1], JUAN CREUS[2], MESRATI NADIR[3] , HIBA MESSAOUDI[4]

[1] *Military Polytechnic School, Algiers, ALGERIA.*
[2] *Engineer science laboratory for environment, La Rochelle, FRANCE.*
[3] *Department of metallurgy, Polytechnic national school, Algiers, ALGERIA.*
[4] *Corrosion laboratory and surface treatment, Skikda, ALGERIA.*

* bekhitidjillali@gmail.com

The introduction of high technology in radiators industry has been accompanied with new corrosion problems associated with modern concepts such as condensation and choice of materials. Thus, we can find in the same aluminum cooling circuit, copper piping, steel or aluminum and polymer materials. We describe an anti-corrosion treatment specifically designed to protect the cooling circuits in these demanding conditions, especially when aluminum is present. The mode of action against corrosion has been shown from a set of complementary experimental results: electrochemical measurements, observation by optical microscope and fluorescence analysis. In our work we focus on cathode deposits on the 6061 series and 2024 for comparison; these deposits are obtained by electro base generation in a solution containing rare earth lanthanum and yttrium. In our deposits we apply different cathodic currents for periods ranging from 10 to 30 minutes, we found that the film quality was directly related to conditions such as the current and time. After making the deposits, we proceeded to the polarization tests to assess the influence of these deposits on the corrosion resistance.

[1] Rangel C M, Paiva T L, Daluz P P. 2000, 29(9) : 507. Anticorrosion treatments for aluminum and aluminum alloys. European Symposium on Corrosion Inhibitor.
[2] Bethencourt M, Botana F J, Cano M J. 2002, 189(1/2): 162. High protective, environmental friendly and short-time developed conversion coatings for aluminum alloys. Applied Surface Science.
[3] Wang Zhenyao, Ma Teng, Han Wei, Yu Guocai. Trans. Nonferrous Met. Soc. China, 2007, l7: 326. Corrosion behavior on aluminum alloy LY 12 in simulated atmospheric corrosion process.
[4] Neil W, Garrard C. Corrosion Science, 1994, 36(5): 837. The corrosion behaviour of aluminum silicon carbide composites in aerated 3.5% sodium chloride.
[5] Sun J, Qi G C, Tan Y. Characterization of chromate conversion film on tinplate substrate by XPS and electrochemistry methods

PT S1-2

Advanced ceramic coatings to prevent corrosion an fouling in offshore components

David VÉLEZ[1]*, Josemari MUÑOZ[2], Rosalina PÉREZ[3], Marian CORRES[4]

[1,2,3,4] *IK4-CIDETEC, San Sebastian, Spain.*

** dvelez@cidetec.es*

Offshore components and devices have serious technical and economic problems as a result of aggressive phenomena of fouling and corrosion. In this sense, there is a growing demand to ensure the high performance and durability of these products, using efficient protective systems. The traditional solutions to avoid biofouling phenomenon use biocides, usually highly polluting substances, most of them included in paints and polymeric agents. Furthermore, another important solution to prevent corrosion is the use of expensive materials, substrates (stainless steels, Ni alloys, Titanium, etc.) and oversized designs for the purpose of increasing the whole life cycle of the component.

Faced with this scenario, there is a need for many industries to develop environmentally sustainable solutions to protect offshore structures. A technical solution based on advanced coatings with corrosion resistance and anti-fouling properties could improve the yield and reduce costs. In this field, the most important solutions have been focused on the development of paints. However, for certain applications, paints may have several disadvantages as their low resistance to scratching and wear, chemical stability problems at certain temperatures, low adherence (mechanical) to the substrate, etc. Thus, usually they have to be replaced regularly to maintain the main properties. In this regard, ceramic coatings could be a good environmentally friendly alternative in certain offshore components with high corrosion and biofouling resistance.

The application of ceramic coatings based on advanced enamels with antifouling properties in offshore structures is completely new. At this stage, IK4-CIDETEC, is actually working on different projects based on the development of ceramic coatings, chemically bonded to the substrate, incorporating active ceramic particles against fouling and environmentally friendly as copper oxides, vanadium, calcium, magnesium, zinc, titanium, iron, etc.

The ceramic coating could be applied by different procedures to allow the highest quality and the lowest cost. Systems based on 2 layers, ground and cover coat, with total thickness around 300 microns combine the desirable characteristics in an enamel coating. The ground coat gives a chemical bonding to the substrate by the formation of a metal/ceramic interface and also a high corrosion protection to chloride systems. Finally, the cover coat, chemically bonded to the ground coat and applied in the same way that the first one (thermal heating over 820ºC) provides the combined properties (anticorrosive/antifouling). The main objective of this technology is to achieve a durability solution that could extend the life of the metal structures in offshore environment.

Some ceramic formulations developed in IK4-CIDETEC with high corrosion resistance under seawater immersion conditions are currently under evaluation in a test bed to analyze the effect of active ceramic nanoparticles in the antifouling properties, showing a good behavior at early stages.

PT S1-3

Application of the conducting polymers in the marine anticorrosion paints

Ahcene SAKHRI*[1], F.X. PERRIN[2], E. ARAGON[2] and A. BENABOURAD[3]

[1] : DRD/Algérien Navy- Alegria,
[2,]: MAPIEM, SeaTech, Université de Toulon Var, France
[3] : USTHB- HOUARI Boumediene- Algeria

** SAKH_21DZ@yahoo.fr*

The corrosion problem affects all domains of the industrial activity and caused serious damages on the economic and ecological fields. The domains of shipbuilding and maritime transport are the most affected by this problem. The damages produced are harmful to the production (losses of equipment, reparation costs, repeated failures), and the conditions of security of the personnel (staff) and the ship's crews.
The aim of this work is the comparison between the protected performances of the marine anticorrosion paints system incorporating zinc phosphate and a new system based on conducting polymers. The anticorrosion performance was evaluated using salt spray and electrochemical methods.
The results obtained by different methods indicate the superiority of paints including conducting polymers in comparison with conventional paints incorporate zinc phosphate in terms of corrosion protection.

Keywords: paint, conducting polymers, anticorrosion pigment, electrochemical impedance spectroscopy.

PT S1-4

Study on the performance of different type epoxy resin coatings under hydrostatic pressure seawater environment

Bin LIU *

Naval Academy of Armament, Beijing, P.R.China.

* *liubindr@outlook.com*

Along with ocean resources development and exploitation day by day, the corrosion protection research aiming at deep sea environment becomes a new topic. The epoxy coatings are widely used under marine environment, while epoxy resin plays an important role to the performance. In this paper, under hydrostatic pressure seawater in the laboratory, the performance of three different type epoxy resin coatings, including E44, E12 and FM-15, were studied by using electrochemical impedance spectroscopy (EIS) and adhesion test. The results showed that the deterioration of coatings' property of corrosion protection under hydrostatic pressure seawater environment was much faster than that of under normal pressured seawater. However, the performance of FM-15 and E12 epoxy resin coatings are better than that of E44 epoxy resin coatings under hydrostatic pressure seawater, which indicating potential application for hydrostatic pressure seawater environment, such as deep sea engineering in the future. The research results are valuable to develop and select anti-corrosion coatings for similar application.

Keywords: Epoxy resin, Coatings, Anti-corrosion performance, Adhesive force, Hydrostatic pressure seawater

PT S1-5

Coatings for corrosion protection of Mg alloys

Aurélie DUPUIS*,[1], Emmanuel ARAGON[1], François-Xavier PERRIN[1]

(1) Laboratoire MAPIEM EA 4323, Seatech-Ecole d'Ingénieurs, Université de Toulon, CS 60584, 83041 Toulon Cedex 9, France

** aurelie.dupuis@univ-tln.fr*

Magnesium and its alloys is used in a wide range of applications due to its low density as well as its good mechanical properties. On the contrary, engineering applications of magnesium have been limited mainly due to the poor corrosion properties of magnesium alloys. Several coating applications have been developed in order to improve corrosion and a very promising application is hybrid organic-inorganic sol-gel coatings [1]. Furthermore, active corrosion inhibiting components are often added to the protective corrosion system, conferring self-healing properties which assure prolonged protection even in the case of partial damage of the coating.
Polyaniline (PANI) has been extensively studied as protective coating for metals and alloys and has remarkable capability to protect steel in acid, alkaline and neutral environments. PANI containing coatings protects metal by forming a passive oxide layer on the metal surface. The corrosion process monitored by electrochemical impedance spectrometry for instance has shown the efficiency of protection of PANI inhibitors. Perrin et al. showed the increase of protection by doping PANI with decylphosphonic acid (DPA) [2]. In the last decade, nanoparticles like nano-SiO_2, nano-TiO_2, nano-Al_2O_3 and nano-ZnO have been used to improve the mechanical properties as well as the anticorrosion performance of the organic paints. Among inorganic nanoparticles, nano ZnO particles have received great attention because of its unique electrical, catalytic, electronic and optical properties, high stability and environmental friendly feature, as well as low cost and extensive applications in different fields. Mostafaei et al. [3] prepared PANI/ZnO nanocomposite by in situ chemical oxidative method. PANI/ZnO nanocomposite pigmented coatings on steel exhibited high corrosion resistance in 3.5% NaCl solution.
The aim of this work is to test corrosion protection of sol-gel coatings reinforced with a combination of PANI and nano-ZnO pigments on Magnesium alloys. Optimization of nano-ZnO and PANI proportions as well as their dispersion in the sol-gel coating have been studied. Corrosion resistance properties of the coatings was investigated by electrochemical measurements and by the study of evolution of coating under salt spray exposure.

[1] S.V. Lamaka, D. G. Shchukin, D. V. Andreeva, M. L. Zheludkevich, H. Mohwald, M.G.S. Ferreira, *Adv. Funct. Mater*. **2008**, 18, 3137-3147.
[2] F.X. Perrin, T.A. Phan, D.L. Nguyen, *Eur. Polym.* **2015***,* 66, 253–265.
[3] A. Mostafaei, F. Nasirpouri, *Prog. Org. Coat.* **2014**, 77, 146–159.

PT S2-1

Dynamics of carbon steel corrosion in an estuarine Amazonian environment (MIC)

Margaux VASTRA[1], Paule SALVIN[1], and Christophe ROOS*,[1]

[1] *L3MA UMR ECOFOG Université des Antilles, Schoelcher, France*

* *christophe.roos@martinique.univ-ag.fr*

MIC is a natural process widely studied in temperate, tidal environments. Recently, in 2009, a bridge with a carbon steel structure made, crossing over an estuary in French Guiana and constituting a major road in the area, had undergone of a material damage (crack on a pylon), strongly suspected to have been induced by microbial induced corrosion (MIC). This phenomenon, rarely studied in warm and sediment rich environments, as presented here, has been the object of our study. The objectives were to demonstrate the part of the microbial biodiversity in the damage and to identify MIC markers in this kind of environment.
In precedent studies, we have demonstrated that at low water level of immersion, where the breakage took place, the conditions lead to the faster corrosion with 0.8 $mm.year^{-1}$ [1]. This water level has been identified frequently as conducive to MIC [2,3]. In addition to this corrosion rate, a low corrosion resistance, an important diversity of the microorganisms and a high concentration of nutrients (especially nitrate) were markers of accelerated low water corrosion (ALWC).
Thereafter, the corrosion dynamics were followed for 50 days at low water level. Experiments were carried out immersing carbon steel coupons at this water level of the estuary in situ and under different conditions in laboratory. A multidisciplinary research with the combination of electrochemistry, chemistry, biology and materials science has been used in order to identify and track corrosion parameters and MIC phenomenon. Throughout the period of 50 days, the surface phenomena appears to be constant whereas corrosion rates increase linearly. Evolution of the chemical and biological compositions of the coupon surface' deposit were observed and compared. The deposit composition on the coupon surface changed from iron oxides and hydroxides to manganese oxides and iron sulfides. A shift in the main bacterial species was observed evolving from β-proteobacteria to α-proteobacteria, with a very minor population of δ-proteobacteria such as sulfate-reducer bacteria, yet often involved in MIC. The corrosion process is an aerobic one with the predominance of aerobic sulfate-oxidizer bacteria, corresponding to the first stages of the Melcher's electrochemical model.

Acknowledgements: This project was supported by the European Union (FSE), the Centre National d'Etudes Spatiales (CNES) and an "Investissement d'Avenir" grant managed by Agence Nationale de la Recherche (CEBA, ANR-10-LABX-25-01).

[1] M. Vastra, P. Salvin and C. Roos, "MIC on bridge-building carbon steel in a tropical/Amazonian environment", European Corrosion Congress (EUROCORR 2014) 8-12 Sept. 2014, Pisa, Italy
[2] I. B. Beech and S. A. Campbell, *Electrochimica Acta* **2008**, vol. 54, no. 1, 14–21. Special Issue BIOCORROSION OF MATERIALS Selection of papers from the International Conference (BIOCORYS 2007) 14-17 June 2007, Paris, France.
[3] H. Wall and L. Wadsö, *Marine Structures* **2013**, 33, no. 0, 21 – 32.

PT S2-2

Influence of *Desulfovibrio* sulphate reducing-bacteria in the corrosion of mild steel coated with self-healing coatings

Tânia OLIVEIRA[1], Maria Júlia FERREIRA[1], Francisco AVELELAS[1], Frederico MAIA[1], Roberto MARTINS[2], Rob ONDERWATER[3], Alexandre BASTOS[4], João TEDIM[4]*

[1]Smallmatek - Small Materials and Technologies, Lda., Rua Canhas, 3810-075 Aveiro, Portugal.
[2]Department of Biology and CESAM, University of Aveiro, 3810-193 Aveiro, Portugal.
[3]MateriaNova ASBL, Rue des Foudriers, 1, 7822, Ghislenghien, Belgium.
[4]Department of Materials and Ceramic Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal.

** joao.tedim@ua.pt*

Bacteria and microalgae tend to fix and grow on the surface of maritime structures during the initial stages of biofouling, forming extensive biofilms able to produce metabolic by-products. The interaction between these by-products and the metal substrate affects the kinetics of cathodic and/or anodic reactions and often accelerates the deterioration of metallic structures, known as microbially-influenced corrosion (MIC) [1]. Several groups of bacteria can be involved in the MIC process. Sulphate reducing-bacteria (SRB) are a ubiquitous group of bacteria that reduces sulphur and oxidized sulphur compounds into H_2S, usually in the total absence of oxygen, posing a big challenge for the stability of natural or man-made metallic structures under anoxic conditions [1,2]. Despite the increasing knowledge regarding this subject, there are few studies on how self-healing coatings based on controlled release of inhibitors can limit the detrimental effect of SRB in the active corrosion protection. Therefore, the aim of the present study is to understand the role of both anaerobic SRB *Desulfovibrio desulfuricans* and *D. desulfuricans aestuarii* in the corrosion process of coated mild steel substrates, under different scenarios.

For this purpose, mild steel was pre-treated according to the standard ASTM G1 and then uniformly coated with different coating systems developed for maritime applications. Coupons were then exposed to different scenarios: (a) abiotic condition by adding to each coupon *Desulfovibrio* medium supplemented with NaCl, without bacteria; (b) biotic condition by inoculating *Desulfovibrio* medium supplemented with NaCl with each bacteria species (*D. desulfuricans* and *D. desulfuricans aestuarii*). Liquid handling was performed under sterile and anoxic conditions inside a glove box. The corrosion protection was investigated by optical microscopy, as well as by different electrochemical techniques, such as electrochemical impedance spectroscopy and direct current polarization (fig. 1).

The obtained results are expected to contribute for the improvement of knowledge about the role of anaerobic bacteria in the degradation of metallic structures used in maritime applications.

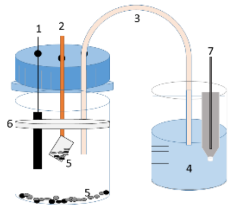


Fig. 1. Scheme of the EIS testing set-up for MIC studies: (1) counter electrode; (2) working electrode; (3) salt bridge; (4) sodium chloride solution; (5) SBR biofilm; (6) mineral oil; (7) reference electrode.

[1] B. Little, J. Lee, Microbiologically Influenced Corrosion **2007**, John Wiley & Sons, Hoboken, NJ.
[2] I. Beech, A. Bergel, A. Mollica, H.-C. Flemming, V. Scotto, W. Sand, *Int. J. Electrochem. Sci*. **2013**, 8, 859-871.

Acknowledgements: This research is supported by the EU FP7 collaborative project “BYEFOULING - Low-toxic cost-efficient environment-friendly antifouling materials”, under Grant Agreement no. 612717.

PT S2-3

Electrochemical aspects of stainless steels corrosion in seawater

Valery KARPOV*[1], Julia KOVALCHUK[1], Victor TIMONIN[2]

1 - A.N. Severtsov Institute of Ecology and Evolution, Moscow, Russia
2 –D.Mendeleev University of Chemical Technology, Moscow, Russia

** Valery.Karpov@bk.ru*

High corrosion resistance of stainless steels in seawater could be explained by their passivity to oxidizing agents (mainly – dissolved oxygen). The presence in the seawater of significant amount of chloride ions that are the local activators of passivation layers gives rise to pitting. It was experimentally proved that fortification of oxygen concentration in seawater (when corrosion potential is shifted to electropositive meaning) intensifies pit corrosion, whereas the reduction of oxygen concentration leads to the general activation of the passive surface. Thus the corrosion resistance is achieved in rather narrow potential range in which there is enough oxygen for passivation process but its quantity is insufficient for shifting to corrosion pitting.
Biofilm on the metal surface has considerable effect on both anodic and cathodic processes of electrochemical corrosion. In natural context in the presence of marine bacteria the corrosion rate of stainless steel samples increases in 2-3 times in comparison to the corrosion of the similar samples in bacteria-free seawater. It is explained by the reduction of oxygen concentration in biofilm on metal surface as a result of aerobic bacteria metabolism, and in the course of time – by growth of anaerobic bacteria as well as by hydrolysis processes under the films of corrosion products and biodeposits.

PT S3-1

Use and misuse of anodic protection in ballast tanks

Kris DE BAERE[1]*, Raf MESKENS[1], Remke WILLEMEN[1],
Helen VERSTRAELEN[1], Geert POTTERS[1,2]

[1] Antwerp Maritime Academy, Antwerp, Belgium.
[2] Dept. Bioscience Engineering, University of Antwerp, Antwerp, Belgium.

** kris.de.baere@hzs.be*

For some 140 years steel is the common construction material for commercial ships. Together with this, relatively stable, substance a persistent enemy popped up: corrosion. Two long-established methods are being used to fight this never sleeping enemy: either through the use of coatings, creating a barrier between the electrolyte and the steel or by way of using sacrificial anodes or impressed current, lowering the potential of the steel structure until it becomes cathodic. This article will focus on the correct use of sacrificial anodes in ballast tanks, since these tanks are the most vulnerable to corrosion, especially on board double hull ships due to increased temperatures, inherent wet/dry situations, omnipresence of seawater, storage compartment for ship's structural elements.
An in situ survey of >170 ballast tanks on board merchant ships lead to two principal conclusions: First, epoxy coatings in ballast tanks, remain overall in intact condition for approximately 5 years and afterwards degrade with 1.7% surface per year. Secondly, statistical analysis of the database did not show any distinctive advantage of the presence of sacrificial anodes, hence leading to the alarming conclusions that, probably, for many years anodes have been used without any significant impact on corrosion or corrosion rates. We studied this phenomenon further in depth and found that a cathodic protection system will only generate a distinguishable advantage if installed and maintained meticulously. Calculating the total mass of zinc required to lower the potential of the metallic structure sufficiently is rather easy, distributing the anodes correctly throughout the tank to obtain an even and correct potential is already a lot more complicated. Till today, any legal obligation to install sacrificial anodes in ballast tanks, is lacking. Consequently there are no rules promoting a correct weighing and spreading out of the sacrificial anodes. Very often, the design and installation of the cathodic protection system is done by the vendors of the zinc or aluminum anodes. Their and the ship's interest are not always the same.
A simulation package, CPMaster, developed by Elsyca, Belgium allows the visualization of the polarization of a metallic structure induced by sacrificial anodes or impressed current. By way of example one of the ballast tanks of the Flanders Harmony, a 28 year old LNG carrier, was modelled and the results were compared with the outcome of a detailed tank inspection held during dry-dock in Bahrain 2013. The resemblance between the in situ observation and the simulation model was satisfying. Although the tank was in a splendid condition, taking into account the age of the ship, there was still plenty of room for improvement. The cathodic protection system was oversized and the anodes were not distributed in a uniform way, the sacrificial anodes might even be responsible for the massive quantity of blisters in the tank.
Finally we conclude that cathodic protection using sacrificial anodes is a useful technique only if the system is well proportioned, installed, maintained and evolves together with and in function of the condition of the tank. If one is not prepared to follow up the system in a proper way it is better to abandon cathodic protection all together and invest the money gained in an improved coating system.

PT S3-2

SRB induced accelerated stress corrosion cracking under cathodic protection potential

Fang GUAN[1,2], Jizhou DUAN*[,1], Yanliang HUANG*[,1], Xiaofan ZHAI[1,2], Baorong HOU[1]

[1] *Institute of Oceanology, Chinese Academy of Sciences, Qingdao, China.*
[2] *University of Chinese Academy of Sciences, Beijing, China.*

** duanjz@qdio.ac.cn, hyl@qdio.ac.cn*

The stress corrosion cracking (SCC) behavior of steel in sulfate-reducing bacteria medium under -1030 mVSCE was studied to simulate the corrosion cracking of steel wirerope with Zn-Al alloy coating in seawater and seamud. Slow strain rate tension (SSRT) technique, scanning electron microscopy (SEM) and electrochemical techmiques were applied foe the tests.Tests were carried out in sea water, sterile or inoculated with sulfate-reduction bacteria (SRB). Results showed that the steel was susceptible to hydrogen embrittlement to some extent. SRB could promote the hydrogen brittle fracture under cathodic protection.

[1] Q. Fu, H. Kobayashi , Y. Kuramochi, J. Xu , T. Wakayama , H. Maeda, K. Sato, *Int J Hydrogen Energy.* ***2013,*** 38, 15638-15645.
[2] Y. Zhu, Y. Huang, C. Zheng, Q. Yu, *Materials and Corrosion* **2007,** 58, 447-451.

PT S3-3

The effect of fouling organisms on calcareous deposit of carbon steel

Jie ZHANG[1]*, Jiangwei WANG[1,2], Shougang CHEN[2], jizhou DUAN[1]

1. Institute of oceanology, Chinese academy of sciences, Qingdao 266071,China
2. Institute of Material Science and Engineering, Ocean University of China, Qingdao 266100, China

** zhangjie@qdio.ac.cn*

Under the condition of cathodic protection, calcareous deposit is formed on metal's surface. Sulfate-reducing bacterial (SRB) are recognized as the most imminent species taking part in microbiologically influenced corrosion. Moreover, the cathodic depolarization theory induced by SRBs is commonly accepted. But few articles about the interaction between SRB with the calcareous deposit were found.

In this experiment，the calcareous deposit precipitated for 72h with the current density of -30uA/cm^2 was prepared, which is with optimum crystal structure and smooth surface. The calcareous deposit is mainly composed of $CaCO_3$ with fine grain and uniform surface.

Fluorescence microscope was used to study the influence of calcareous deposit on the attachment of SRB. The samples coated with calcareous deposit were immersed in the culture medium containing SRB for different hours, so the pictures of fluorescence microscope was taken. From these pictures, we could conclude that the samples with calcareous deposit are beneficial to SRB colonization.

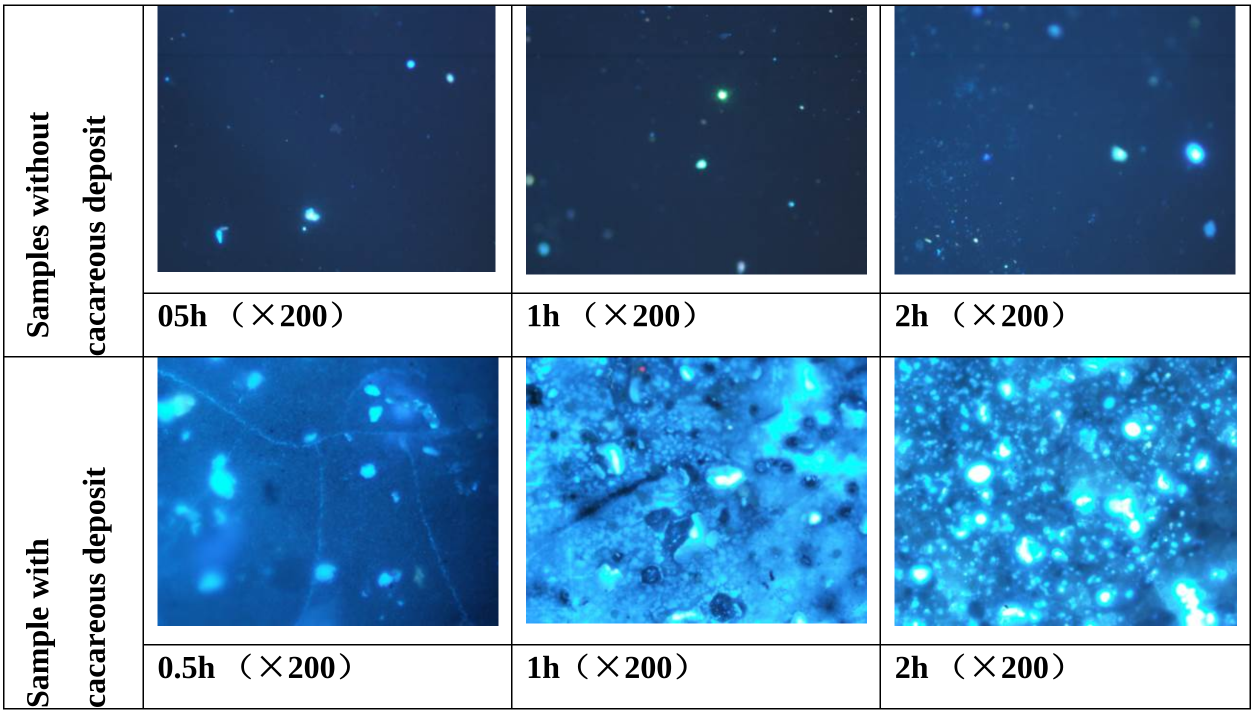


Figure. Fluorescence microscopy images of SRBs stained with DAPI on samples

Acknowledgements: This study was supported by National Natural Science Foundation of China (No. 41376003 and 41006054).

PT S4-1

“Marine Fouling Species from the Brazilian Coast” database: a web-based system for marine biosecurity management

Luciana V R De MESSANO[1,2,*] , Alexandre D KASSUGA [1,2]; Lais PDO NAVAL-XAVIER [1,2]; Luciana V GRANTHOM-COSTA[1,2]; Julio Cesar MONTEIRO[2]; Moacir APOLINARIO[3] and Ricardo COUTINHO[2]

[1] *FUNDEP- Fundação de Desenvolvimento da Pesquisa, Belo Horizonte/ MG, Brazil*
[2]*IEAPM- Instituto de Pesquisas do Mar Almirante Paulo Moreira, Arraial do Cabo/RJ, Brazil*
[3] *CENPES/PDEDS/AMA, Rio de Janeiro/RJ, Brazil*

** lvicentebm@gmail.com*

Marine bioinvasions caused by biofouling transportation on vessels are reported around the world and represent a risk to environmental biosecurity. Prevention is considered the best alternative for this problem. In order to accomplish that it is crucial to understand species distribution patterns and history of invasion of non-indigenous species (NIS). The database “Marine Fouling Species from the Brazilian Coast” was built to fill in these gaps and help the management and control of fouling organisms and NIS along Brazilian coastal waters. Our database is a web-based system implemented to provide open access to information on the geolocation of marine fouling species on Brazilian natural and artificial substrates and also check on the taxonomic status of these species. The system is a friendly platform designed to easily upload information directly by individual insertions or by multiple insertions using an Excel spreadsheet. The final result is a table composed by the species' taxonomic classification as well as a mapping system to visualize the data and download them. Published data have been inserted by our group, but any researcher can login as a collaborator in the system and insert data. Other information can be included such as the status in relation to introduction, sampling site details and photographs. The system can be accessed in the website www.incrustantesdobrasil.com.br wherein previously authorized information is available to any visitor in Portuguese or English versions. Nowadays the database contains 568 fouling species distributed over more than 290 localities along the Brazilian coast. The conceptualization and development of the system and the website are part of GEBIO project that also supported the implementation of a scientific collection housed at IEAPM (Brazilian Navy) to store mostly marine fouling specimens and a tissue collection. A module was designed in the restricted area of the system to catalogue the collection items. The Curation area was developed to assist curator activities, providing a database to organize the collection which currently holds more than 800 specimens. Like other users, curators can login in the system, catalogue their own items and authorize (or not) the data to be open accessed through the portal. This solution give support to an effective dissemination and utilization of the information associated with the collections, an old problem in collections management worldwide [1]. The whole system with all functionalities effectively integrates essential information to improve management and control of fouling species distribution in Brazil. The system also provides an accurate background for risk assessment analysis in different Brazilian coastal areas helping in the creation of “watch lists" of species that biosecurity management can use for NIS surveillance [2]. Future steps in system development include a specific module to attend the requirements to assess marine biosecurity risks and another module to support a citizen scientists program.

[1] M. Hamer, *S. Afr. j. sci.* [online]. **2012**, 108, 71-82.
[2] F. Azmi, C. Primo, CL Hewitt, ML Campbell, *ICES Journal of Marine Science* **2015**, *72*(3), 1078-1091.

PT S4-2

At the border: assessing vessel biofouling risks in an operational context

Daniel KLUZA*[1], Andrew CURTIS[1], and Eugene GEORGIADES[1]

[1] *Ministry for Primary Industries, Wellington, New Zealand.*

* *daniel.kluza@mpi.govt.nz*

Vessel biofouling is a significant pathway for the introduction of non-indigenous marine species, and this topic is receiving increasing attention at national and international levels. New Zealand has become the first nation to regulate the vessel biofouling pathway, with controls coming into force in May 2018. To implement these controls, biosecurity targeting operations require a set of biofouling risk indicators to identify potentially noncompliant vessels for further investigation. Here, we discuss the performance of the initial biofouling risk indicators being trialled by the New Zealand Ministry for Primary Industries (MPI), the operational practicalities of assessing vessel biofouling in the border clearance process, and we review MPI's commissioned research on the development of practical risk management solutions.

PT S4-3

Ship biofouling: what are the biosecurity risks?

John A LEWIS[1]*

[1] *ES Link Services Pty Ltd, Castlemaine, Australia*

* *jlewis@eslinkservices.com.au*

Any surface immersed in the sea becomes a potential settlement site for marine organisms with the hulls of vessels no exception. Since mariners first set sail, their boat hulls became a welcome home for many species that liked a floating lifestyle on substrates initially free of established communities and epibenthic predators. The character of the hull habitat, with few natural analogues, has since globally fostered the formation of an association of organisms with composition and characteristics unique to that community. The stresses of the peripatetic lifestyle inhibit the regular patterns of ecological succession and complex communities often only develop in protected niche areas.

The effect of biofouling to the ship operator is an increase in hull friction, degradation of performance, and added fuel and maintenance costs. A further consequence is the increased emission to the atmosphere environmentally harmful gases, notably SOx, NOx and greenhouse gases. Antifouling coatings have been the primary defence against biofouling since the mid-19th century but, despite significant advances in antifouling technology over the last 50 years, they still have limitations in effective life, cost, and efficacy for both hulls and within hull niches. The vast array and taxonomic diversity of potential biofouling species, combined with environmental concerns and limitations on the use of broad spectrum biocides ensures there is no simple solution.

The anthropogenic movement of aquatic invasive species and the significant economic and environmental impact documented for some species has precipitated global actions to minimise further introductions and spread of non-indigenous species. Translocations and biogeographic spread have been associated with aquaculture, the opening of inter-ocean canals, the aquarium industry, and vessels. International shipping has been targeted as a major vector for the transportation of marine species in either ballast water or as hull fouling and the need for management of these has been promoted through the IMO Ballast Water Management Convention and the Guidelines for the Control and Management of Ships' Biofouling. It is accepted that the introduction of the majority of non-indigenous marine species found in ports around the world is most likely via ship biofouling, but these predominantly establish on only artificial substrates or in anthropologically disturbed environments. They can therefore be considered a consequence, not a cause, of environmental disturbance. The question therefore arises whether the expenditure of resources on all-encompassing regulatory systems directed at international trading ships is justified, or whether a more focused approach that targets higher risk vessels and vectors is a more judicious approach.

PT S5-1

An impact of nautical tourism on copper concentrations in the Krka River estuary (Croatia)

Nuša CUKROV[1], Jasmin PAĐAN[1], Ana-Marija CINDRIĆ[1], Marija Marguš[1], Neven CUKROV[1], Dario, OMANOVIĆ*,[1], Cédric GARNIER*,[2]

[1] Ruđer Bošković Institute, Division for Marine and Environmental Research, POB180, Zagreb, Croatia
[2] Université de Toulon, PROTEE, EA 3819, 83957 La Garde, France

** omanovic@irb.hr; cgarnier@univ-tln.fr*

Copper (Cu) is a micronutrient required in a number of cellular processes that are key for phytoplankton growth. As phytoplankton is the first level of the food chain, deficiency in copper can lead to numerous unfavourable biological conditions in the sea ecosystem. At physiologically high concentrations, copper is toxic and may affects both planktonic abundance and diversity in coastal waters. Range of copper concentrations between these two extremes is relatively narrow [1, 2, 3]. Copper contaminates coastal waters mainly by anthropogenic inputs. It is used as an anti-biofouling agent with Cu-based paint covering the hull of boats, releasing considerable quantity in coastal waters. The areas which are potentially endangered are those with high copper input and weak water exchange. One of these potentially endangered areas is the Krka River estuary. Estuary is protected as NATURA 2000 site under name Krka Mouth. In the site, two areas protected in the category of Significant landscape are situated – "Krka – lower part" landscape from the Skradin bridge to the Šibenik bridge and "Channel-Harbour" in Šibenik. Considering the value of the Estuary, increased development of nautical tourism poses a threat for this protected area. Preliminary studies carried out in Krka River estuary in last several years, have showed that during summer season concentrations of copper are up to 20 times higher compared to winter season [4]. Unfortunately, the number of vessels (per day/month/year) in the Estuary is unknown.

To evaluate relation between copper contents in water, the number of vessels during one-year period and other parameters such are salinity, rainfall, Krka River flow, wind strength and direction, a monitoring system has been established, based on the two main activities: (1) video surveillance/observing system for vessels counting, (2) monitoring of copper content in water. The video observing system provided continuous information about entrance/exit and statistics of the vessels (hour, day, month, year). In surface water samples, which have been collected every 2-3 days within the Šibenik bay, concentrations of copper and other trace metals were measured. The established monitoring has confirmed strong relation between the nautical tourism and concentrations of copper in the surface layer (Figure 1). The results from this research can be used as support in planning sustainable tourism in this, as well as in other protected areas.

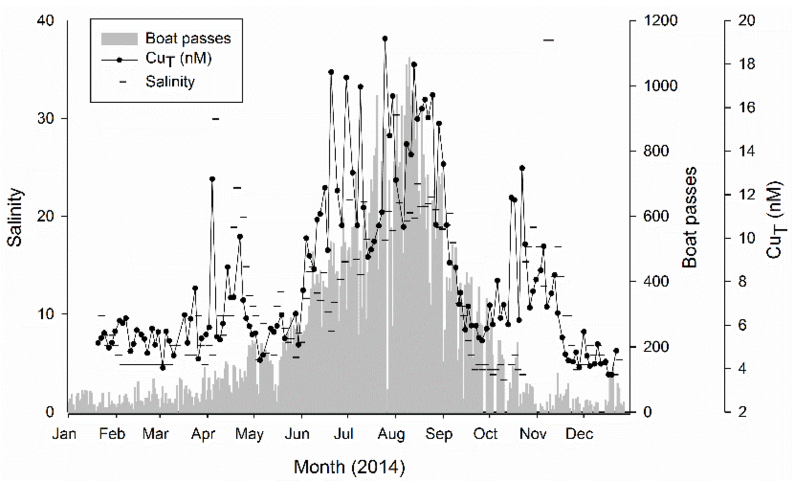


Fig. 1: Boat passes, Cu concentrations and salinity in surface layer

[1] J. Donat, C.Dryden, *MC&G* **2001**, 77-81
[2] W.G. Sunda, P.A. Tester, S.A. Huntsman, *Mar. Biol.* **1987**, 94, 203-210
[3] A. Tessier, D.R.Turner, Metal Speciation and Bioavailability in Aquatic Systems. **1996**, John Wiley & Sons, Chichester, UK.
[4] A.-M. Cindrić, C. Garnier, B. Oursel, I. Pižeta, D. Omanović, *Mar. Poll. Bull.* **2015**, 94, 199-216

PT S5-2

Zinc governs the release rate of copper in a generic antifouling paint

J. Fredrik LINDGREN*[1], Mia DAHLSTÖM[1], Anna-Lisa WRANGE[1], Albin HOLMQVIST[1], Peter DAHL[2], Magnus DAHLSTRÖM[3] and Erik YTREBERG[3]

[1] SP Technical Research Institute of Sweden, Borås, Sweden
[2] Department of Chemistry and Molecular Biology, University of Gothenburg, Göteborg, Sweden
[3]Department of Shipping and Marine Technology, Chalmers University of Technology, 412 96 Gothenburg, Sweden

** fredrik.lindgren@sp.se*

The issue with biological fouling on manmade structures is a well-known problem that has been combated in various forms since man started to use sea transport [1].
Following the ban of TBT by the International Maritime Organization (IMO) in 2008 [2] the usage of copper was reintroduced as the main used biocide in antifouling paints. It has its main antifouling effect on barnacles, tube worms and species of algae [3]. The copper used in antifouling paints is usually in the form of metallic copper, copper thiocyanate or cuprous oxide and the copper content can vary between approximately 4 to 75 %, depending on the fouling pressure on the geographical location [4]. Copper is an essential micronutrient used in metabolic processes within an organism, hence low concentrations of it is needed. However, higher concentrations of copper is toxic to organisms where cyanobacteria and embryos/larvas of mussels, oysters and sea urchins are known to be highly sensitive [5]. Therefore to minimise the copper leakage from antifouling paints is of importance. Zinc is a component in antifouling paint that is included in various concentrations. However, the importance of Zinc in governing the release rate of copper is not fully examined. Therefore, the purpose of this study was to evaluate to what extent zinc content contributes to leakage rates of copper and to relate it to effects in recruitment of fouling organisms.
A field test was performed at the Swedish west coast during june-september in 2015. Copper concentrations of 8.5, 11.7 and 16.3% with 0, 10 or 20% Zinc were added to a generic paint. The paint was applied with a paint applicator (100µm) to Plexi glass® panels and each treatment was replicated 24 times. After initial X-ray fluorescence (XRF) measurements the panels were submerged in the marina. At each sampling occasion (after 4, 7, 14, 28, 56 and 98 days), four replicates were retrieved and once again measured for Cu and Zn content. Leakage rates were calculated and steady state release rates appeared after 28 days. The recruitment of fouling organisms to each panel was calculated under a dissecting microscope.
In the treatments where no zinc was mixed into the generic paint the release rate of copper was highly elevated in the first week. The total amounts of released copper were also larger in the no-zinc treatments. In all treatments where zinc was mixed into the generic paint the copper release was more uniform over time. All treatments were successful in deterring fouling over a period of 98 days.
Results shows that zinc is highly involved in governing the release rate of copper. In addition, the results indicates that including zinc in antifouling paints increase the period of time where it is effective in combating fouling.

[1] D.M. Yebra, S. Kiil, K. Dam-Johansen, *Progress in Organic Coatings.* **2004**, 50(2), 75-1004.
[2] IMO, 2001 International Convention on the Control of Harmful Anti-fouling Systems on Ships. IMO. **2001.**
[3] N. Voulvoulis, M.D. Scrimshaw, J.N. Lester, *Applied organometal chemistry* **1999**, 13, 135-143.
[4] M. Srinivasan, G. W. Swain, *Environmental management* **2007** 39, 423-441.
[5] K.V. Thomas, S. Brooks. *Biofouling* **2010**, 26(1), 73-88.

PT S6-1

Role of hydrodynamic condition on biofilm formation of *Bacillus sp.* in a rotating disk system

Leila ABDOLI, and Hua LI*

Key Laboratory of Marine Materials and Related Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China.

** lihua@nimte.ac.cn*

Hydrodynamic strength is one of the key parameters that influence microbial adhesion and biofilm formation [1]. In order to adhere to surfaces and subsequently to form biofilms, microorganisms in high-velocity flowing systems must overcome shear stress at the fluid surface interface. In this study we examined the effect of shear, created by the tangential liquid flow in a rotating disk system (RDS) on adhesion and biofilm formation of *Bacillus sp*. biofilms were formed on stainless steel 316L while being exposed to different shear stresses generated by two rotational speeds (350rpm≈37 rad/s and 800rpm≈84 rad/s). The coupons were examined by confocal laser scanning microscope (CLSM) and SEM for 7 days. Results showed the early stage of biofilm development practically unaffected by shear stress. However, in a mature biofilm, shear stress determined the disposition of biofilm cells onto the surface. Moreover, shape of biofilms was probably governed by the continuous applied shear stress. Finally, biofilms formed under higher shear stress differs significantly in their arrangement, as compared with those formed under lower shear conditions.

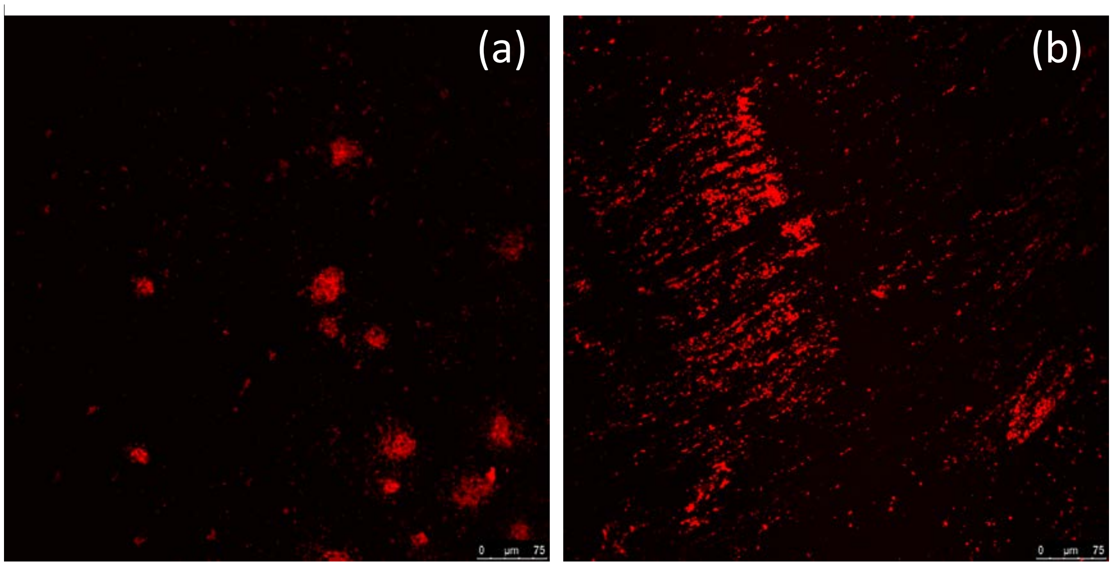


Fig. 1: CLSM images of Bacillus sp. biofilms formed on stainless steel after 7days at 350 rpm (a) and 800 rpm (b).

[1] S. Wäshe, H. Horn, D-C. Hempel, *Water Res.* **2004**, 36, 4775–4784.

PT S6-2

Deep sea biofouling - state of the art and where are we going?

Nikoleta BELLOU[1] *

[1] *Hellenic Centre for Marine Research, Institute of Oceanography, Anavyssos, Greece*

** bellou@hcmr.gr*

Biofouling is one of the major concerns when it comes to deploy artificial substrates into the deep-sea marine environment, while at the same time *in situ* biofouling experiments can be used to investigate the ecology of hardbottom communities. In the deep sea, the number of artificial substrate deployments is increasing vast and at the same time the knowledge on which species live in such environments, as well as the parameters that are influencing their settling and growth is still limited below 100m depth. This limitation occurs mainly due to the technical difficulties associated with performing deep sea *in situ* experiments.

In shallow waters, the factors that have been investigated and defined to influence the settling process and the hardbottom communities have a wide range including depth, seasonality, substrate type, orientation and position of substrata, nutrient availability and pollution, grazing and competition.

Compared to the coastal environment and global wide, information about the factors that are influencing the deep-sea biofouling communities are very limited. A few experimental pioneer studies were performed in the 70s along a bathymetrical transect from the euphotic to the aphotic zone and in the 60s that investigated biofouling of artificial materials deployed in the deep-sea environment of the Pacific Ocean. Then, in the beginning of the 20th century experiments started scarcely to be performed in deep-sea extreme environments. The first pioneer and groundbreaking study [1] that performed *in situ* deep sea biofouling experiments with scope to determine factors which are influencing the biofouling (biofilm) communities and are comparable to those defined in coastal zones was performed recently at the deepest point of the Mediterranean [2,3]. But the deep-sea biofouling research is still limited and gapping and thus, although an increasing number of deep-sea studies have highlighted the importance of investigating deep-sea biofouling.

A review is being presented on the scarce available literature about deep-sea studies that described the deep sea biofouling communities and investigated the factors that are influencing the biofouling process. Furthermore it underlines the need of a uniform way to perform deep sea *in situ* experiments that will enable to compare the rare data and the importance of expanding our knowledge on deep sea biofouling, as human actions in the deep sea environment have expanded radically in the past decade.

[1] Traverso, P., & Canepa, E. *Ocean Engineering* **2014** *87*, 10–15.
[2] Bellou, N., Colijn, F., & Papathanassiou, E. *Nuclear Instruments and Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* **2011** *626-627*, 102–105.
[3] Bellou, N., Papathanassiou, E., Dobretsov, S., Lykousis, V., & Colijn, F. *Biofouling* **2012** 199–213.

PT S6-3

Impacts of a multi-contamination gradient in a North-Western Mediterranean bay (Toulon Bay, France) on biofilm microbial communities analyzed by flow cytometry.

Clément COCLET[1,2]*, Benjamin MISSON[2], Gaël DURRIEU[2], Christophe LE POUPON[2], Sébastien D'ONOFRIO[2], Thomas POLLET[1], Cédric GARNIER[2] and Jean-François BRIAND[1]

[1] Université de Toulon, MAPIEM, EA 4323, La Garde, France.
[2] Université de Toulon, PROTEE, EA 3819, La Garde, France.

** clement.coclet@univ-tln.fr*

The Toulon Bay is submitted to various anthropogenic inputs, particularly associated to industrial and maritime activities (civil and military harbours). As a result, the Toulon Bay is strongly polluted by metals and organic contaminants. Remarkably, previous investigations showed that both chemical and biological gradients could be observed between the harbors and the entrance of the Bay.
In order to study the impact of this multi-contamination gradient on the biofilm microbial communities, five specific and chemically contrasted sampling stations (41p, 15, 12, MIS and 6ext) were selected, considering the following specificities: station 41p is open to the sea and nearly unpolluted, station 15 is located close to a fish/mussel farming area and intermediately contaminated, station 12 is also intermediately contaminated and close to the harbours, station 6ext is located in an enclosed dock of the French Navy area close to a sediment storage tank and heavily contaminated, and MIS station is also heavily contaminated and located in a very enclosed dock. In June 2015, water was sampled at two depths (1m above the sediment and 1m below the surface) at the five stations every week for physico-chemical and planktonic community structure analyses. Biofilm colonizing polycarbonate plates at the same sampling stations and depth were collected after one month of static immersion. Physico-chemical analyses consisted in multiprobe field measurements and determination of total organic carbon and total nitrogen (using TOC-V_{CSH} analyzer), nitrates and phosphates (colorimetric methods) and trace metals (voltammetry and HR ICP-MS) concentrations. Planktonic and biofilm communities were analyzed by flow cytometry (FCM). FCM provides fast enumeration and structural characterization of autotrophic communities at the single-cell level by using only optical properties like autofluorescence of pigments. In contrast, as heterotrophic bacteria are not naturally fluorescent, it is necessary to use fluorochromes to count and discriminate them. Relationships between biological and physico-chemical parameters were studied to assess impact of anthropogenic pressure on the abundance and structure of both planktonic and biofilm microbial communities in the specific context of the Toulon Bay.

PT S6-4

LC-MS based metabolic profiling of marine bacterial strains demonstrates variation between free-living and biofilm lifestyles

Laurie FAVRE[1]*, Annick ORTALO-MAGNE[1], Jean-Charles MARTIN[2], Jean-François BRIAND[1], Raphaël LAMI[3], and Gérald CULIOLI[1]*

[1] Université de Toulon, MAPIEM, EA 4323, La Garde, France.
[2] Aix-Marseille Université, UMR INSERM 476/INRA 1260, Marseille, France.
[3] Laboratoire de Biodiversité et Biotechnologies Microbiennes (LBBM), USR3579 UPMC-CNRS, Banyuls, France.

** favre@univ-tln.fr, culioli@univ-tln.fr*

Biofilm formation constitutes a crucial step of the biofouling process. Most of the previous studies dealing with marine biofilms have mainly included genomics and post-genomic functional approaches. Nevertheless, analysis of the metabolic production of such biofilms could conduct to a better understanding of their mechanisms of formation, composition (species diversity) and chemical interactions with surfaces and other colonizing organisms [1].
In the present work, a LC-MS based metabolomics approach was chosen in order to face the chemical complexity of these natural matrices. The aim was to identify metabolic differences between free-living and biofilm cultures of several Mediterranean marine biofilm-forming bacteria. As several experimental constraints (eg. high-nutrient media, low number of chemical standards available …) have to be overcome, sampling, analysis and statistic treatment steps were specifically optimized. The bacterial metabolomes were then analysed by LC-ESI-MS at different stages of growth in both planktonic and biofilm modes of life.

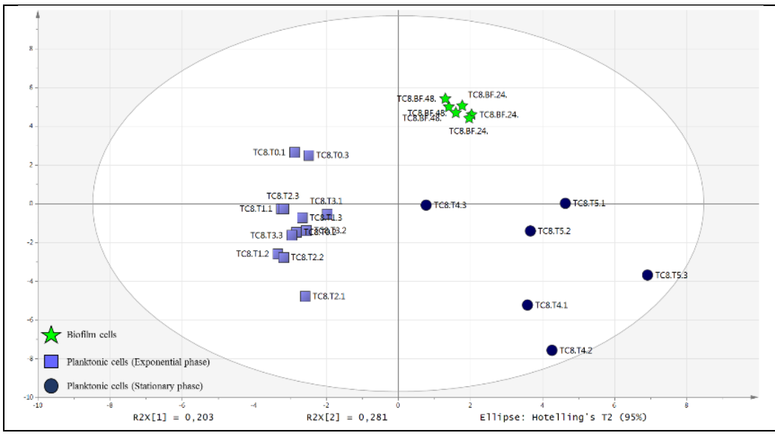


Figure 1. PLS-DA comparison of Pseudomonas lipolytica *TC8 cells (biofilm vs planktonic) using UPLC-QToF+ESI mode*

The main results showed that the most efficient protocol consisted in the whole extraction of the bacterial cells and the culture media with ethyl acetate. Moreover, bacterial cells grown in biofilms showed a significantly different chemical composition compared to planktonic cultures. For this type of study, metabolite annotation constitutes a crucial step because of the low level of knowledge of marine bacterial compounds. Nevertheless, a high-resolution analysis (UPLC-TOF) allowed us to characterize several specific biomarkers of bacterial life-style.

[1] S. Goulitquer, P. Potin, T. Tonon, *Mar Drugs* **2012**, 10(4) : 849-880

PT S6-5

The effects of long-term grooming on the diatom community structure and biofilm adhesion to ship hull coatings

Kelli HUNSUCKER*, Geoffrey SWAIN

Center for Corrosion and Biofouling Control, Florida Institute of Technology, Melbourne Florida USA

* *khunsucker@fit.edu*

Grooming is a proactive method to keep a ship hull free of fouling. This approach uses a frequent and gentle wiping of the hull surface to prevent the settlement of fouling organisms (Tribou and Swain 2010). While grooming has proven to be effective at preventing the settlement of macrofoulers, it appears to cultivate tenacious biofilms (Hearin et al. 2015). A long-term study was designed to better understand how grooming impacts diatom communities and their associated adhesion to ship hull coatings. Two commercially available coatings, a fouling release and an antifouling, were applied to two large-scale test panels (Hearin et al. 2015). Each panel was subdivided into four sections each subjected to a different grooming regime: un-groomed (control), groomed once a week, groomed twice a week, and groomed every other week. All grooming was performed using a hand operated, electrically powered, rotating brush tool. In-water biofilm samples were collected monthly and the diatom community structure was analyzed. The diatom community structure was found to change based on coating type and grooming regime. After one year of immersion and grooming, the panels were lifted out of the water and biofilm adhesion was measured. The frequency of grooming had an impact on the biofilm adhesion strength. Frequently groomed sections (once or twice a week) developed a stronger biofilm than those groomed every other week or not at all. This trend was seen for both the fouling release and the antifouling coating.

Acknowledgements: This research was funded by the Office of Naval Research (Grant No. N00014-02-1-0217).

[1] M. Tribou and G. Swain. *Biofouling* **2010**, 26, 47-56
[2] J. Hearin, K. Hunsucker, G. Swain, A. Stephens, H. Gardner, K. Lieberman, M. Harper. *Biofouling* **2015**, 31, 625-638

PT S6-6

Antibacterial activity of green algal extracts against fouling bacteria isolated from bay of Carthage (northern coast of Tunisia)

Wafa CHERIF [1,2,3], Monia El BOUR[1], Abdellatif BOUDABOUS[2],
Micheline GRIGNON-DUBOIS[3], Leila KTARI[*1]

[1] *INSTM, National Institute of Marine Sciences and Technologies Tunis, Tunisia.*
[2] *FST, Faculté des Sciences de Tunis, Tunisia.*
[3] *Univ. Bordeaux, EPOC, Talence, France*

* *leila.ktari@instm.rnrt.tn*

The need of non-toxic antifouling substances to control marine fouling is one of the major concerns for marine industry. Moreover, in order to understand the specific ecological mechanism of fouling and how to prevent it, biofilm communities should be specified. Thus, This work deals with marine biofouling in two simultaneous ways: one is the contribution to improvement of knowledge of biofilm by isolating and identifying fouling bacteria and the second is the research for natural prevention substances from seaweeds.
In the present study, 13 fouling bacteria were isolated from immersed steel and glass plates in shallow water. Bacterial strains were isolated, cultured and identified based on their 16S rDNA sequences. Disc diffusion method was used to test antibacterial activity of dichloromethane extracts of 8 green macroalgae (*Cladophora laetivirens, Chaetomorpha linum, Bryopsis muscosa, Codium bursa, Codium fragile, Caulerpa prolifera, Caulerpa racemosa and Halimeda tuna)* collected from northern coasts of Tunisia.
Isolated bacteria belonged to three taxonomic groups: Bacteroidetes, Proteobacteria and Firmicutes. Three fouling bacteria were sensitive to macroalgal extracts. *Maribacter sp.* was significantly inhibited by *Bryopsis muscosa* extract (15mm inhibition diam.). *Vibrio alginolyticus* and *Vibrio sp.* were inhibited by *Codium fragile* and *Bryopsis muscosa* extracts. This work highlights the potential use of macroalgae to prevent biofouling.

PT S6-7

A robust quorum quenching enzyme for antifouling applications

Laure PLENER[1], David DAUDE[1], Mikael ELIAS[2] and Eric CHABRIERE*[,3]

[1] Gene&GreenTK, Faculté de Médecine, 27 boulevard Jean Moulin, 13385 Marseille Cedex 5, France
[2] University of Minnesota, Department of Biochemistry, Molecular Biology and Biophysics & Biotechnology Institute, St. Paul, MN 55108, USA
[3] Aix Marseille Université, URMITE, UM63, CNRS 7278, IRD 198, INSERM 1095, Marseille, France

** eric.chabriere@univ-amu.fr*

Marine bacteria play an important role in the initial biofilm development and the maintenance of a biofouling community[1]. Bacterial communication, known as Quorum Sensing (QS), is based on the diffusion of small molecules between cells and is essential to the formation and maintenance of the biofilm. Disruption of this communication, called Quorum Quenching (QQ) has been shown several times to reduce drastically biofilm formation and can be achieved by using enzymes that degrade the communication molecules. One class of these molecules, used by Gram negative bacteria, are acyl-homoserine lactones (AHLs). They are composed of a lactone ring and an aliphatic chain which length and nature may vary.

We have isolated, characterized and engineered a proficient and stable QQ lactonase called *Sso*Pox. This enzyme, isolated from the hyperthermophilic archeon *Sulfolobus solfataricus*, is active over a wide range of temperature (-18°C to 100°C) and pH values (5.0-9.0)[2]. Furthermore, *Sso*Pox exhibits a strong tolerance to proteases, surfactants as well as organic solvents.

In vitro and *in vivo* assays proved that *Sso*Pox was efficient to disrupt communication on the model bacterium *Pseudomonas aeruginosa* PAO1 thus preventing cells from expressing virulence factors and from forming biofilm[3]. Similar results were obtained using clinical isolates, highly divergent from the laboratory model strain.

Preliminary tests showed that *Sso*Pox was able to drastically reduce biofilm formation when coated onto plates dipped over 2 months in marine water. Finally, we used a lab-scale filtration system using whole cells expressing *Sso*Pox entrapped into silica beads which served as a filtration matrix. Biofilm formation was highly reduced when the water, inoculated with a multispecies bacterial population, was filtered through the matrix containing *Sso*Pox. Finally, toxicity assays showed that the enzyme is non toxic to oyster and urchin larvae.

Altogether these data support that the enzyme *Sso*Pox could be used as an environmentally friendly way to limit biofouling with efficiency on environmental bacterial isolates. Thanks to its resistance the enzyme could easily be incorporated instead of copper in paints and coatings or bio-based materials.

[1] S. Dobretsov, M. Teplitski, M. Bayer, S. Gunasekera, P. Proksch, V.J. Paul, *Biofouling,* **2011**, 893–905
[2] L. Merone, L. Mandrich, M. Rossi, G. Manco, *Extremophiles*, **2005**, 297–305
[3] S. Hraiech, J. Hiblot, J. Lafleur, H. Lepidi, L. Papazian, J.-M. Rolain, et al., *PloS One*, **2014** e107125

PT S6-8

Biofouling, deposition and corrosion in cooling water cycles using brackish seawater

Pauliina RAJALA[1] *, Elina HUTTUNEN-SAARIVIRTA[1] and Leena CARPÉN[1]

[1] *VTT Technical Research Centre of Finland, Espoo, Finland*

* *pauliina.rajala@vtt.fi*

Water cooling using natural waters is typically utilized for cooling large industrial facilities such as power plants, chemical factories and refineries. Cooling water systems remove heat from components, processes and industrial equipment. Power plants, such as nuclear power plants and fossil fuel plants, transfer excess heat to cooling water in their condensing systems. Due to the moderate temperature of the water running in cooling water systems, the materials are susceptible to biofouling and also scaling [1]. Biofouling, inorganic fouling and scaling can reduce heat-transfer and enhance corrosion. Microfouling, i.e. microbial biofilm formation, on the water cycle surfaces can enhance corrosion of materials in various conditions. Corrosion reduces lifetime of the systems and also further increases scaling and fouling by providing uneven surfaces more favorable to attachment of microorganisms. Microfouling and inorganic scaling precedes the attachment and growth of macrofouling organisms, such as mussels and macroalgae. Macro-organisms are known to favor surfaces where biofilm is already formed [2, 3]. Macrofouling reduces the heat-transfer efficiency of cooling systems and reduces the flow rate of cooling water and thus the prevention of biofilm formation is needed.

Here the results of field studies in power plant utilizing brackish sea water from Baltic Sea are presented. Hypochlorite treatment is used to prevent the biological fouling in cooling water system during summer months when the sea water temperature rises and biofouling is more intensive. Here we studied the effect of chlorination to species composition of microfouling formed on the surface of pipe material and to the inorganic deposits.

[1] P. Rajala, M. Raunio, E. Sohlberg, O. Priha and L. Carpen**.** *16th NCC.* **2015**, paper nro 18.
[2] Y. Sawall, C. Richter, A. Ramette. *PLoS ONE*. **2012**, 7(7): e39951
[3] M. Salta, J. A. Wharton, Y. Blache, K. R. Stokes, J.-F. Briand. *Environ Microbiol*. **2013**, 15: 2879–2893.

PT S6-9

Dynamic biofilm growth and collection using a strut arrangement on a catamaran vessel

Serkan TURKMEN *,[1], Atlar MEHMET[1] and Irma YEGINBAYEVA[1]

[1] *Newcastle University School of Marine Science and Technology, Newcastle upon Tyne, United Kingdom.*

* *serkan.turkmen@ncl.ac.uk*

The hydrodynamic drag of coating differs depending on the condition of the coated surface whether it is clean or biofilmed. The effect of biofilm on drag performance of coatings applied on test panels can be evaluated using laboratory based testing facilities (e.g. purpose built flow cells etc.). Collecting biofilm, preferably on flat test panels attached to ship hulls, therefore will enable to conduct drag tests to evaluate the effect of biofilm as well as that of clean coating on the skin friction drag. However, attaching test panels on a ship hull is challenging due to the attachment procedure and techniques (e.g. using magnets, screwing and welding) as well as removing difficulties and inconveniences (e.g. need for dry-docking, using divers, waiting periods etc).

In order to explore the effect of biofilm on coating performance and easing some of the above stated challenges of collecting dynamic biofilm samples, Newcastle University has been contributing in the EU-FP7 project SEAFRONT[1] and hence recently designed and manufactured a flexible strut arrangement. This arrangement is deployed underneath the moon pool plug of the University's research catamaran, The Princess Royal, as shown in Figure 1(left). The twin struts of the arrangement can accommodate (2x4 =) 8 off, so-called "UNEW standard test panels" as also shown in Figure 1(right).

This study presents a review of the design, manufacture and operation of the strut arrangement in collecting dynamic biofilm in North East coast of England. The experience shows that the strut arrangement effectively facilitates growing and collection of biofilms on the standard test panels under authentic conditions in a short period of time.

Fig. 1: The twin strut system with dynamically grown biofilms on coated surfaces deployed underneath (on the left) and deployedon board (on the right) of the RV Catamaran Princess Royal for inspection.

[1] Seafront "Synergistic Fouling Control Technologies ", 2013, Annex-I Description of Work, EU-FP7 Collaborative project, Grant agreement no: 614034

PT S7-1

Extracellular polymeric substances from a marine biofilm-forming strain, *Pseudoalteromonas ulvae* TC14: Characterization of exopolysaccharides and antifouling activities

Gennaro ROBERTO.ABBAMONDI[1], Gérald CULIOLI[1], Robert BUNET[2], Stéphane CERANTOLA[3] and Annick ORTALO-MAGNE*[1]

[1]*Université de Toulon, MAPIEM, EA 4323, F-83957 La Garde, France*
[2]*Institut Océanographique Paul Ricard, Ile des Embiez, F-83140 Six-Fours-Les-Plages, France*
[3]*Laboratoire de Résonance Magnétique Nucléaire, Université de Bretagne Occidentale, CS 93837, F-29238 Brest cedex 3, France*

* *ortalo@univ-tln.fr*

In marine environment, biofilms cover inert or living surfaces with the formation of multicellular aggregates, commonly referred to as biofilms. Bacteria in biofilms are embedded in a matrix of extracellular polymeric substances (EPS) with protective and adhesive proprieties. In this work, a marine bacterial strain identified as *Pseudoalteromonas ulvae* (TC14), initially isolated in the early stages of fouling [1], was selected for its ability to produce abundant carbohydrate-rich EPS. This study allowed the characterization of these EPS, the aim being the identification of exopolysaccharides with antifouling properties. This study completes a previous work in which the polysaccharidic fractions of EPS harvested from biofilm cultures of *P. ulvae* TC14 showed a strong antibiofilm activity [2].
EPS were here harvested from planktonic culture medium as soluble EPS. Their content in proteins, carbohydrates, uronic acids and lipids were quantified. A chloroform/methanol/water partition allowed their separation into water- and low-water-soluble polymers which were further purified and separated by anion-exchange and gel permeation chromatography in order to isolate polysaccharidic fractions. The nature, purity and molecular weight distribution of the content of these fractions were estimated through GC-MS, NMR and HPSEC analyses. Finally, whole EPS samples and the purified polysaccharides were assayed for their anti-adhesion activity against marine bacterial strains and for their anti-settlement activity against barnacle larvae.
Results showed that *P. ulvae* TC14 strain was able to produce one major acidic exopolysaccharide having glucose as the main component. This polysaccharide, and the whole EPS sample from which it was purified, either stimulated or prevented adhesion of the tested marine organisms. Extended studies have to be pursued in order to finalize the structure of this active polysaccharide and to assess its possible involvement among the total EPS as inhibitor of fouling.

[1] F. Brian-Jaisson, A. Ortalo-Magné, L. Guentas-Dombrowsky, F. Armougom, Y. Blache, M. Molmeret, *Microb Ecol.* **2014**,68, 94-110.
[2] F. Brian-Jaisson, M. Molmeret, A. Fahs, L. Guentas-Dombrowsky, G. Culioli, Y. Blache, S. Cérantola, A. Ortalo-Magné, *Biofouling* **2016**, 32, 547-560.

PT S7-2

Inhibition of bacterial quorum sensing by macroalgae: importance of associated microbial communities

Sergey DOBRETSOV[1]*, Daniela BATISTA [2], Anna Polycarpa CARVALHO[2], Rafaela COSTA[2], Ricardo COUTINHO[2]

[1] Department of Marine Science & Fisheries, College of Agriculture & Marine Sciences, Sultan Qaboos University, Muscat, Oman.
[2] Marine Biotechnology Division, Institute of Marine Studies Admiral Paulo Moreira, Rua Kioto nō 253, Praia dos Anjos, CEP 28930-000, Arraial do Cabo, RJ, Brazil

** sergey@squ.edu.om*

Quorum sensing (QS) is a bacterial cell-to-cell communication that is based on the production, release and perception of small signal molecules. Acyl homoserine lactones (AHL) are the most common and studied QS signals of Gram negative bacteria. It has been proposed that QS inhibitors can prevent biofilm formation and biofouling (Dobretsov et al. 2009). In this study we investigated the ability of polar (1:1 water/methanol) and non-polar (dichloromethane) extracts of macroalgae from Arraial do Cabo, Rio de Janeiro, Brazil, to inhibit bacterial QS. In order to test the role of surface associated communities, half of the algae were treated with 30% ethanol to remove microorganisms before the experiment (Keintz et al. 2011). Ninety per cent of tested polar extracts inhibited the QS of the AHL producer and reporter strain *Chromobacterium violaceum* CV017 with minimal inhibitory concentrations (MIC) ranging from 0.28 μg ml^{-1} (*Ulva fasciata*) to 189 μg ml^{-1} (*Codium* sp.). The MICs of nonpolar extracts were 14 - 246-fold higher than for polar extracts. Usually, extracts from algae with associated bacteria had a higher bioactivity than ones without them. Among 11 algal species tested, 50% of extracts with associated bacteria were toxic at the effective concentrations to the strain *C. violaceum* CV026. None of the extracts contained AHLs, which was shown using reporters *C. violaceum* CV026 and *Agrobacterium tumefaciens* NTL4 (pZLR4). Our data suggest that algal associated communities are important for QS inhibition and protection of host macroalgae.

Acknowledgements: This research was supported by the “Ciencias sem Fronteiras” program of Conselho Nacional de Desenvolvimento Cientifico e Tecnologico-CNPq for collaborative research with SD.

[1] S. Dobretsov, M. Teplitski and V.J. Paul. *Biofouling* **2009**, 25, 413–427.
[2] B. Kientz, M. Thabard, S. M. Cragg, J. Pope and C. Hellio. *Bot. Mar.* **2011**, 54, 2655–2661.

PT S7-3

Application of green fluorescent protein as a viable marker in a pioneer marine species, *Pseudoalteromonas* sp. D41 for adhesion and biofilm dynamics analysis

Catherine DREANNO[1]*, Marcel KOKEN[2], Chantal COMPERE[1], Gwendal LENAOUR[1]

[1] *IFREMER, RDT/LDCM, Brest, France*
[2] *LABOCEA R&D - CNRS, Plouzané, France*

* catherine.dreanno@ifremer.fr

Surface colonization by microorganisms is considered one of the first steps in marine fouling formation. At the beginning, bacteria colonize the surface and build up a biofilm. In the frame of a long term study of biofilm formation in a coastal marine environment, a few species were isolated from stainless steel, glass and Teflon® coupons immersed in natural seawater in the bay of Brest (France). Amongst the several novel pioneer marine species identified, *Pseudoalteromonas* sp. D41 was selected for its adhesion and physico-chemical characteristics (*i.e* hydrophobicity) and its ability to inhibit the biofilm formation of competitive bacteria. The strain was transformed with green fluorescent protein expression vectors (pCJS10) to investigate the biofilm dynamics and adhesion regulation. The clones that were obtained were compared to the parental strains for their growth characteristics, basic metabolism, antibiotic-resistance and adhesion properties to validate them as genuine equivalents of the wild type strains. This validation is crucial since GFP expression is known to induce sometimes phenotypic modifications and aberrant effects. Moreover, the GFP encoding plasmid should be stably retained by the bacteria under non-selective growth conditions to be able to follow the biofilm formation *in situ* over a long period of time. Therefore, the plasmid retention time has been examined over 15 days. The strain started only to loose plasmids after 12 days of daily re-inoculation, but the percentage of plasmid containing bacteria remained high, *i.e.* 92 % of GFP-tagged *Pseudoalteromonas* sp D41 on day 15. Taking into account growth and phenotype characterization, several clones were then selected to develop a GFP-based assay to screen antifouling and antimicrobial compounds. Cell viability estimated by colony forming units was completely correlated to GFP fluorescence intensity as measured by spectrofluorimetry. Several anti-biofilm and bactericidal compounds were then tested to characterize the assay. GFP-tagged *Pseudoalteromonas* sp D41 was first used to follow its invasion effectiveness during the establishment of a complex natural biofilm community on glass slides. In a second test its ability to intervene with the development of a natural biofilm on glass slides was tested when this had already established as a biofilm.

In conclusion, the GFP-tagged *Pseudoalteromonas* sp. D41 allows quick quantification and viability assessment and represents an ideal non-invasive tool to investigate and monitor biofilm development.

PT S7-4

Hanging on by a thread: the ecomechanics of mussel byssus glue

Matthew N. GEORGE[1,2,*] and Emily CARRINGTON[1,2]

[1] *University of Washington, Department of Biology, Seattle, WA, USA*
[2] *Friday Harbor Laboratories, Friday Harbor, WA, USA*

* *mngeorge@uw.edu*

In hydrodynamically turbulent marine environments, the settlement and survival of marine organisms depend on a strong attachment to the ocean floor. Marine mussels achieve this by anchoring themselves to rocks with stretchy, collagen-like fibers (known as byssal threads) that are tipped with a natural adhesive. Synthesized in seawater and curing within days, the glue that byssal threads use is a biomechanical marvel that has inspired the synthesis of several novel synthetic glues due to its unique ability to adhere to a variety of conventionally challenging surfaces (e.g. glass, plastics, wood, and Teflon), all while in the presence of excess water, salts, and polar organic molecules. However, despite the adhesive's notoriety little is known about how the glue matures or "cures" in natural environments and under what seawater conditions this process is either accelerated or retarded – information that could be ecologically and economically relevant as seawater conditions change as a result of ocean acidification, the expansion of hypoxic zones, and increases in sea-surface temperatures predicted by climate models. Here we describe laboratory experiments wherein mussels made byssal attachments to mica sheets that then matured in a range of different temperature, dissolved oxygen, and seawater pH conditions for up to two weeks and were then pulled to failure using a materials testing machine. Results from these assays provide insights into which environmental factors promote strong byssal attachment and inform commercial aquaculture facilities about which seawater variables should be monitored to better identify and adapt to unfavorable growing conditions.

PT S7-5

Investigation of different marine bacterial strains behaviors in biofilm

Richard GUILLONNEAU[1*], Claudine BARAQUET[1] and Maëlle MOLMERET[1]*

[1] *Université de Toulon, MAPIEM EA 4323, 83957 La Garde, France*

* richard.*guillonneau@univ-tln.fr, molmeret@univ-tln.fr*

In the marine environment, all surfaces submerged are rapidly colonized by bacteria and others microorganisms (biofilm) and then by macro-organisms (biofouling).These complex communities of organisms formed on inert immersed surfaces have important environmental and economic ramifications (degradation of port infrastructures, drag reduction of ships…). Therefore, understanding how are formed these communities and how these organisms interact with each other should help finding new eco-friendly strategies to limit biofouling development on surfaces.

Previous studies in our lab have shown different patterns of biofilm formation on polystyrene in rich medium of bacterial strains isolated from the Mediterranean sea (Toulon collection, TC). The aim of this study is first to understand and characterise their adhesion and biofilm formation in artificial seawater (a medium closer to the marine environment). The study by fluorescence microscopy of adhesion and colonization by these bacterial strains (*Shewanella* sp., *Polaribacter* sp. and *Pseudoalteromonas* sp.) in artificial seawater showed an important behavioural heterogeneity between strains, which can also vary in function of the medium and the surface. A preliminary study also showed that only TC5 and TC11 formed patches and produced D-Glc and D-Man types of EPS in this medium. These results need to be completed by the study of the secretion of other types of EPS. The second objective is to characterize bacteria-bacteria interactions of these strains as well as their relationship with *Acanthamoeba castellanii* a model amoeba ubiquitous of the environment, which usually feed on bacteria. Using co-culture assays for numeration of each of the organisms and observation by epifluorescence microscopy, interactions between bacteria and amoeba has been studied. All the strains studied are phagocytized by *A. castellanii*, with the exception of TC4 (*Persicivirga mediterranea*), that is able to prevent it. Preliminary results showed a potential cytotoxic effect of TC10, T11 and TC14 against protozoa. Confirmation of these results using other approaches is necessary. If confirmed, the identification of the molecules involved in these interactions could be of interest.

These organisms are present in biofilms but their interactions in the marine environment are poorly understood. Multi-species/organisms studies may unravel new types of molecular and cellular interactions that could lead to new anti-biofilm strategies.

PT S7-6

Biofilm formation and c-di-GMP signaling in marine bacteria

Manar HARB[1], Olivier BOTTZECK[1], Annie PRAUD-TABARIES[1], Yves BLACHE[1], Maelle MOLMERET[1] and Claudine BARAQUET[1]*,

[1]*University of Toulon, Toulon, France*

manarhareb@gmail.com, baraquet@univ-tln.fr

Biofilms are surface-attached bacteria embedded in a self-produced matrix of polysaccharides, proteins and nucleic acids. In marine environment biofilms, and subsequent colonization by algae or other organisms (micro or macro fouling), causes economic and environmental drawbacks for marine industries such as decreasing hydrodynamic efficiency of ships or affecting equipment function.

Understanding how marine bacteria adhere and form biofilms on the surface of certain materials is crucial to develop new coatings with targeted anti-biofilm properties.

In many bacteria, biofilm formation is regulated by c-di-GMP (cyclic-di-guanosine monophosphate). C-di-GMP is an ubiquitous second messenger in bacteria, where it affects the transition between a motile planktonic lifestyle and an adhesive biofilm lifestyle. High intracellular c-di-GMP is usually associated with biofilm production. C-di-GMP is synthesized by diguanylate cyclases (DGC), degraded by phosphodiesterases (PDE). Because of the widespread conservation of c-di-GMP signaling in bacteria and their critical role in biofilm formation, inhibition of this pathway offers an attractive approach to interfere with biofilm formation. In addition, associated enzymes are not encoded in eukaryotic organisms and these processes are not essential for growth, reducing the risk of toxicity and the risk of selection for resistant organisms.

The project is based on the screening of chemically engineered and natural compound libraries, the rational optimization of the identified inhibitors, as well as the selection of anti-biofilm efficiency of combined inhibitors. The first step of this project is to construct a c-di-GMP reporter strain that can be introduced in different marine bacterial species to measure the intracellular concentration of c-di-GMP. To identify new molecules, which antagonize c-di-GMP signaling, we will perform structure-activity relationships (SAR) studies oriented toward c-di-GMP signaling as well as a broader screen of rationalized chemical libraries using the c-di-GMP reporter strain.

We hope to obtain new molecules able to decrease intracellular c-di-GMP concentration and therefore able to decrease biofilm formation. Inhibitors can target signal synthesis, signal perception, signal sequestration as well as inducing signal degradation.

PT S7-7

"Quorum Sensing" system characterization of *Shewanella woodyi* and its role in biofilm formation

Mahmoud HAYEK[1], Olivier BOTTZECK[1], Annie PRAUD-TABARIES[1], Claudine BARAQUET[1], Yves BLACHE[1] and Maelle MOLMERET[1]*

University of Toulon, Toulon, France

hayek@univ-tln.fr, molmeret@univ-tln.fr

Quorum sensing (QS) or cell-to-cell communication is a process by which bacteria produce and detect signal molecules and thereby coordinate their behavior in a cell-density dependent manner. Two main QS systems can be distinguished: the acylhomoserine lactone (AHL) and the autoinducer-2 (AI-2). The sequenced genome of the marine bioluminescent MS32 strain of *S. woodyi* contains genes coding for these two main QS systems. This work aims at identifying the QS communication systems present in this bacterium and understanding its role in biofilm formation. The objective is also to find molecules that interfere with these QS processes to inhibit adhesion and biofilm formation.
Preliminary results showed that *S. woodyi* is able to adhere and to form a mature biofilm in a rich or poor culture media. The use of bacterial biosensor suggested that one or more type(s) of AHL and an AI2 molecule are synthesized by this bacterium.
Several commercial molecules, identified for their inhibitory effect on the AI2 QS system of *V.harveyi* inhibited the luminescence of *S. woodyi* and reduced adhesion and biofilm formation suggesting the existence of a functional AI2 QS system.
Therefore, *S. woodyi* appears containing two functional QS systems. It remains to identify the nature of the autoinducers and their receptors.
The effect of commercial AHLs on luminescence and biofilm formation will be tested to confirm the existence of the AHL QS system and to study the effect of different AHLs on these phenotypes. Finally, the identification of bio-inspired molecules that are able to inhibit both QS systems will provide a first basis on which other molecules can be tested. The long term goal of this study is to find new ecofriendly strategies using non-toxic bio-inspired molecules to limit biofilm development on surfaces colonized by micro-organisms in the marine environment.

PT S7-8

Marine *Roseobacters*' lifestyles in biofilms forming conditions

Margot DOBERVA[1], Laurie FAVRE[2], Jean-Luc ROLLAND[3], Yoan FERANDIN[1], Didier STIEN[1], Elodie BLANCHET[1], Gérald CULIOLI[2], and Raphaël LAMI[1*]

[1] Laboratoire de Biodiversité et Biotechnologies Microbiennes (LBBM)
USR3579 UPMC-CNRS, Banyuls, France.
[2] Université de Toulon, MAPIEM, EA 4323, La Garde France
[3]UMR 5244 IHPE, Equipe MIMM, Ifremer, Université de Montpellier, CNRS, UPVD

** raphael.lami@obs-banyuls.fr*

Roseobacters constitute a taxonomically large, geographically widespread, marine microbial group. It has been shown that *Roseobacter* species could harbor either a free-living or a biofilm lifestyles on various marine surfaces. These prokaryotes play a key role in many important biogeochemical reactions.
Our project aims to investigate differences between *Roseobacter* strains collected in biofilms-forming conditions and free-living ones. To this extent, we investigated by LC-MS-based metabolomics a Mediterranean *Roseobacter*, *Marivita cryptomonadis*, cultured in biofilm or in free-living conditions. These results are currently in course of acquisition in our labs and will be presented in our poster.
Then, we tested whether or not the expression of cell signaling processes (quorum-sensing) in the *Roseobacter* group is linked to a biofilm life style. Quorum-sensing allows prokaryotic cells to perceive their abundance, and to coordinate their behavior and physiological activities. First, expression analysis of quorum-sensing is currently analyzed using molecular biology approach (qPCR) onto *M. cryptomonadis* samples, and targeted metabolomics will also be conducted. Also, we designed qPCR primers to investigate expression of *Roseobacter* quorum sensing in natural samples over the course of phytoplankton blooms. More particularly, we are investigating if quorum-sensing is expressed in *Roseobacter* associated to the phycosphere, which could constitute a particular type of natural biofilm in the nearby environment of small algae.
Collectively, all these data should provide new insights on phenotypic differences between free-living and biofilm-forming *Roseobacter*.

PT S7-9

Implication of extracellular components of *Shewanella frigidimarina* NCIMB400 membrane on adhesion and biofilm formation.

Aurore PUYMEGE[1], Justine DEFRANCE[1] and Maëlle MOLMERET[1,*]

[1] *Université de Toulon, Laboratoire Mapiem, EA4323, La Garde, France.*

* *maelle.molmeret@univ-tln.fr*

In the marine environment, all surfaces immersed in water are rapidly colonized by bacteria resulting in formation of complex structures called biofilms. In the marine sector, biofilm formation lead to numerous economic and ecological consequences. Different strategies exist to limit biofilm development. One of them is the use of self-polishing coatings (SPC), which release toxic biocide. A second one, less toxic for the environment is the use of Fouling Release Coatings (FRC), whose surface properties allow the release of most organisms settled on it.
Initial attachment of bacteria is a key step of biofilm formation, which involves different bacterial abilities such as mobility provided by flagella or cohesive adhesion using proteins (adhesins) located on curli or pili. All these play an important role in adhesion or biofilm formation. *Shewanella frigidimarina* a facultative anaerobic Gram negative bacteria, isolated from the marine environment, in particular from biofilm, has been shown to form biofilm *in vitro*. A proteomic analysis reveals that some components such as a polysaccharide export protein or the ones belonging to the type VI secretion system are upregulated in sessile compared to planktonic conditions [1].
We have conducted experiments to understand the importance of some of these components in particular the flagella, the curli, and one key component of the type VI secretion system, in adhesion and biofilm formation. Several mutated strains of *S. frigidimarina* NCIMB400 have been constructed to check their involvement in adhesion and biofilm formation. Furthermore, adhesion tests were performed on different types of antifouling surfaces (SPC and FRC). Understanding the mechanisms of cell adhesion on multiple surfaces should help developing new ecofriendly antifouling strategies.

Keywords: adhesion, biofilm, biofouling, marine bacteria

[1] D. Linares, N. Jean, P. Van Overtvelt, T. Ouidir, J. Hardouin, Y. Blache, M. Molmeret, *Environ Microbiol Rep.* **2015**

PT S8-1

Study of gene expression along the settlement process of barnacle *Balanus improvisus*

Anna ABRAMOVA[1,*], Magnus Alm ROSENBLAD[1], Emil KARLSSON[1], Ulrika LIND[1], Per JONSSON[2], Anders BLOMBERG[1]

[1]*Department of Marine Sciences, University of Gothenburg, Gothenburg, Sweden*
[2] *Department of Marine Sciences, Sven Loven marine station-Tjärnö, University of Gothenburg, Strömstad, Sweden*

* *anna.abramova@marine.gu.se*

The barnacle *Balanus improvisus* is a common species in biofouling communities along temperate waters. The barnacle cyprid larva displays a complex exploratory behaviour prior to selection of a suitable settlement site. Cyprids of *B. improvisus* demonstrate clear preferences for some types of surfaces and actively reject surfaces with particular properties. However, there is a lack of knowledge on molecular mechanisms underlying the settlement behaviour. We performed deep RNA-sequencing to compare transcriptome profiles from four different stages along the settlement process, namely i) free swimming, ii) close exploration, iii) attached cyprids and iv) early juveniles. Methods were optimized so that sufficient and high-quality RNA was obtained from only 20 cyprids. Preliminary analysis revealed interesting changes in gene expression pattern along the settlement progression. The transcriptome profiles of the free swimming cyprids and cyprids during close exploration were similar. However, there are certain genes specifically upregulated in the close exploration stage. The transcriptome of attached cyprid was considerably distinct from the other stages in terms of a large number of upregulated genes. Majority of these genes are involved in molting and tissue remodelling during metamorphosis. In summary, for the first time a trascriptomic approach has been used to analyse gene expression during the surface exploration phase of settlement process in barnacles. Our study provides new insights into mechanisms of barnacle settlement and creates a basis for designing new targets for antifouling research.

PT S8-2

Fouling in finish aquaculture: a case study from Adriatic Sea

Daniela PICA*, Alessandra BELLUCCI, Tommaso PINTO and Stefania PUCE

Università Politecnica delle Marche, Ancona, Italy.

** daniela.pica@gmail.com*

Biofouling affects several maritime industries producing significant operational problems and additional costs [1]. Moreover, not only the infrastructures represent an ideal substrate for fouling but also, in the aquaculture, the reared organisms causing a loss of biomass. In fact, in marine aquaculture, fouling can cause a negative impact on fish or shellfish welfare and compromise the structures stability and lifetime [2, 3, 4].
Many studies have been conducted to analyse the effects of biofouling in aquaculture but few in the Mediterranean Sea and in particular in the Adriatic Sea, where the knowledge is still very scant [5]. Therefore, the aims of our study are to identify the main organisms that compose the fouling community in a finfish farm sited in front of Gargano Promontory (Adriatic Sea, Italy) and to analyse the temporal and depth trend of the biofouling biomass during a year.
A set of polyethylene net panels were placed in April 2015 at two different depths (2 m and 6 m) in the farm, next to the fish cages. The choice of the depths is related to the characteristic of the water column in Adriatic Sea. The panels were made with the same net of the fish cages and they had a size of 20x20 cm. Each month three panels were randomly collected from the experimental set, photographed, and then fixed in alcool 70°. For each panel the organisms of the faunal community were identified, the wet weight of both total organisms and of organisms split in the identified taxa was measured.
The preliminary results show that the fouling community is dominated by animal species while algae are scarce. The fouling is composed mainly by hydroids, polychaetes, crustaceans, molluscs, bryozoans and ascidians. Amphipods with their soft tubes result the first colonizers of the experimental substrates. After few months, the ascidians are the main component of the biofouling followed by molluscs and polychaetes at both the considered depths. Molluscs result much more abundant in shallow water such as erected bryozoans and polychaetes.
During the first three months, the biomass of the fouling is comparable between the two studied depths then it increases considerably more rapidly at 2 m than at 6 m. Moreover, the pattern of colonisation results different at the two studied depths.

[1] I. Fitridge, T. Dempster, J. Guenther, R. De Nys, *Biofouling* **2012**, 28, 649-669.
[2] E. Lacoste, N. Gaertner-Mazouni, *Reviews in Aquaculture* **2014,** 6, 1-10.
[3] E.J. Baxter, M.M. Sturt, N.M. Ruane, T.K. Doyle, R. McAllen, H.D. Rodger, *Fish Veterinary Journal* **2012**, 13, 17-29.
[4] N. Bloecer, Y. Olsen, J. Guenther, *Aquaculture* **2013**, 416-417, 302-309.
[5] M. Sliskovic, G. Jelic-Mrcelic, B. Antolic, I. Anicic, *Environmental Monitoring and Assessment* **2011**, 173, 519-532.

PT S8-3

A multivariate analysis of the attachment of biofouling organisms in response to surface properties

Caitlyn M. GATLEY[1], Eric R. HOLM*[2], and Michael R. DETTY[1]

[1] *Department of Chemistry, SUNY at Buffalo, Buffalo, NY, USA.*
[2] *Naval Surface Warfare Center, Carderock Division, West Bethesda, MD, USA.*

* *eric.holm@navy.mil*

Previous investigations suggest that variation in surface properties (for example, surface energy, charge) affects the attachment of biofouling organisms. Individually these studies typically have focused on one or two species, and there has generally been little commonality across species in the test materials employed. As well, the surface properties of the test materials have usually been examined as if they were independent of one another, despite the fact that (depending on the suite of materials in use) many such properties are correlated. Thus it has not been possible to combine the results of these investigations to produce a comprehensive view as to how surface chemistry influences patterns of biofouling attachment. We have addressed these issues by exposing several species of biofouling organisms to a library of xerogel coatings, spanning a wide range of surface properties, and submitting the results to multivariate analysis.

Xerogels provide smooth, reproducible, optically-clear surfaces for experimentation. Our analysis included 10 xerogel coatings and a clean glass surface. These 11 materials produced a wide range of surface properties. Surface energy, and polar and dispersive components of surface energy, were determined by contact angle analysis. Surface charge was estimated based on theoretical expectations. Attachment assays with all materials were executed for 5 common biofouling organisms; the barnacles *Amphibalanus amphitrite* and *Amphibalanus improvisus*, the bryozoan *Bugula neritina*, the green macroalga *Ulva linza*, and the diatom *Navicula incerta*.

Multivariate analyses of the surface property characterization and the biological assays, by principal coordinate analysis (PCO), resulted in different groupings of the xerogel coatings. In particular, the biofouling organisms were able to distinguish 4 coatings that were not distinguishable by their surface properties. We used canonical analysis of principal coordinates (CAP) to identify surface properties governing attachment across all 5 biofouling species. The CAP pointed to surface energy and surface charge as important drivers of patterns in biological attachment, but also suggested that differentiation of the surfaces was influenced to a comparable or greater extent by the dispersive component of surface energy.

Acknowledgments: This investigation was supported by funding from the Navy Undersea Research Program, Office of Naval Research.

PT S8-4

Investigating the *Amphibalanus improvisus* octopamine receptor – comparison between receptor binding, efficacy and physiological output

Lena LINDBLAD[1*], Jonne LAURILA[2] and Mika SCHEININ[2],

[1]I-Tech AB, AZ BioVenture Hub, Mölndal, Sweden.
[2]University of Turku, Turku, Finland

** Lena.Lindblad@i-tech.se*

Medetomidine (Selektope®) was recently approved as a new antifouling agent. Medetomidine is a potent α_2-adrenoceptor agonist commonly used as a veterinary sedative agent in vertebrate animals. However, invertebrates have no adrenoceptors, so there must be a different receptor mediating medetomidine's effects in invertebrates. Lind et al. presented in 2010[1] that the target for medetomidine in invertebrates is a family of octopamine receptors that regulate the behaviour of the barnacle cyprid larvae. Five different octopamine receptor subtypes were found. Among those, the alpha-like R0 receptor is especially interesting since the R0 receptor increases intracellular calcium in contrast to the beta-like subtypes R1 - 4 which increase intracellular cAMP. Further, medetomidine has a higher efficacy compared with the endogenous ligand octopamine for activating the R0 receptor. Therefore, there is a special focus towards the R0 octopamine receptor regarding inhibition of settling of barnacle cyprid larvae.

The R0 receptor was expressed in a DiscoverX in vitro assay system and a number of different ligands were tested. Among those tested, dexmedetomidine, medetomidine and octopamine were full agonists, and dexmedetomidine showed the highest potency. A number of other adrenergic alpha2-agonists also bound to the R0 receptor, but in contrast to octopamine and (dex)medetomidine, they emerged as partial agonists. For example, clonidine, lofexidine and naphazoline had relatively high affinity but induced only half of the maximal response. When the same substances were tested *in vivo* in the kicking assay and the settling assay, clonidine and lofexidine affected the barnacle larvae similarly, evoking slight responses in the kicking assay and inhibition of settling at high nM concentrations. Naphazoline was even less efficacious in vivo. Other substances with lesser affinity and efficacy in the *in vitro* DiscoverX assay also showed poorer efficay *in vivo*.

It thus appears that only full agonists towards the R0 octopamine receptor induce a satisfactory antifouling effect represented by (dex)medetomidine or the endogenous ligand octopamine, with partial agonists having considerably weaker efficacy than (dex)medetomidine *in vivo*. However, this might only be part of the explanation since (dex)medetomidine also activates the other octopamine receptor subtypes, R1-4; of these the R4 receptor has the highest expression level in cyprids which indicates that this receptor might also be important as a target for antifouling agents.

PT S8-5

Coastal marine fouling monitoring: validation of an innovative field exposure system and comparison between covering assessment methods

Veronica PIAZZA*[1], Giovanni PAVANELLO[1], Elisa CERVETTO[1], Silvia MORGANA[1], Francesca GARAVENTA[1] , Maria Chiara CHIANTORE[2], Valentina ASNAGHI[2], Laurent DELAUNEY[3], Kada BOUKERMA[3] and Marco FAIMALI[1]

[1]ISMAR CNR, Genova, Italy
[2]DISTAV, University of Genoa, Genova, Italy
[2]IFREMER, Brest Center, France

** veronica.piazza@ge.ismar.cnr.it*

In the framework of the European Project JERICO (Toward a Joint European Research Infrastructure network for Coastal Observatories, www.jerico-fp7.eu), aimed to create an european network for monitoring of coastal marine fouling, ISMAR-CNR developed a special sampling system named Biofouling Monitoring Box (BMB), designed to provide substrates with spatial and structural heterogeneity that can simulate the complexity of the sensors and sensor housing/containers. This work presents annual monitoring data, obtained by means of a photographic monthly sampling, for BMB immersed at ISMAR-CNR Genova marine station, placed inside Genoa harbour. The system is evaluated for its validity as biofouling monitoring device, taking into account the influence of variables (light, substrate material, horizontal/vertical panel) on quali- quantitative fouling composition. Moreover, the influence of geographical latitude is considered, by comparing fouling community developed on BMB immersed by ISMAR-CNR Genova (harbour, Mediterranean Sea) and IFREMER France (open sea, Atlantic Ocean). Finally, covering percentages registered for ISMAR-CNR Genova BMB at the end of experiment (12th month) with two different estimate methods, analysis of photographical material through a specific software (Photogrid®) and manual counting with Dethier method, are compared, to highlight respective advantages and limits. Results allow to highlight the different characteristics of the biological colonization process and the biodiversity of fouling community that develops on different materials at different exposure conditions. Light resulted to play a key role in the composition of the fouling community, hard fouling was the main component of the panels exposed both in the horizontal and vertical planes. The metal panels were the substrate mainly colonized by hard foulers, while the glass panels the less colonized. A different situation occurred in the interstitial space: here the panels presented lower percentage of hard fouling. The comparison between data from ISMAR-CNR Genova and IFREMER allows to underline differences in fouling community depending on latitude: after 3 months of exposure, coverage was significantly lower for IFREMER BMB panels and especially hard fouling percentages were scarce. The geographical gradient also showed to influence the composition of communities. The comparison between the two methodologies points out advantages and limits of each technique: Dethier's method is able to supply more detailed data but is more time consuming and requires more expertise, analysis of photographic material is non-destructive, allows to monitor panels in time and is able to supply reliable data, especially if a macro-cathegories classification is required.
BMB proved to be a valid tool for coastal marine fouling monitoring, able to supply useful informations on communities that make up the biofouling of the sensors in different exposure conditions and at different latitudes.

PT S8-6

Preparing samples of antifouling systems for successful testing in the marine environment

Abraham STEPHENS*, Kelli HUNSUCKER, Emily RALSTON, Melissa TRIBOU and Geoffrey SWAIN

Center for Corrosion and Biofouling Control, Florida Institute of Technology, Melbourne, FL, USA

* *astephens@fit.edu*

The development of new antifouling technologies is a multi-billion dollar a year industry that culminates in testing these systems in marine environments. Between the lab and commercial use, these systems are subjected to real world conditions. Occasionally, these systems suffer from failures that are not specifically related to the attributes which researchers have specifically targeted to protect against fouling. This poses challenges for acceptable *in situ* data collection. This may be remedied with adequate planning and sample preparation. Observations from decades of panel immersion have been assimilated and guidance for successful testing will be presented.

PT S8-7

The seasonal variation of offshore macrofaunal fouling assemblages in the South China Sea

Min TANG[1], Chaochao WANG[2], Xin CHEN*[1]

1. Faculty of Material and Chemical Engineering, Hainan University, Haikou, China.
2. College of Agriculture, Hainan University, Haikou, China.

** 982912387@qq.com*

The South China Sea supports highly diverse fouling assemblages with tropical/subtropical characteristics, and the rapid development of various communities under relative stable climate attributes serious fouling problem and also ideal community model to them. However, even now their dynamics have not been well investigated. This study attempted to explore the tempo-spatial variation of macrofaunal fouling assemblages by deploying panels in two depths at two offshore sites (H-site, L-site) in the South China Sea for one year.

The features of fouling assemblages were analyzed seasonally. The abundance of all samples in MDS was clustered according to 60% similarity percentages, and it was found that the samples at L-site were clustered as one group, while three groups were identified at H-site. Such pattern may be related to the more stable environment at L-site than that of H-site. Though the species composition of fouling assemblages showed vastly different at two sites, the sole dominant species at each site kept consistent respectively throughout the studying year. Furthermore, the biomass of dominant species varied with depth. The dry weight of *Balanus reticulatus*, the dominant species at H-site, showed significant difference between two depths in summer, autumn and winter, and also the significant seasonal difference showed in the depths of both 0.5 m and 2.0 m; while the dry weight of *Hydroides elegans*, the dominant species at L-site, was significantly higher in the depth of 2.0 m than that of 0.5 m in both summer and winter, and the significant seasonal difference only found in the depth of 2.0 m. The Shannon index, H', at H-site was significantly higher in the depth of 2.0 m than that of 0.5 m in both winter and spring. On the contrary, at L-site H' was significantly higher in the depth of 0.5 m than that of 2.0 m in both winter and summer. At H-site the significant difference of seasonal H' was only found in the depth of 2.0 m, and at L-site the seasonal H' showed significantly different in the depths of both 0.5 m and 2.0 m. Apparently even at such small-scale vertical stratification of fouling assemblages demonstrated the seasonal dynamics.

In brief, the seasonal variation of fouling assemblages in the South China Sea kept a relative stability as far as the dominant species was concerned, but temporal dynamics of biomass and abundance showed complicated tempo-spatial patterns. At present the reason for such patterns remains unclear; the results demonstrated that there was a resilience of fouling assemblages to tropical environment processes to some extent, and the abundant local species inventory, the rapid larval recruitment and powerful space occupation may contribute to the temporal consistency of dominant species in fouling assemblages.

Acknowledgements: This work was supported by the grants (No. 31160098 and No. 31360105) from NSFC and the grant (No. 313104) from the Natural Science Foundation of Hainan Province.

PT S8-8

The primary study on the characteristics of biofouling community in the nearshore aquaculture in the South China Sea

Chaochao WANG[1], Xin CHEN[2, 3], Guiyuan BAN[3], Min TANG*[2, 3]

1. College of Agriculture, Hainan University, Haikou, China.
2. Key Laboratory of Advanced Matericals of Tropical Island Resources, Ministry of Education, Hainan University, Haikou,China.
3. Faculty of Material and Chemical Engineering, Hainan University, Haikou, China.

** 1251054716@qq.com.*

The problem of marine fouling has caused great concern with the rapid development of aquaculture in the South China Sea. In addition, it is supposed that the fouling community in aquaculture area may be affected by the local culture environment.
We conducted one-year experiment to investigate the macrofouling communities and plankton in the nearshore shellfish culture and its surrounding areas to the south of Hainan Island. It was found that (1) the structure of fouling community showed no significant difference between mariculture area and non-mariculture area, and dominant species included *Hydroides elegans, Styelec plicata Lesueur, Balanus reticulatus and Gammaridae*; (2) The biomass of fouling organisms in mariculture area was significantly greater than that of the non-mariculture area; (3) The biomass of fouling organisms in dry season (November-April) was significantly less than that of the rainy season (May-October); (4) The biomass of *B. reticulatus* demonstrated significantly positive correlation with dissolved oxygen; (5) The plankton communities showed high biodiversity and similar structure in the mariculture areas and its periphery. The dominant species were *Rhizosoleniaceae, Tharassiosira, Cyclotella , Leptocylindrus danicus, Tharassionema nitzschioides, Coscinodiscus, Skeletonema costatum, Favella ehrenbergi, Naupliar Leprotintinnus, Oikopleura, Balanus larva, Helicostomella longa, Globigerinida and Copepoda*; (6) There was no significant correlation between phytoplankton abundance and the biomass of fouling community. The results enlighten the seasonal variation of biofouling community and influential factors in shellfish culture area in the South China Sea.

Acknowledgments: This work was supported by the grants (No. 31160098 and No. 31360105) from NSFC and grant (No. 313104) from the Natural Science Foundation of Hainan Province.

PT S8-9

Varying mussel settlement responses to marine biofilms on polyurethane, epoxy resin and PDMS

Jin-Long YANG[*,1,2], Xing-Pan GUO[1] , Xiao LIANG[1] , Shu-Xue ZHOU[3] , Wei-Yang BAO[4], and De-Wen DING[2]

[1] *Shanghai Ocean University, Shanghai 201306, China.*
[2] *The First Institute of Oceanography, State Oceanic Administration, Qingdao 266061, China.*
[3] *Fudan University, Shanghai 200433, China.*
[4] *Yangzhou University, Yangzhou 225009, China.*

** jlyang@shou.edu.cn*

In the present study, we investigated the formation of natural biofilms developed on polyurethane, epoxy resin and PDMS in the marine environment, and explored the settlement response of the mussel *Mytilus coruscus* plantigrades to these above biofilms. Biofilms developed on coatings including polyurethane, epoxy resin and PDMS significantly reduced mussel plantigrade settlement when compared with biofilms on the non-coating control (Glass). The reduced settlement rates ranged from 20% to 41%, and the biofilm on PDMS showed the best antifouling performance. The dry weight and chlorophyll *a* concentrations of marine biofilms on epoxy resin and PDMS were significantly reduced, while polyurethane showed no significant inhibitory effect. The bacterial and diatom densities of marine biofilms on three coatings were significantly reduced. Among these three coatings, PDMS showed the best inhibitory effect on biofilm biomass such as bacterial and diatom density and chlorophyll *a* concentrations. Miseq sequencing revealed that the bacterial phylum Bacterodetes and Proteobacteria were the two dominant groups in control, polyurethane, epoxy resin and PDMS communities. The composition of bacterial communities was impacted by three coatings; the abundance of Firmicutes was increased and the abundance of Planctomycetes was reduced comparing with the control. PDMS altered the composition of bacterial communities by increasing the abundance of Bacterodetes and Proteobacteria and reducing the abundance of Firmicutes comparing with polyurethane and epoxy resin. Therefore, the present finding suggests that coatings impact the biofilm formation, and the changes in biomass and bacteiral community of biofilm on coatings lead to the different settlement response of the mussel *M. coruscus* plantigrades.

Acknowledgments: This study was supported by National Natural Science Foundation of China (No. 41476131), Innovation Program of Shanghai Municipal Education Commission (No.14ZZ143), and Shanghai Municipal Science and Technology Commission (No.12230502100).

PT S8-10

Automatic Classification of the Settlement Behaviour of Barnacle Cyprids

Ahmad ALSAAB*, Nick ALDRED, Anthony S CLARE

School of Marine Science and Technology, Newcastle University, UK

* *ahmad.alsaab1@ncl.ac.uk*

Barnacles are among the most widespread and troublesome of marine biofouling organisms. Their ability to colonise a wide variety of surfaces, fast growth to a relatively large size, and shell growth characteristics contribute to their traditional prominence as targets for fouling control. The current emphasis on research and development of non-polluting coatings that prevent fouling through non-toxic means is focussing attention on deterrence and/or interference with adhesion during settlement. Despite decades of research on barnacle larval settlement, there is still much to learn that new techniques or technologies applied from other disciplines could facilitate. The pre-settlement behaviour of the cypris larva can be classified under four broad categories: swimming; wide search; close search; and inspection Cyprids spend most of the time swimming and therefore tracking only one cyprid for a short time is not an efficient method. Alternatively, tracking multiple cyprids poses the difficult challenge of separating touching or overlapping cyprids. Further, treatment of cyprids as signal points (as is the case for most commercial software) and estimating behaviour based only on speed and trajectory inevitably produces an unacceptable degree of error. Here, we outline the development of a new tracking system and novel classification system for identifying and quantifying the exploratory behaviour of cyprids. The tracking system is specifically designed to follow cyprids and record their motion. Using only a single camera the system can reliably track multiple cyprids simultaneously for long periods. The tracking system thus enables the user to conduct long-term experiments (hours) with minimal intervention and opens the door to the in-depth study of pre-settlement behaviour. In the classification system, each cyprid is represented by three key points, and then the relationships between movements of these points are analyzed to automatically and reliably partition exploratory behaviour into wide search, close search and inspection events; thus enabling more advanced and informative studies of the pre-settlement interaction of barnacle larvae with developmental antifouling coatings.

PT S9-1

Development of standard and novel laboratory methods to evaluate anti-macrofouling efficacy

Robert BUNET[1]*, Jean-François BRIAND[2] and Jean-Luc BONNEFONT[1].

[1] Institut océanographique Paul Ricard, 83140, Les Embiez, France.
[2] Université de Toulon, MAPIEM EA 4323, 83957, La Garde, France.

**robert.bunet@institut-paul-ricard.org*

Current antifouling paints contain toxicants that represent a threat for marine life. New molecules and structured surfaces proposed by scientists and engineers as an alternative to harmful biocides need to be evaluated for their effectiveness in preventing biofouling.
At the Institut Océanographique Paul Ricard, we have developed laboratory settlement assays using barnacle larvae of two different species (*A. amphitrite* and *B. perforatus*) to assess both innocuousness and anti-adhesion efficacy of natural molecules isolated from a marine organism [1].
However, such a conventional method using these well-known and widespread macrofoulers needs effort to rear barnacle larvae up to the required cypris stage along with meticulous and time consuming microscopic observations.
Therefore, we are now developing an innovative high-throughput screening protocol to consistently evaluate antifouling properties of new available molecules or textured coatings by taking advantage of the fluorescence that spores of the fouling macroalgae *Ulva rigida* emit.

[1] A. Othmani, R. Bunet, J-L. Bonnefont, J-F. Briand, G. Culioli, *J Appl Phycol.* **2015**, in press

PT S9-2

Assessing the performance of low-toxic, cost-efficient and environment friendly antifouling materials

Séverine LARROZE[1]*, Tania TEIXEIRA[1], Manuela MARANHÃO[1], Mélanie DEMEULDRE[2], Jérôme DELROISSE[2], Eldad GUTNER-HOCH[3,4], Chen PILLER[3], Yehuda BENAYAHU[3], Francisco AVELELAS[5], Tânia OLIVEIRA[5], Roberto MARTINS[5,6], João TEDIM[5,7] and Patrick FLAMMANG[2]

[1]AquaBioTech Group, Mosta, Malta.
[2]University of Mons, Research Institute for Biosciences, Mons, Belgium
[3]Department of Zoology, Tel Aviv University, Ramat Aviv, Tel Aviv, Israel
[4]Interuniversity Institute for Marine Science in Eilat, Eilat, Israel
[5]Smallmatek - Small Materials and Technologies, Lda., Rua Canhas, 3810-075 Aveiro, Portugal.
[6]Department of Biology and CESAM, University of Aveiro, 3810-193 Aveiro, Portugal.
[7]Department of Materials and Ceramic Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal.

** sbl@aquabt.com*

Biofouling impacts many maritime activities, being the major cause for maintenance expenses of submerged man-made surfaces. It poses a significant problem for aquaculture industry, the broadest and the most documented impact being in marine finfish aquaculture, in particular sea cage-based aquaculture.
Within BYEFOULING, innovative antifouling approaches have been focused on studies related to surface structuration, protein-adsorption inhibitors, quorum-sensing inhibitors, natural biocides and living active species. New antifouling agents have been either synthesized or isolated and then screened. They have been encapsulated into nanostructured inorganic, hybrid or polymeric materials before being incorporated into coatings to impart a control over the antifouling leaching rate of the agents. In this study, we present the assessment of antifouling performance of new materials developed so far within BYEFOULING project. Standard anti-micro and macrofouling tests have been performed under laboratory conditions and field trials with coatings have been initiated in three geographical regions, using PVC panels and fish nets. Results of laboratory tests including half maximal effective concentrations (EC_{50}) were calculated and data from the field tests were analyzed in order to evaluate the performance of each type of compound developed. Ecotoxicity tests on different trophic levels were also performed to assess the possible impact of the new antifouling materials on the marine ecosystems.
The success of BYEFOULING will be reached through a smart integration of the novel biocides and antifouling technologies into industrial coatings. The integration will also involve the planning of the necessary registration of the new biocides according to the European biocide directive. The project combines a multidisciplinary leading research teams from 11 European countries, which are already acting worldwide in the scientific and technological communities, featuring highly relevant technological and academic skills.

Acknowledgements: This research is supported by the EU FP7 collaborative project "BYEFOULING - Low-toxic cost-efficient environment-friendly antifouling materials", under Grant Agreement no. 612717.

PT S9-3

Marine biofouling on flat panels with graded concentration of biocides

Yi YANG[1], L. GRANTHOLM[2], S. DOBRESTOV[3], R. COUTINHO[2], M. BERGLIN[1], J. GOTTFRIES[1], E. YTREBERG[4] and H. ELWING[1]

[1]Dep of Chem and Cell Biol, Univ of Gothenburg, Sweden. [2]Div Biotecnol Marinha, Arraial Do Cabo, RJ, Brazil [3]Dep of Marine Sci and Fisheries, Muscat, Oman, [4]Chalmers Univ. of Tech, Sweden

hans.elwing@cmb.gu.se

During the last 15 years we have developed two biocide-paint additives, medetomidine ("selectope") [1] and Ivermectin [2] supposed to inhibit barnacle colonization. Our collective experience is that field experiments of barnacle colonization at biocide containing coatings are often laborious, and unreliable for seasonal and geographic aspects. Even the simplest type of field experiments, for example determination of the effective concentration of an added biocide, involve that a large number painted panels have to be made, deployed and evaluated. For this reasons we have adopted current theories in Design of Experiments (DoE) used in Pharmacology [3]. As a first step, in this line, we have designed a new field test method called the "panel gradient method" involving that paint formulations, containing increasing amounts of biocides are applied on the same panels.
Copper oxide (Cu_2O) was used as a "model biocide" in the experiments. Cu_2O was added to a rosin based paint formulation in concentrations ranging in ten steps (on a logarithmic scale) from 60 % to 1.4 % (w/w, fig). The different paint formulations was then applied as adjacent 2 cm broad bands with the use of an applicator to tests panels made of Plexiglas and sized about 20 X 30 cm. The panels were then deployed outside Araial do Cabo in Brazil, or the Swedish west-coast for at least three month , followed by photographic recordings (barnacle colonization) of the test panels. The copper-concentration in the paint layers was also quantified with the use of a hand held X-ray fluorescence analyzer [4].

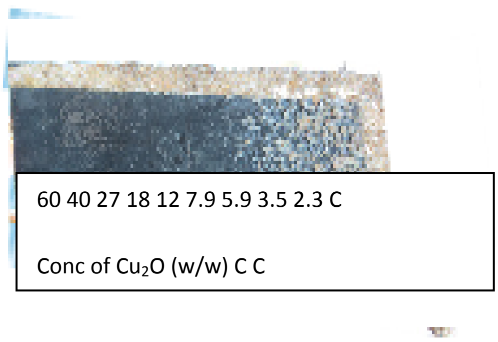


Fig (left) Photograph of a panel (Sweden) coated with Cu_2O containing paints. The coating were performed in the pattern of 10X2 cm broad "bands" that Contained different amounts of Cu_2O (%) as indicated in figure. Note that the anti-barnacle colonization effect Occurred at Cu_2O concentrations ranging from 60 – 7.9%.

In the determination of the minimal amounts of biocides needed in an anti-fouling paint the, DoE inspired "panel gradient method" may significantly reduce the number of needed field test panels without affecting the significance of the results. The leached amount of Cu (µg/cm^2) could also conviently be determined with the use of the XRF- device according to ref 4.
So far, we have not found any statistical significant difference (qualitative or quantitative) in biofouling results obtained by the "panel gradient method" compared to the use of panels with constant concentration of copper.

[1] Mia Dahlström, Mårtensson LGE, Jonsson PR, Arnebrant T and Hans Elwing *Biofouling* **2000** 16, 2-4, 191.
[2] Emiliano Pinori, Berglin M, Brive LM Hulander M Dahlström M and Hans Elwing *Biofouling* 27, 9, 491-953.
[3] Marcus Crompton, Dunstan RH, Macdonald MM, Gottfries J, von Eiff and Roberts TK, *PLOS ONE* **2014**, 9, 14.

PT S9-4

A TLC-agar method as an alternative to liquid-culture method for the evaluation of algaecidal activity

Isabel FREIRE*, Maribel REYERO, Andrea MURAS and Ana OTERO

Department of Microbiology and Parasitology – University of Santiago de Compostela, Spain.

**isabel.freire@usc.es*

Microalgae adherence and growth play an important role in the early stages of biofouling and therefore, the development of new compounds targeting the inhibition of microalgal biofilm formation is of great interest. The inhibition of microalgal biofilm formation and/or algaecidal activity is generally evaluated using liquid cultures and estimated through cell number counts or chlorophyll a measurements, in a technique similar to the technique established for the evaluation of ecotoxicity of compounds on phytoplankton [1]. Nevertheless, the liquid culture technique is complex and extremely time-consuming. Moreover, results may be strongly dependent on the physiological state of the microalgal cultures and incubation conditions. In this work we have optimized and compare two different protocols to evaluate the activity against microalgal biofilms: the liquid culture technique and a new TLC-agar based biofilm technique.

The liquid culture methodology was carried out in 24-well culture plates. The optimal conditions to promote growth and biofilm formation: irradiance, photoperiod, incubation time and shaking were evaluated for 6 species of marine microalgae: *Navicula perminuta, Nitzschia* sp., *Isochrysis galbana* clon T-ISO*, Porphyridium cruentum, Tetraselmis suecica* and *Nannochloropsis gaditana*. The results demonstrated that high irradiance, continuous light, 7-days incubation and steady conditions were the most suitable for the production of strong microalgal biofilm in the culture plates. *T. suecica, N. gaditana, P. cruentum* and *Nitzschia* sp., were selected on the basis of the high chlorophyll levels achieved. In addition, different commercial biocides and antibiofilm compounds were evaluated with this methodology: TBTO, Chlorothalonil, Zineb, Zinc Pyrithione, copper (II) sulphate anhydrous, Nordox cuprous oxide, SeaNine 211, Kojic acid and Furanone. The effect of the biocides was strongly species dependent.

A second technique was developed in our lab based on the application of the compound to be evaluated on silica-TLC plates and overlaid with microalgae included in soft agar (0.8 %, 2-5 mm depth). In this method, the growth inhibition can be directly evaluated as a white spot in the microalgal layer. The TLC-agar method is very fast and simple, does not require special equipment for the measurement of the growth and produced very robust results allowing to exclude the compounds with intermediate inhibitory activity. Therefore, we propose the TLC-agar as a suitable tool for the high throughput screening for novel anti-algal compounds with clear advantages in comparison to the liquid culture method.

Acknowledgements: This work has been supported from the European project BYEFOULING "Low-toxic cost efficient environment-friendly antifouling materials" (FP7-OCEAN-2013 612717).

[1] OECD, Guidelines for the testing chemicals. Proposal for updating guideline 201. Freshwater Alga and Cyanobacteria, Growth Inhibition Test, 2002.

PT S9-5

Increased settlement rates of field-caught barnacle larvae in settlement assays adding metamorphosed juveniles

Kristina GALL*,[1], Constanze FUERLE[1], and Burkard WATERMANN[2]

[1] *LimnoMar, Laboratory for Aquatic and Marine Research, Experimental Station Norderney, Germany*
[2] *LimnoMar, Laboratory for Aquatic and Marine Research, Hamburg, Germany*

* *kristina.gall@limnomar.de*

Barnacles are known to cause severe problems in the shipping industry and industrial aquatic processes due to their settlement on ship hulls and other underwater constructions. Settlement on ship hulls can lead to an increase in fuel consumption and operational costs. Operational costs may also increase by shortened dry dock intervals.
Barnacles are often used as a model in antifouling research to examine the efficacy of new antifouling substances testing the prevention of barnacle fouling in laboratory bioassays. However, in many assays settlement rates of barnacle larvae were quite low [1, 2]. The aim of this study was to increase the settlement rate with field-grown cypris larvae of the species *Austrominius modestus* (Darwin, 1854). The larvae were collected in the harbour of the island Norderney, North Sea. This invasive and competitive species which spread widely in European waters since their invasion in the 1940s showed high resistance to variations in temperature and salinity. 25 larvae were put in each petri dish in addition to five metamorphosed juveniles, which have settled 1 – 3 days before in petri dishes containing adults. After one week settlement rates up to 96% were reached which can be explained by the release of chemical substances by the settled juveniles [3]. This natural process is suspected to ensure the settlement of cypris larvae close to existing colonies in favour of enhanced reproduction.
Furthermore, preliminary observations showed that the settlement of barnacle larvae in the field is not dependent on so called precursor stages in succession pattern of biofouling. The suspected succession is described as a process of the formation of an organic conditioning biofilm followed by settlement of microorganisms and larvae of macroorganisms [4]. The biofilm formation has been described as a prerequisite to the settlement of benthic invertebrates larvae. However, a settlement of cypris larvae on freshly exposed panels within the first 24 hours could be observed at the seaside of the island Norderney several times; thus, the skipping of one or more stages of general fouling succession may happen.

Acknowledgements: The work presented in this study has been funded by the German Federal Ministry for Economic Affairs and Energy, R&D Project FoulProtect (Grant Agreement No. 03SX370).

[1] D. Rittschof, A.S. Clare, D.J. Gerhart, S.A. Mary, J. Bonaventura, *Biofouling* **1992**, 6 (2), pp. 115–122.
[2] C. Pansch, P. Jonsson, E. Pinori, M. Berglin, H. Elwing, poster session on “New Methods for Evaluation of Antifouling and Biocorrosion” at the 17th International Congress on Marine Corrosion and Fouling **2014**, Singapore.
[3] C. Dreanno, R.K. Richard, A.S. Clare, *J. Exp. Mar. Biol. Ecol*. **2007**, 351(1), pp. 276-282.
[4] M. Wahl, Fouling Organisms of the Indian Ocean: Biology and Control Technology **1997**, R. Nagabhushanam, M. Thompson (Eds.), Oxford & IBH Publ Co, New Delhi, pp. 31–84.

PT S9-6

Early detection of bacterial biofilms in seawater lines: a powerful tool for preventing problems

Giovanni PAVANELLO* [1,2], Francesca GARAVENTA[1], Angelo MOLLICA[2], Alessandro MOLLICA[2], Marco FAIMALI[1]

[1] Italian National Research Council - Institute of Marine Sciences (CNR-ISMAR), Genova, Italy
[2] ALVIM Srl, Genova, Italy

** giovanni.pavanello@alvim.it*

Where seawater is used as a process element, there bacterial biofilms appears, sooner or later. Among the others, large industrial cooling water systems and ship piping systems are some of the fields where marine biofilms cause the largest damages. This biological phenomenon can cause important problems, ranging from deterioration of structures to increase in power consumption, e.g. due to decrease in thermal exchange. Large amounts of chemical substances (biocides) are usually employed to prevent biofilm development inside water lines, but often such treatments do not give the expected results. In most cases biocides application is carried out regularly (daily, weekly, ...) or when visible problems arise, and neither the real need of the treatment nor its effectiveness are really verified. An optimization of such treatments can lead to a reduction of their environmental impact, since those chemical compounds are finally discharged into the sea, allowing to cut, at the same time, the total cost of the “biofilm problem”. Thanks to the technology transfer of the results of more than 30 years of scientific research on biofilms and biofilm-related issues, the Institute of Marine Sciences of the Italian National Research Council (ISMAR-CNR), in collaboration with Italian SMEs, has developed a new biofilm monitoring technology [1], able to point out bacterial growth on surfaces since its early stages (>1% of surface covered by microorganisms), on line and in real-time. The proposed system has been applied in several different fields, including industrial cooling waters and seawater desalination, allowing to adopt a completely new approach towards the problem of biofilm prevention and cleaning, promoting a wise use of biocides and preventing potential problems.

[1] G. Pavanello, M. Faimali, M. Pittore, A. Mollica, A. Mollica, A. Mollica, *Water Res.* **2011**, 45, 1651-1658.

PT S9-7

The Mediterranean Sea Urchin *Paracentrotous lividus*: an effective embryotoxicity model

Eldad GUTNER-HOCH[1,2], Eirin LANGSETH[3], Michal WEIS[1], Frederico MAIA[4], João TEDIM[4], Severine B. LARROZE[5], Aikaterini-Flora TROMPETA[6] Costas A. CHARITIDIS[6], Yehuda BENAYAHU*[1]

[1]*Department of Zoology, Tel Aviv University, Ramat Aviv, Tel Aviv, Israel*
[2]*Interuniversity Institute for Marine Science in Eilat, Eilat, Israel*
[3]*SINTEF Materials and Chemistry, Nano and Hybrid Materials Group, Oslo, Norway*
[4]*Smallmatek - Small Materials and Technologies, Lda Rua Canhas, Aveiro, Portugal*
[5]*AquaBioTech Group, Naggar Street,Targa Gap, Mosta, Malta G.C.*
[6]*Research Unit of Advanced, Composite, Nano-Materials & Nanotechnology, School of Chemical Engineering, National Technical University of Athens, Zographos, Athens, Greece*

* yehudab@tauex.tau.ac.il

Evaluating the toxicity of antifouling compounds is essential in order to produce environmentally- friendly materials. Several approaches are currently in use to assess toxicity levels, assaying a variety of model organisms, including both marine invertebrates and vertebrates. By testing the toxic effects of a given compound in relation to its concentration in the early embryonic stages of a model organism, both cytotoxic and embryotoxic effects can be determined. This is in contrast to other toxicity tests that only examine organism mortality. In this study we present an embryotoxicity assay on *Paracentrous lividus,* a temperate water sea-urchin. Eggs and sperm were mixed and inseminated in seawater with BYEFOULING test products, including nanomaterials such as carbon nanotubes and encapsulated compounds. The assay examined toxicity level, indicated by percentage of fertilized eggs cleaving to a 2-cell stage (first cleavage) and percentage of fertilized eggs reaching the pluteus larval stage. Thus, percentage inhibition of normal pluteus formation was indicative of toxicity. In addition, malformed and pre-pluteal embryos were microscopically checked. This assay is established as simple, straightforward, and swift.

Acknowledgements: This research is supported by the EU FP7 Programme/ THEME [OCEAN 2013.3] within the collaborative project “BYEFOULING - Low-toxic, cost-efficient, environment-friendly antifouling materials” (www.byefouling-eu.com) under Grant Agreement no. 612717.

PT S9-8

Characterization of marine biofilms grown under different hydrodynamic regimes and their impact in ship operational efficiency

Jack HAYDEN*, Marie DALE, Barry KIDD, Alistair FINNIE

International Paint Ltd., Stoneygate Lane, Felling, Gateshead, NE10 0JY, UK

* jack.hayden@akzonobel.com

It is well recognised that the combination of the nature of the micro and macro physical roughness elements on the underwater surface of a ship's hull and the type and extent of any biofouling that is present will strongly influence the overall frictional resistance and operational efficiency of the vessel. Traditionally, such biofouling has been sub-categorised as "macrofouling" (e.g. calcareous fouling or weed) or "microfouling" (e.g. bacterial and algal biofilms. While a number of historic studies have been performed to quantitatively assess the impact of macrofouling on frictional resistance ship operational efficiency, the impact of microfouling is less well understood. In order to address this, a series of biofilms are being grown under controlled laboratory conditions involving exposure to seawater at different flow rates ranging from 0 to 2.6 ms^{-1} (0 to 5 knots). A detailed biological and physical investigation of the resulting marine biofilms will be performed, including metagenomic characterisation, measurement of biofilm thickness, surface roughness and topography, and direct measurement of the frictional resistance and hydrodynamic drag penalty upon subsequent high-speed seawater exposure. The poster will present the preliminary results of this investigation and discuss the potential impact of similar biofilms on ship operational efficiency.

PT S9-9

A flow-through method of laboratory testing for the efficacy of antifouling paints using three types of fouling organisms: barnacle, mussel and green algae

Seiji KOBAYSHI [1], Ryuji KOJIMA [2], Cyril Glenn Perez SATUITO [3], Tomoaki MATUMURA[1], Ichiro KATSUYAMA*[1], Hirotomo ANDO[2], Yasuyuki SEKI [4] and Tetsuya SENDA [2]

[1]Japan NUS Co., Ltd., Shinjuku, Tokyo, Japan
[2] National Maritime Research Institute, Mitaka, Tokyo, Japan
[3]Nagasaki University, Nagasaki, Japan
[4] Chugoku Marine Paints, Ltd, Otake, Hiroshima, Japan

***** katuyama@janus.co.jp

Antifouling (AF) paints are widely applied on the ships' hull surfaces to prevent the unwanted aquatic organisms through biofouling of ships. To develop more effective AF paints, it is very important to quantify the efficacy of new AF systems including biocides. In order to establish the test methods, test panels were prepared by the different formulations of AF paints by varying content of Cu_2O, and cured dynamically before the experiment. After that, a behavioral test was conducted using three types of fouling organisms; cypris larvae (*Balanus (=Amphibalanus) amphitrite*), juveniles of mussel (*Mytilus galloprovincialis*), and spores of green algae (*Ulva prolifera*). A behavioral test was assessed from the surface of each panels under flow-through coditions against control groups by ways as follows, (1) the rate of cypris metamorphosed settlement, (2) the number of attached byssal threads, and (3) the number of spots adhered *Ulva* spores. As a result, the number of byssal threads and spores, and the rate of settlement generally decreased with increasing Cu_2O content. In the case of cypris larvae and mussel, the critical value of settlement was observed at 30 wt.% of Cu_2O. On the other hands, the critical value of settlement was observed at 5 wt. % of Cu_2O in the case of *Ulva* spores. These results imply that Cu_2O content in each assays may be the critical value for laboratory behavioral test of the efficacy of AF paints. Furthermore, the validation of laboratory assay was evaluated compared to field experiments, and showed the good agreement with field experiments. The author will propose conventional and universal test protocols on the basis of these results.

PT S9-10

Development of bacteria and microalgae biofilm in photobioreactor to evaluate antifouling surfaces

Tiffany LE NORCY[1*], Claudia ZEA[1], Claire HELLIO[2], Isabelle LINOSSIER[1],Karine REHEL[1] and Fabienne FAŸ[1]

[1] Laboratoire de Biotechnologie et Chimie Marines, Institut Universitaire Européen de la Mer, Université de Bretagne-Sud, 56100 Lorient, France
[2] Laboratoire des sciences de l'Environnement MARin, Institut Universitaire Européen de la Mer, Université de Bretagne Occidentale, 29280 Plouzané, France

[*] *tiffany.le-norcy@univ-ubs.fr*

Marine biofilms are multispecies communities composed of bacteria and microalgae. These biofilms are a binding site for macroorganisms which participate to the biofouling formation. Biofouling is a process which induces consequences on the economy and the ecology.
Antifouling coatings which contain several active molecules are in constant development to prevent biofouling formation. The evaluation of these coatings requires long and complicated validation processes. In this context, new methods are necessary to evaluate rapidly the activity of new coatings in controlled conditions.
This method of evaluation takes place in a photobioreactor where three marine bacteria (*Paracoccus* sp. 4M6, *Pseudoalteromonas* sp. 5M6 and *Bacillus* sp. 4J6) and a microalgal strain (*Cylindrotheca closterium* AC 170) were inoculated. Several parameters were controlled: the temperature, the pH, the oxygenation and the illumination.
The biofilm formation was performed during 14 days in dynamic condition. Three supports were immersed, two negative standards: a glass slide and a coating without the molecule and a coating with the molecule. The activity of compounds was evaluated by observation in Confocal Laser Scanning Microscopy (CLSM) and the determination of bacteria and microalgae biomass by the COMSTAT program.

PT S9-11

Effect of cuprous oxide particles on the roughness, boundary layer and drag characteristics of marine antifouling coatings

Chang LI *,1, Mehmet ATLAR [1], Irma YEGINBAYEVA [1], and Colin ANDERSON [2]

[1] School of Marine Science and Technology, Newcastle University, UK
[2] American Chemet Corporation, USA

** c.li16@newcastle.ac.uk*

Copper and copper compounds are commonly approved as antifouling active substances. Copper is a naturally occurring material and is an essential element required for normal growth by all plants and animals at low concentrations. At high concentrations it prevents biofouling growth, and cuprous oxide is globally used as the majority ingredient in many marine antifouling coatings for underwater hull protection.

Even though cuprous oxide coatings can provide a relatively effective mechanism for fouling free surfaces, resulting in substantial fuel savings and consequently reduced emissions of greenhouse gases (GHG) and prevention of transfer of invasive species, the roughness effect of different sizes of cuprous oxide particles on the drag performance of antifouling coatings, and hence on ship hull drag, has not been systematically studied. In order to shed light on this effect a postgraduate research project has been recently started at Newcastle University to conduct systematic experimental research on the effect of particle size of cuprous oxide particles on the boundary layer and drag characteristics of commercial marine antifoulings.

This paper will report on the first part of the research where the roughness effect is explored. Varied sizes of commercial cuprous oxide particles (D_{50} ranging from 2µm to 250 µm) were applied on 14 standard flat test panels (600mm x 210mmin size L x B) using suitable binders and different application methods. The roughness characteristics of the test panels were analysed to assess the detailed roughness statistics of the surfaces. The test panels were then fitted to a special wall type insert (3m long) where they were subjected to dynamic flow conditions with different flow speeds, in the medium size testing section (800mm x 800mm in size B x H) of the Emerson Cavitation Tunnel (ECT) of Newcastle University. Under these conditions the boundary layer characteristics of the coated surfaces and reference smooth surface were measured by using the two-dimensional Laser Doppler Velocimetry (LDV) system of the ECT.

Based on the analysis results of the systematic roughness and boundary layer measurements, an attempt is made to establish a correlation between the relevant roughness parameters and roughness functions of the tested surfaces, and thus provide insight into the effect of the cuprous oxide particle size on the skin friction drag characteristics of antifouling surfaces.

PT S9-12

Combatting fouling on fish cages in three seas: towards protocol for long term static immersion tests

Rachel MAILICK[1], Eldad HOCH-GUTNER[1,2], Michal WEIS[1], Xabi FERNANDEZ[3], Severine LARROZE[4], Tania TEIXEIRA[4], Manuela MARANHÃO[4] and Yehuda BENAYAHU*[1]

[1]Department of Zoology, Tel Aviv University, Ramat Aviv, Tel Aviv, Israel
[2]Interuniversity Institute for Marine Science in Eilat, Eilat, Israel
[3]Zunibal, Idoro, 1 Derio, Bizkaia, Spain
[4]AquaBioTech Group, Naggar Street, Targa Gap, Mosta, Malta G.C.

** yehudab@tauex.tau.ac.il*

The mariculture industry is one which has been growing rapidly and has become a principle contributor to the world's food supply. One of the primary costs and concerns affecting the growth of this industry is the problem of biofouling. If not addressed, continued build-up of fouling can result in numerous deleterious consequences, including the loss of fish stock due to oxygen deprivation or disease, as well as increased costs for the cleaning, replacing or repairing of nets. One way to decrease the severity of fouling affecting the mariculture industry is to coat the cages before use with an antifouling paint. Although effective in mitigating the rate of fouling if reapplied regularly, these paints are most often copper based and have their own negative consequences on non-target organisms as well as on the farmed fish. As new environmentally friendly antifouling strategies are being developed, there is a need to standardized experimental procedures.
Static immersion testing has been employed in the Red Sea (Eilat, Israel), central Mediterranean Sea (Malta) and the Atlantic (Spain) to test different antifouling shelf products (FlexGard Original, FlexGard Superior, Flexdip and Notorious 1). Underwater structures containing five 15x15 cm net squares for each type of paint, as well as control ones were deployed. Nets were photographed monthly and analyzed to determine percent net occlusion over time, and samples were removed every 4 months in order to determine taxa composition, biomass accumulation and chlorophyll content. The performance of the antifouling paints was then compared in all three locations. Our experimental approach provides a protocol to test the efficacy of newly developed antifouling paints for use in the mariculture industry.

Acknowledgements: This research is supported by the EU FP7 Programme/ THEME [OCEAN 2013:3] within the collaborative project "BYEFOULING - Low-toxic cost-efficient environment-friendly antifouling materials" (**www.byefouling-eu.com**) under Grant Agreement no. 612717.

PT S9-13

Development of a test platform for anti fouling coatings.

Raf MESKENS*[1], Remke WILLEMEN[1], Lisa DEVRIEZE[3], Jorne BEYEN[4], Helen VERSTRAELEN[1], Geert POTTERS[1,2], Kris DE BAERE[1]

[1] Antwerp Maritime Academy, Antwerp, Belgium.
[2] Dept. Bioscience Engineering, University of Antwerp, Antwerp, Belgium.
[3]ILVO, Institute for Agricultural and Fisheries Research, Ostend, Belgium.
[4]DEME, Dredging, Environmental & Marine Engineering, Zwijndrecht, Belgium.

** raf.meskens@hzs.be*

Marine fouling, or the growth of marine organisms on fully or partly submerged structures, is an unwanted phenomenon in the marine industry. Bio fouling will increase the hydrodynamic drag of ships, causing an increased fuel consumption, promote the corrosion of the metallic structures and trigger undesired transport of invasive species. The impact is economic as well as environmental. More fuel consumption is synonym for more CO_2 and other detrimental emissions, corrosion entails coating and the introduction of toxic substances in the sea and air and the transport of hitch-hikers: non-indigenous species towards locations without natural enemies will harm the local delights of the marine environment. In 2001 the IMO adopted the "International Convention on the Control of Harmful Anti-Fouling Systems on Ships". This convention entered into force 17 September 2008 and prohibited the use of harmful organotins in anti-fouling paints used on ships. A mechanism was established to prevent the future use of other potential harmful substances in anti-fouling systems.

The ban on organotins confronted the marine industry with a major challenge. TBT's (TriButylTin) have a negative impact on the marine biotope but till today no equally efficient, harmless, substance has been found. The search for an efficient, economic and ecological friendly novel anti-fouling paint is high on the agenda of IMO, governments, paint producers, ship owners and environmental organizations. All major marine coating producers bring to the market very similar products. Broadly speaking, the present hull anti -fouling systems focus on the following three generic types of AF-coating: firstly, hard coatings, usually biocide-free vinyl esters, reinforced with glass platelets. In actual fact this is not a real anti-fouling coating since fouling will appear over time but it resists mechanical cleaning, even with hard brushes, exceptionally well. Secondly, we have a whole range of soft/smooth paints, often based on silicones or fluoropolymers, rendering the hull surface so slippery that latching onto becomes difficult. Basically this type of coating cleans itself by means of the speed of the ship, the organisms with little adhesion will flush of easily. Finally, the most popular type of fouling protection, have a toxic additive incorporated in the topcoat. Predominantly these additives are copper based products reinforced with booster biocides. Three different techniques are being used to release these toxins in a more or less controlled way. The most primitive system, dating from the 1950's, consist out of a soluble matrix, in general colophony mixed with copper, arsenic, zinc, mercury or iron oxides. A few years later, the binder became non-soluble, acrylic resins, vinyl resins or chlorinated rubber polymers were being used together with copper and zinc oxides with or without organometallic compounds. Presently mainly self-polishing copolymers are being used whereby biocides are leached under a controlled manner. While sailing the paint abrades and constantly a new layer of coating, mixed with zinc- or copper oxides emerges.

Each of the above described AF-coatings has a very specific and limited field of application. Selecting the correct coating for a specific ship is far from self-evident. Important differences do exist within each coating type, dependent on the manufacturer. Unfortunately, no real objective means of comparing these products exists, neither on performance nor on ecological impact. The aim of this project is to establish an impartial test-protocol and build a platform for testing AF-coatings in a statically and dynamically manner. With knowledge of type, composition and performance of the anti-fouling paints tested we can advise the ship owners in an objective way and evaluate the ecological impact of a paint through a well-founded life cycle analysis.

PT S9-14

Optimization of the screening method for anti-biofouling compounds using the xCELLigence® system

Andrea MURAS[1*], Celia MAYER[1], Isabel FREIRE[1], and Ana OTERO[1]

[1] *Universidade de Santiago de Compostela, Santiago de Compostela, Spain.*

* *andrea.muras@usc.es*

The formation of bacterial biofilm is the first step in the development of the biofouling process on submerged surfaces and its control is a global economic problem due to its negative impact not only in the industries but also in environmental pollution. The formation and maturation of bacterial biofilm is often controlled by a cell-to-cell chemical communication mechanism known as quorum sensing (QS). Therefore, the interference with QS, a process generically known as Quorum Quenching (QQ) has been proposed as a novel anti-fouling strategy.

The direct effect of biofilm-inhibitors is generally measured using fluorescent stains and image analysis of microscope observations, but these techniques are very time consuming and present high variability, not being suitable as high throughput screening (HTS) methods. As a complementary approach, we propose to use a HTS method for bacterial biofilm inhibitors based on the on-line measuring equipment xCELLigence System RTCA SP (ACEA, Biosciences Inc). This machine uses the electronic impedance measured between electrodes to provide important information about the biological status of cells adherence and allow real-time measurements throughout the experiment capturing data from start to finish. The optimization of the method was done selecting several marine biofilm-forming bacterial strains: *Vibrio anguillarum* 90-11-287, *V. aestuarianus* CECT625, *V. tubiashii* CECT631, *Cobetia marina* CECT4278, *Shewanella putrefaciens* CECT5346, *Pseudoalteromonas flavipulchra* and *P. maricaloris*. One of the limitations of the method is that it only can measure the biofilm formed on the bottom of the well, being unable to detect the air-liquid phase biofilms since the sensor arrays are integrated in the bottom of special plates (E-plates). Moreover, the electrode measurements are affected by salinity at values higher than 10 g/L of NaCl. In order to evaluate if these marine biofilm-forming marine strains could be used to sense simultaneously anti-biofilm and quorum quenching activities, they were characterized regarding the presence of QS or QQ systems. AHLs production by marine bacteria was detected by streaking against the biosensor strains *Chromobacterium violaceum* CV026 and VIR07 and by HPLC-MS analysis. AHL degradation bioassays were carried out using *C. violaceum*-based solid plate assays. Four of them were selected (*V. aestuarianus*, *V. tubiashii, P. flavipulchra* and *P. maricaloris*) on the basis of strong biofilm formation, as detected by xCELLigence equipment, and sensitivity to QQ enzymes and QS inhibitors such as furanone (0.1 µM) and kojic acid (1mM). Results indicate that the xCELLigence system measures the biofilm formed by these four marine bacterial strains with high reproducibility. As a conclusion, the xCELLigence system is an effective, simple, fast and reliable method to quantify bacterial biofilm formation in low-salinity culture media and can be an invaluable tool to be used in the HTS for anti-biofilm eco-friendly compounds.

Acknowledgements: This work has been supported from the European project BYEFOULING “Low-toxic cost efficient environment-friendly antifouling materials” (FP7-OCEAN-2013 612717).

PT S9-15

Matching forces applied in underwater hull cleaning with adhesion strength of marine organisms

Dinis OLIVEIRA*,1 and Lena GRANHAG[1]

[1] *Department of Shipping and Marine Technology – Chalmers University of Technology, Gothenburg, Sweden.*

** dinis@chalmers.se*

Biofouling on ship hulls leads to increased fuel consumption and greenhouse gas emissions. Between successive dry-dockings, strategies to combat biofouling largely rely on antifouling paints and underwater hull cleaning. The latter strategy is not always efficient in controlling growth, in part due to the fact that today's cleaning methods might result in damage to the antifouling coating. Shear forces imparted by some brush systems correspond to ~10,000 Pa [1,2], while available literature indicates that adhesion strength (i.e. resistance to cleaning) of microfouling species is, in most of the cases, lower than 300 Pa. Therefore, there is a need for matching the forces applied during cleaning to the values of adhesion strength of marine organisms.
The current research project aims at optimizing underwater hull cleaning regarding both force and frequency. Thus, regional biofouling communities will be characterized regarding composition (taxonomic groups), hydrodynamic properties (contribution to frictional drag) and adhesion strength of marine organisms. An innovative sampling method will enable to collect intact biofouling communities from selected areas of ship hulls. This method consists in deploying magnetic settlement plates (MAGPLATE), attached to the hull by means of a set of magnets [3]. MAGPLATEs have previously been used in assessing *en route* survivorship of biofouling organisms, in studies where plates were preconditioned with a fouling community grown under static conditions [4]. In the present study, MAGPLATEs will be used for the first time in sampling intact biofouling communities during normal operation of vessels. Thus, on dry-docking and repainting of vessels, MAGPLATEs will be coated using the same procedure as applied to the hull surface. At the end of the exposure period, during which the vessel operates, fouled MAGPLATEs will be retrieved by divers. Finally, biofouling communities will be transferred to the lab for identification of marine *taxa*, drag & boundary layer studies and adhesion strength testing.
The next steps within the project include both numerical and field validation of the MAGPLATE design, before deployment of MAGPLATEs on several vessels in the North Sea region. In the future, other studies could benefit from using a similar method, e.g. for comparing the performance of different hull coatings on specific vessels and routes.

[1] M. Tribou, G. W. Swain, *Biofouling* **2015**, 31 (4), 309–319.
[2] E. R. Holm, E. G. Haslbeck, A. Horinek, *Biofouling* **2003**, 19(5), 297–305.
[3] A. D. M. Coutts, M. D. Taylor, C. L. Hewitt, *Mar. Pollut. Bull.* **2007**, 54(1), 97–100.
[4] A. D. M. Coutts, R. F. Piola, M. D. Taylor, C. L. Hewitt, J. P. Gardner, *Biofouling* **2010**, 26(5), 539–553.

PT S9-16

Adhesive properties of three marine bacteria towards FRC-SPC hybrid antifouling coatings

Aurore PUYMEGE[1], Sofiane EL-KIRAT-CHATEL[2], The Hy DUONG[1,3], Lénaïk BELEC[1], Christine BRESSY[1], Yves F. DUFRENE[4] and Maëlle MOLMERET*[,1]

[1] Université de Toulon, Laboratoire MAPIEM, EA4323, La Garde, France.
[2] Université catholique de Louvain, Institute of Life Sciences, Louvain-la-Neuve, Belgium
[3] The University of Danang, University of Science and Technology, 54 Nguyen Luong Bang, Danang, Vietnam
[4] Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Croix du Sud 2/18, B-1348 Louvain-la-Neuve, Belgium

** maelle.molmeret@univ-tln.fr*

All surfaces immersed in seawater are exposed to the settlement of marine organisms, such as microorganisms or macrofoulers, known as biofouling. Antifouling coatings have been developed due to the economic and environmental impacts of biofouling. Different strategies of antifouling coatings dedicated to the protection of ship hulls exist but two are mainly used: self-polishing copolymer (SPC) and fouling release coating (FRC). SPC coatings are chemically active coatings which release biocidal products by combining diffusion and erosion processes in a controlled manner. FRC coatings are non-toxic and efficient in particular when the ship is moving. New environmentally friendly coatings, FRC-SPC hybrid coatings, which combine erosion properties and fouling release properties, are currently developed. In this study, we have characterized two hybrid coatings. Adhesion of three marine bacterial strains on these surfaces has been studied using different approaches [1]. These bacteria, belonging to the *Polaribacter* or *Shewanella* genus, exhibited different profiles of adhesion and biofilm formation on polystyrene. Adhesion properties of these three strains were evaluated on the new copolymer-based hydrid surfaces. Atomic force microscopy (AFM) in single-cell force spectroscopy (SCFS) mode was also used to quantify the adhesive properties of individual bacterial cells towards surfaces [2-3]. For this purpose, a viable single cell was picked up on a colloidal probe coated with polydopamine bioadhesive and force-distance curves between the bacterium and the surfaces were measured. We showed different adhesive properties between strains on the two surfaces. For at least one strain, pili seems to govern adhesion at short contact time. At longer contact time, adhesion seems to be reinforced by cell wall and surface molecules. For the less adhesive strain, we can postulate that adhesion involve cell wall hydrophobicity and some adhesive molecules. This approach allow us to determinate some important bacterial properties to adhesion on different surfaces.

Keywords: hybrid antifouling coating, adhesion, marine bacteria

[1] TH. Duong, C. Bressy, A. Margaillan, Polymer, **2014**, 55, 39-47
[2] J. Helenius, CP. Heisenberg, HE Gaub, DJ Muller, Journal of cell science, **2008**, 121, 1785-1791
[3] DJ. Muller, J. Helenius, D. Alsteens, YF. Dufrêne, Nature chemical biology, **2009**, 5, 383-390

PT S9-17

3D printing of biofouling organisms for hydrodynamic testing

Scott STORMS*[1], Eric HOLM[2]

[1] *Naval Surface Warfare Center – Philadelphia Division, Philadelphia, PA, United States.*
[2] *Naval Surface Warfare Center – Carderock Division, West Bethesda, MD, United States.*

** scott.storms@navy.mil*

The general effects of hull roughness due to fouling, as it is related to ship power requirements, have been well documented. However, in order to determine specific effects of various types of fouling organisms, their distribution, or abundance on ship performance, hydrodynamic testing of the actual fouling organisms is desirable. The difficult part of such testing lies within the test subjects themselves – living organisms may be difficult to maintain during testing, which render replicated tests challenging. Likewise organism size may be inappropriate for the facilities at hand. Laser metrology and additive manufacturing (or 3D printing) provides solutions to these difficulties.
Laser metrology (3D scanning) was used to capture the geometric shapes of fouling organisms attached to panels. These panels were then digitally recreated in 3D CAD software. These 3D CAD models will be used to 3D print the fouled panels for testing in a channel flow apparatus. The design of the apparatus, created by the Naval Surface Warfare Center – Carderock Division, requires a dovetailed plate to attach to the biofouled plate. In order to accomplish this, the dovetail plate 3D CAD model was merged with the biofouled plate 3D CAD model. This CAD model will then be imported into the Objet350 Connex3 3D printer at the Naval Surface Warfare Center, Philadelphia Division. This printer uses photo-cured polymers to physically create the digital 3D models in 30 micron layers. The Objet350 Connex3 also has the ability to print a flexible polymer, or rubber-like material. Using this material, fouling organisms such as arborescent bryozoans can be printed such that they mimic the actual behavior of the bryozoans in moving water.
The ability to create multiple arrangements of the fouled panel on the dovetail plate enables the testing to be carried out with various configurations of channel flow over biofouling. Randomized plate orientations can be easily created in the 3D CAD software, and then 3D printed. The use of 3D printing also enables significantly more confidence in the results to be achieved during repeated testing. Likewise, it permits for scaling of fouling panels to conform to size limitations associated with the channel flow apparatus.

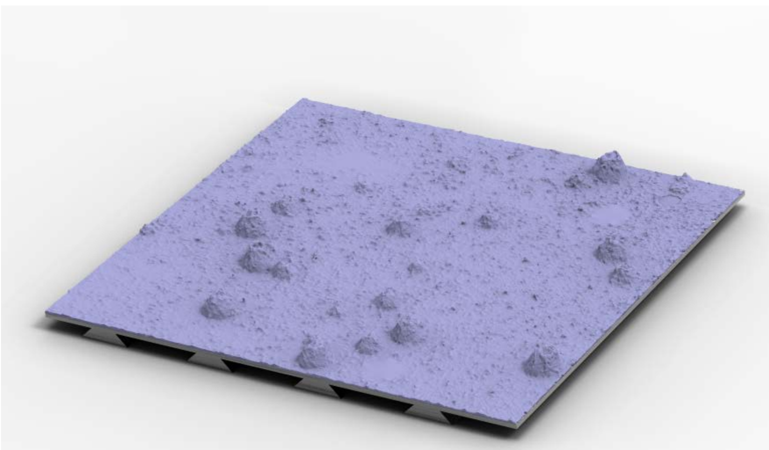


Fig. 2: 3D CAD model of biofouled plate and dovetail plate attachment.

PT S9-18

Targeted in-field macro-fouling tests in Singapore

Wensley Louis WIDJAJA*[1], David Anthony STARK[1], and Jennifer LONGYEAR[2]

[1] AkzoNobel, International Paint Singapore Pte Ltd., 21 Tuas South Street 3, Singapore 638023
[2] AkzoNobel, International Paint Ltd., Stoneygate Lane, Felling, Gateshead, Tyne and Wear, NE10 0JY, United Kingdom

** widjaja.louis@akzonobel.com*

Single species laboratory based bioassays are advantageous as initial screens of marine coatings, experimental substrates, or novel surfaces in part because they are repeatable and comparable tests. Longer-term in-field immersion testing is more representative of the fouling challenges encountered by vessels and provides broad confidence of coating antifouling efficacy, but site fouling pressures determine the species make-up of the tests. This study assesses the viability of conducting robust, taxon-targeted in-field biofouling tests at two field locations in Singapore.

The fouling profiles of two sites in Singapore were evaluated based on biofouling diversity and coverage. A diverse mix of fouling species encompassing a wide taxa of organisms were found on these sites, providing an all-rounded assessment for the experimental surface of interest, allowing the antifouling performance of experimental surfaces to be evaluated against a wide range of fouling organisms.

Long term assessments of these sites also identified seasonal biofouling effects, which provided opportunities to test substrates against particularly harsh taxon-specific hard fouling challenges, such as tubeworms, barnacles and mussels. Thus, experimentation may be adjusted to optimise field tests to be targeted against particular fouling organisms of interest.

In conclusion, by incorporating ecological observations into testing protocols, immersion testing of experimental surfaces at these two marine sites can deliver a more nuanced, taxon-targeted testing similar to single species assays, in addition to experimental confidence of their resistance against the majority of biofouling.

PT S9-19

The use of a simple x-ray fluorescence method (XRF) for quantification of Cu, Zn and Sn (TBT) content in marine coatings.

Erik YTREBERG[1*], Magnus DAHLSTRÖM[1], Peter DAHL[2] Leif ERIKSSON[2] and Hans ELWING[2].

[1] Department of Shipping and Marine Technology, Chalmers Univ. of Technol, Gothenburg, Sweden
[2]Department of Chemistry and Molecular Biology, University of Gothenburg, Sweden

**erik.ytreberg@chalmers.se, hans.elwing@cmb.gu.se*

Simple hand-held XRF equipment has been successfully used in such diverse areas as mining and exploration, scrap sorting and environmental and soil screening. One of its advantages is versatility since almost any “heavy” elements from Magnesium to Uranium could be detected in a solid sample with the use of XRF. The simplicity and accuracy of the XRF inspired us to use a hand-held XRF for the detection and quantification of heavy metals such as Cu, Zn and Sn of antifouling paints applied at marine construction (ship hulls) or at submerged experimental panels coated with anti-fouling paints. Our results so far could be summarized as followed:

1. XRF was very useful for determination and quantification of Cu, Zn and Sn at paint layers applied at ship hulls. The presence of Sn was also well correlated to the presence of old, or new Tributyltin-tin (TBT) containing paints [1].
2. We also made XRF determinations on panels coated with antifouling paints before and after several month deployments in sea water. The Leaching rates of Cu and Zn from these panels could conveniently calculate and expressed in release units such as µg metal/cm^2/day [2].
3. We have also performed antifouling experiments on panels painted with paints containing graded concentration of Cu_2O in ten steps. XRF measurements were successfully used to quantify the copper contents in the localized paint areas before and after several month deployments in the sea. Traditionally used quantification methods for leached Cu could not be used for this application [3].

The versatility and simplicity of the hand-held XRF make it an attractive analytical method for research, fate and development of heavy metal based anti-fouling coatings.

[1] E. Ytreberg, L. Lundgren, MA Bighiu and B. Eklund, *Talanta* **2015**, 143, 121-126.
[2] E. Ytreberg et *al.* This meeting
[3] Yang et al. This meeting

PT S10-1

The impact of microbial biofouling on marine resource extraction: a case study involving seawater uranium adsorbents

Jiyeon PARK[1], Gary A. GILL[1], Jonathan E. STRIVENS[1], Li-Jung KUO[1], Robert T. JETERS[1], Andrew AVILA[1], Jordana R. WOOD[1], Nicholas J. SCHLAFER[1], Christopher J. JANKE[2], Erin A. MILLER[3], Mathew THOMAS[3], R. Shane ADDLEMAN[3], George BONHEYO*[1,4]

[1] Pacific Northwest National Laboratory-Marine Science Laboratory, Sequim, WA, United States.
[2] Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States.
[3]Pacific Northwest National Laboratory, Richland, WA, United States
[4]Washington State University, Pullman, WA, United States

**George.Bonheyo@pnnl.gov*

Seawater provides a mostly untapped resource for several valuable chemical commodities, but many of these chemicals exist at concentrations of <10 ppb. High affinity and high capacity adsorbent materials are one means to extract significant quantities of a desired chemical from large volumes of seawater, but specialized adsorbents can be expensive to produce. To compete economically with traditional terrestrial mining operations, the adsorbents must be able to maintain a maximum rate of uptake and total capacity for the target chemical while allowing efficient extraction and reusability. However, biofouling on the adsorbents may 1) alter fluid dynamics across the adsorbent surface, 2) create a physical barrier that reduces diffusion, 3) chemically interfere with uptake and recovery, 4) cause damage to the ligand chemistry or adsorbent structure, and 5) increase operating costs due to necessary cleaning.

A specific case example entailing the impact of microbial biofouling on adsorbent materials for seawater uranium extraction is presented. Dissolved uranium is found in seawater at a concentration of ~3.3 ppb, amounting to a global marine resource of an estimated 4.5 billion metric tons. The U.S. Department of Energy's Office of Nuclear Energy is supporting the development of high affinity and high capacity adsorbent materials to provide a sustainable and economically viable supply of uranium for nuclear reactors. A study performed at the Pacific Northwest National Laboratory's Marine Science Laboratory in Sequim, WA found that biofouling decreased uptake on a leading adsorbent material by up to 30%. A comparison was made using adsorbents exposed to light (simulating shallow deployment in the marine photic zone) and adsorbents kept in darkness. Adsorbents kept in the light accumulated 27% more biomass (measured as non- purgeable total organic carbon) and supported a distinct microbial community in comparison with the unlit adsorbent materials. Preliminary examinations found no damage to the adsorbent material. Although placement into aphotic water may significantly decrease the impact of fouling, this would add to deployment costs and the colder temperatures found in deeper water are less favorable for uranium uptake. The results provide a demonstration of effects and a first estimate for the economic impact that fouling may have on adsorbents used for resource extraction from a marine environment.

PT S10-2

The impact of fouling control coating selection on hull roughness: an updated review

Haoliang CHEN*, Barry KIDD, Alistair FINNIE, Yuhuai SEAH

International Paint Singapore Pte Ltd., Global Marine Coatings Research Center, Singapore

* *Haoliang.chen@akzonobel.com*

The prediction of the total roughness change over a drydock cycle is one of the key inputs into any model that seeks to predict ship operational efficiency. Total roughness can be broken down into hull and coating micro, macro and fouling roughness. The general impact of macro roughness on ship resistance and powering requirements is well known, as is the need to prevent biofouling through the application of an effective fouling control coating. The initial average hull roughness (i.e. macro roughness) and rate of change during the full in service period of a ship is linked to several contributing factors, such as the selected fouling control coating type, the number of applied coats and applied thickness (including underlying anticorrosive coatings and primers), the degree and type of surface preparation (spot blasting, full blasting, power tooling etc.), vessel age, vessel type and operational profile, etc. Townsin's seminal work in the 1980s quantified the effect of increasing hull roughness on ship powering requirements and assessed the typical increase in roughness over time for the main coating technologies then in use. Since then significant advances in ship design, manufacturing approaches, materials and fouling control coating technologies have been made. Additionally the available dataset of hull roughness measurements has grown substantially over the years as many ship owners pay ever closer attention to the indocking and outdocking condition of their ships. It is therefore appropriate to revisit Townsin's work and re-appraisal its accuracy and applicability in the light of these developments.

A preliminary review was undertaken in 2014 [1] which presented fresh insight into the effects of substrate preparation, coating technology type and vessel age on surface roughness. Making use of a significantly expanded set of hull roughness surveys and improved data cleansing routines, a more detailed review will now be presented which additionally allows the data to be broken down by vessel type and provides a more detailed exploration of the range and extent of substrate preparation. This creates a comprehensive and updated macro roughness model for in service ship hulls, which when combined with appropriate models for other key parameters contributes toward the development of an overall model of total roughness change during a drydock cycle. If further combined with an appropriate ship powering requirement model, then the impact of fouling control coating choice on ship operational efficiency can be assessed.

[1] PREDICTING THE IMPACT OF HULL ROUGHNESS ON THE FRICTIONAL RESISTANCE OF SHIPS, PA Stenson, B Kidd, HL Chen, AA Finnie, R Ramsden, *International Conference on Computational and Experimental Marine Hydrodynamics, MARHY 2014*, **3-4 December 2014**, Chennai, India
.

PT S10-3

Advanced coatings for offshore renewable energy

Alvaro RODRIGUES[1*], Henry BEGG[2], Yi YANG[3], Mattias BERGLIN[3] and Hans ELWING[3]

[1]Centro Tecnologico de Componentes, Santander, Spain, [2]TWI Ltd, Cambridge, UK
[3]University of Gothenburg, Sweden

arodriguez@ctcomponentes.com, hans.elwing@cmb.gu.se

There is a vast energy potential in the utilization of wave and tidal devises in the oceans. Many mechanical designs for offshore uses involve turbines, and adjacent low water friction solid surfaces of different designs. The demands of certain sea water contacting surfaces are very high since such materials should resists corrosion, erosive cavitation and marine biofouling for a several years with a minimum of maintenance time. We have developed a coating based on “thermally sprayed aluminum” (TSA). The TSA coating provides excellent corrosion resistance, working as both a barrier to seawater and by corroding sacrificially to protect regions of exposed steel (fig 1). The corrosion resistant service time for the TSA coating is estimated to be at least 30 year. The TSA coating is furthermore eroded at a rate of about 2-10 microns per year. In the present investigation we have tried to make the TSA surface resistant to marine biofouling. The barnacle was regarded to be one of the most serious biofouling organisms at coated surfaces since barnacles may penetrate and destroy paint-based coatings (fig 2). We speculated in that an antibarnacle substance (biocide) with very high efficacy included in the TSA coating at high concentration, may be barnacle resistant for years due to erosion and diffusion. A series of anti-barnacle substances (biocides) where therefore included in the TSA-coating. We also established a novel field tests facilities in Santander, Spain involving the biofouling can be assessed at three different exposure zones: the splash zone, the tidal zone and the submerged zone (fig 3).
The results indicated that the corrosion resistance of the TSA coating was excellent. There was also an indication of that the TSA coating by itself seems to have some anti-fouling properties possibly related to erosion of the TSA layers. Significant results of the antibarnacle properties of the developed coating were not obtained in 2015, due to unexpected low level of barnacle colonization in the Swedish and Spanish test facilities.

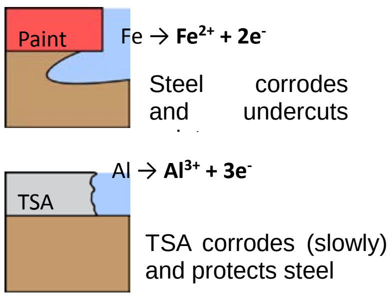


Fig 1. TSA Anti-corrosion

Fig 2. Barnacles

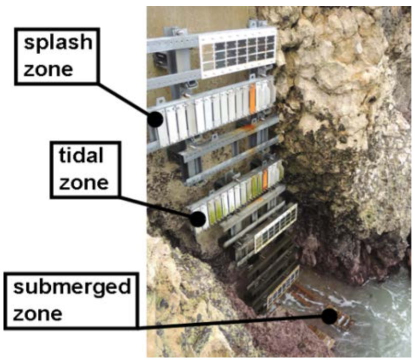


Fig 3. Santander test site

Acknowledgements: ACORN (**A**dvanced **C**oatings for **O**ffshore **R**enewable e**N**ergy), is an industry-led project supported by the European Commision (http://www.acorn-project.eu/)

PT S10-4

Using three dimensional printing to investigate the hydrodynamic effect of biofouling (*Chirona Hameri*) in relation to tidal energy.

Rebecca FRANCIS[1], Martyn HANN*[1], Thomas VANCE**[2]

[1] *Plymouth University, Plymouth, United Kingdom.*
[2] *Plymouth Marine Laboratory Applications Ltd, Plymouth, United Kingdom*

**martyn.hann@plymouth.ac.uk*
**thva@pml.ac.uk

Following a rapid expansion of the marine renewable energy (MRE) industry a call for research has highlighted the need to investigate effects of biofouling on MRE devices [1]. Biofouling is a significant problem in relation to shipping and static marine structures [2]. However the unique location and design of MRE devices poses different opportunities for biological colonisation, the effects of which are largely unknown [3].
Biofouling generally increases the surface roughness of a structure thus; increasing friction, drag and causing changes to hydrodynamics surrounding the structure [4]. This study explores the effect of biofouling on boundary layer hydrodynamics using a calcareous barnacle (*Chirona hameri*) biofouling sample and a series of 3D printed replicas.
The original sample was collected from deployment at the European Marine Energy Centre (EMEC) tidal test site at Orkney, Scotland (Fall of Warness, 59º 08’ 05.1211’ N and 002º 48’ 20.9126’ W).
Two techniques were adopted to generate 3D computerised models of the original sample; 3D scanning and a photogrammetric technique. From these models two full scale and two scaled samples were 3D printed in plastic using a Makerbot Replicator 2.
Surface elevation of all samples was measured using a laser distance scanner. From these data the root mean square deviation was calculated to determine the degree of deviation in surface height between the original sample and printed models. Deviation from the original sample increased with increased scale factor and no model accurately represented the surface elevation of the original sample.
A 20m recirculating flume at Plymouth Universities COAST Laboratory was used to investigate the effect of barnacle biofouling on hydrodynamics. The effect of the samples on a generated flow of ~0.32m/s was measured in the boundary layer using an Acoustic Doppler Velocimeter (ADV) and strain gauge. ADV data was collected along the central transect of the samples including 50mm upstream, along the full length of the sample (100mm) and 200mm downstream of the sample.
A decrease in average X velocity of 0.14m/s was observable over the course of the original sample and continued, to a lesser extent, downstream. A similar pattern is observable across full scale models. Where surface elevation increases average X velocity decreases.
Understanding the effect of biofouling on MRE devices will allow for a more accurate calculation of their efficiency and longevity. This study supports a hypothesis that the presence of biofouling alters hydrodynamics in the boundary layer with potential implications on device efficiency and loading. A more in depth study of this kind into downstream effects of biofouling may help to quantify potential array effects.

[1] Renewable UK **2015,** *Available online at www.renewableuk.com/en/renewable-energy/wave-and-tidal/*
[2] M.Legg, M.K.Yucel, I. Garcia de Carellan, V.Kappatos, C.Selcuk, T.H.Gan. *Ocean Engineering*. **2015**, 103. 237-247.
[3] M.E. Callow, J.A.Callow, *Biologist.* **2002**, 49.1.
[4] H.Ameryoun, F.Schoefs, *International conference on Ocean, Offshore and Arctic Engineering conference paper*. **2013**, 9-14 June 2013. 1.

PT S10-5

Settlement of an alien mollusc in a Mediterranean industrial plant: strategy for the optimization and management of antifouling treatments

Francesca GARAVENTA*[1], Arianna CASELLA[2], Veronica PIAZZA[1], Elisa COSTA[1], Silvia MORGANA[1], Paolo FISICARO[2], Salvatore DI MARCO[2], Andrea GAROFALO[2] and Marco FAIMALI[1]

[1]ISMAR CNR, Genoa, Italy
[2]Nalco Champion, Sicily, Italy

**francesca.garaventa@ismar.cnr.it*

The presence of biofouling in heat exchange systems using seawater as coolant is a worldwide and well-known problem that may undoubtedly cause both economical and ecological damages. Antifouling treatments for industrial plants using sea water as cooling fluid, are exclusively based on chemical toxic substances (biocides) and often well-established antifouling strategies reveal themselves to be ineffective when dealing with alien species, such as the bivalve *Brachidontes pharaonis*, classified by CIESM as an exotic species introduced in Mediterranean sea by maritime transports (ballast waters).
In 2006 a strong settlement phenomenon of this species has been observed in an industrial plant in South Italy. This massive presence of bivalves inside the plants caused the stop of the plant with consequently high economical impact.
The routine chemical treatment (hypochlorite) and the supplying methods (concentration and timing) resulted to be completely ineffective
Furthermore, there was a complete lack in the knowledge of the ecology of the fouling community inside and around the plant.
The present work describes the approach used in the plant to solve the fouling problems and to correctly manage the bivalves pressure along the following 10 years.
To do that the identification of the effective dose/timing of the biocide was performed under laboratory condition taking into account also the environmental effects at the discharge and then applied in the plant; in fact, only the accurate knowledge of the lethal and sublethal responses of the target species to the biocide is essential for the development of a rational antifouling strategy.
In parallel, a biological monitoring of the fouling bivalves community has been set up analyzing, monthly or twice monthly both benthic and planktonic samples collected before and after the biocide injection points in different Plant areas. The precise knowledge of the presence of juveniles and larvae of bivalves allowed to modulate the timing and dosing of the treatment thus making it more effective and reducing the useless injection (and consequent discharge at Sea) of an excess of biocide.

PT S10-6

In-service performance evaluation of low frictional AF marine coating based on ISO/DIS19030

Inwon LEE*,[1], and Hyun PARK[2]

[1] GCRC-SOP, Pusan National University, Busan, South Korea.
[2] GCRC-SOP, Pusan National University, Busan, South Korea.

*inwon@pusan.ac.kr

In the previous study of the authors, a novel FDR-SPC was first synthesized. The drag reducing functional radical such as PEGMA (Poly(ethylene) glycol methacrylate) has been utilized to participate in the synthesis process of the SPC. In the high-Reynolds number flow measurement with a flush-mounted balance and a LDV (Laser Doppler Velocimeter), the skin friction of the present FDR-SPC is found to be smaller than that of smooth plate throughout the range of Reynolds number, with the average drag reduction efficiency being 13.5% over the smooth plate. These results strongly support that the present FDR-SPC gives rise to the Toms effect based on chemical reaction at the surface of the coating. The low frictional AF coating based on the FDR-SPC has been comerciallized as Bn Green Guard FS, which is found to give 25% skin friction resuction compared with conventional AF coating. After the antifouling efficiency had been confirmed through the patch test during a couple of years, this product was chosen to be painted on the whole underwater surface of a 176k bulk carrier (M/V "PAN BONA") to evaluate the full-scale energy saving performance during service. The repainting was finished in December 2015. The propulsion performance of M/V "PAN BONA" as well as the weather condition is being recorded during service. It is imperative that the hull coating performance be evaluated without being affected by the additional resistance component associated with such weather condition as wind and wave. It is ISO/DIS19030 that is being proposed as a new international standard for that purpose. Based on this standard, the in-service navigation data collected from M/V PAN BONA is going to be analyzed to give an assessment of energy saving performance of the present low frictional AF coating.

Fig. 1: Photographs of M/V "PAN BONA" after painted with low-friction AF coating

[1] I. Lee, H. Park, H. Chun, *Proceedings of 9th International Symposium on Turbulent Shear Flow*, **2014**, paper 5A-1

PT S10-7

Review and assessment of mechanical methods for underwater cleaning of marine structures

Tom MARQUARDT[1], Andreas MOMBER[1]

[1] Muehlhan AG, Schlickstraße 3, 21107 Hamburg, Germany.

marquardt@muehlhan.com

The growth of micro- and macro-organisms (biofouling) and their settlement on the underwater surfaces of marine structures significantly affects the performance of the structures. For vessels, biofouling increases friction losses and fuel consumption, and invasive organisms are spread along trade routes all over the world. For offshore structures, biofouling modifies the flow dynamics around legs and may promote scour formation; it also impedes inspection and cleaning.
A number of methods are available for the removal of biofouling. This poster is concerned with a systematization and assessment of the methods. According to the tribological principles behind the material removal mechanisms, cleaning methods are subdivided into three categories, namely mechanical methods (abrasion), jet-based methods (flow erosion), and cavitating methods (cavitation erosion). Typical devices and tools for each category are discussed in terms of physical, energetic, economic, ecologic and process-based parameters. A procedure for the ranking of the methods is proposed and first results are provided. The poster also reports about application trials with abrasion-based and flow-based tools.

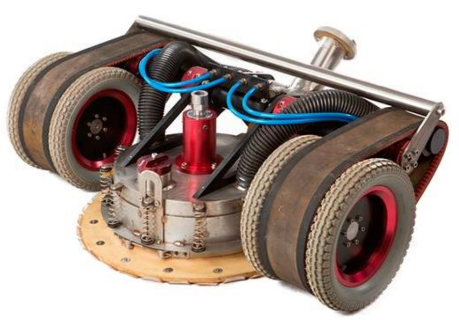


Fig. 1: Tool based on flow erosion: M4 Magnet Crawler Vacuum (OFTEC GmbH)

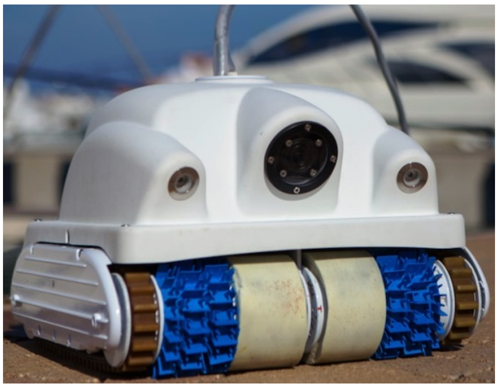


Fig. 2: Tool based on abrasion: Keelcrab One (Aeffe S.r.l.)

Acknowledgements: The work presented in this study has been funded by the German Federal Ministry for Economic Affairs and Energy (BMWi) through the Project “FoulProtect” (Grant Agreement No. 03SX370).

PT S10-8

Similarity transform method to predict full scale ship performance based on various lab skin friction tests

Hyun PARK[1] and Inwon LEE*,[2]

[1] GCRC-SOP, Pusan National University, Busan, South Korea.
[2] GCRC-SOP, Pusan National University, Busan, South Korea.

*inwon@pusan.ac.kr

With the advent of various types of low frictional AF marine coating, there have been proposed a variety of measurement techniques to evaluate frictional performance in laboratory scale, including a towed flat-plate drag measurement, a flush-mounted skin friction balance, a rotor torque measurement and a model ship total drag measurement. However, differences in the flows associated with such various setups make it extremely difficult to compare one test results with the other. When it comes to the extrapolation from lab scale results to the full scale ship performance, there hardly exist a systematic method ever proposed. In this study, a similarity transform is attempted to predict full scale ship performance based on such lab test method as towed flat-plate drag measurement and rotor torque measurement. This is an extension of the Granville similarity transform method used in [1]. Greater care is also taken to account for the low frictional AF coatings.

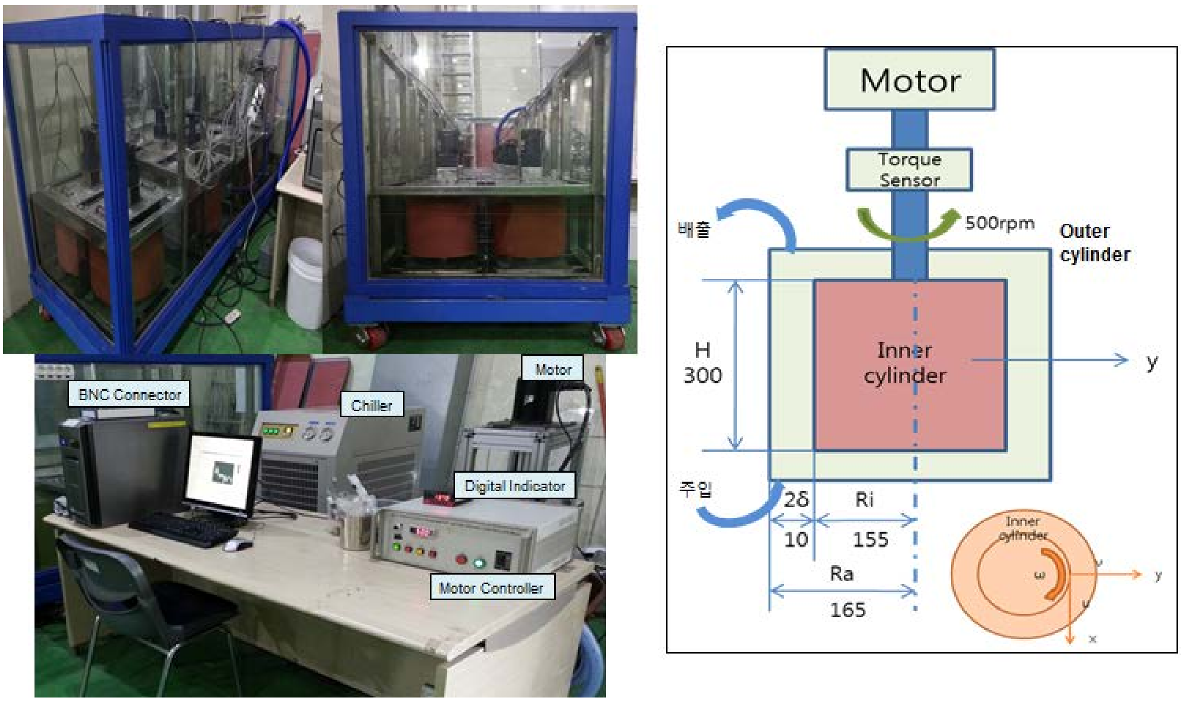


Fig. 1: Rotor test apparatus for long-term skin frictional performance assessment

[1] M. Schultz, *Biofouling*, **2007**, 23(5), 331-341

PT S10-9

Additive manufacturing for the control of biofouling in problematic vessel niche areas

Richard PIOLA*[,1], Martin LEARY[2], Steven TOPPI[3], Alexander DEL FRATE[2], Clare GRANDISON[1], Scott MAYSON[4], Jeff SHIMETA[5], Milan BRANDT[2]

[1] *Environmental Signature Control Group, Defence Science and Technology Group, Melbourne, AUSTRALIA.*
[2] *Advanced Manufacturing Precinct, Royal Melbourne Institute of Technology, Melbourne, AUSTRALIA.*
[3] *Department of Mechanical and Aerospace Engineering, Monash University, Melbourne, AUSTRALIA*
[4] *School of Architecture and Design, Royal Melbourne Institute of Technology, Melbourne, AUSTRALIA.*
[5] *Applied Sciences, Royal Melbourne Institute of Technology, Melbourne, AUSTRALIA.*

* *richard.piola@dsto.defence.gov.au*

The accumulation of biofouling on marine vessels and structures results in reduced operational efficacy and increased running costs, in addition to posing significant environmental risks through the transport of unwanted marine pest species. Vessel niche areas have long posed a problem for biofouling control as they are often difficult to access, and their diverse shape and size result in variable water flow regimes that are poorly suited to minimising biofouling settlement and for efficient performance of antifouling coatings. Additive Manufacture (AM) refers to a manufacturing paradigm by which components are manufactured in a layer-by-layer method. The fundamental differences between traditional and additive manufacture have seen AM labelled a disruptive technology with novel opportunities for innovation and cost reduction. In particular, AM provides opportunities for the manufacture of: (i) Prototype components, for design validation prior to large-volume manufacture; (ii) Complex shapes that are not technically feasible with traditional methods, and (iii) Low-volume production without the cost-penalty associated with traditional manufacture. This presentation discusses ongoing research and development investigating opportunities for the use of additive manufacturing techniques for the control of biofouling in problematic vessel niche areas.

PT S10-10

Assessment of fouling release coating degradation caused by grooming

Melissa TRIBOU*[1], Geoffrey SWAIN[1]

[1] Melbourne, Florida, USA.

** mtribou@fit.edu*

Grooming of fouling release coatings has been shown to be an effective method to reduce fouling [1]. Grooming uses rotating soft-bristled polypropylene brushes to remove newly settled fouling organisms, and is performed on a frequent basis, at least once weekly. Previous studies showed no coating damage from grooming brushes with a stiffness parameter of 7N/m [2,3]. However, improvements to grooming performance required stiffer brushes and it was unknown how this would impact the coating. This study was designed to measure the effect of a 9N/m stiff grooming brush on 200 and 275-μm thick silicone fouling release coatings. Rotating brushes were laterally translated across the coatings at 3 different compression forces. The experiment ran continuously to simulate weekly grooming for twelve years. Coating degradation was assessed using microscopic imaging, glossmeter readings, captive bubble method, and pseudo-barnacle adhesion measurements. All surfaces were then deployed to accumulate fouling at the Florida Institute of Technology's estuarine static immersion test site. Fouling assessments and biofilm adhesion measurements were performed after three weeks immersion. Visual appearance, surface gloss, and pseudo-barnacle adhesion differed among coating thicknesses and compression forces. There was; however, no significant differences in fouling coverage; and biofilm adhesion was only affected by coating thickness, and not effects due to brush compression forces. These results indicate that grooming brushes may be used successfully without degradation to silicone fouling release coatings.

[1] Tribou, M. and Swain, G. (2010). Biofouling 26(1), 47–56.
[2] Tribou, M. and Swain, G. (2015) Biofouling 31:4, 309-319.
[3] Tribou, M. 2015. Brush development for underwater ship hull coating maintenance [Doctoral dissertation]. [Melbourne (FL)]: Florida Institute of Technology.

PT S10-11

Investigation of the biofouling and corrosion performance of thermal spray coatings subjected to static immersion in Australian marine sites

Andrew S.M. ANG*[1,5], Richard PIOLA[2], Christopher C. BERNDT[1,5], Hugo HOWSE[3], Peter RICHINGS[4], and Scott A WADE[1,5]

[1] *Swinburne University of Technology, Melbourne, Australia.*
[2] *Defence Science and Technology Group, Melbourne, Australia.*
[3] *United Surface Technologies Pty Ltd, Melbourne, Australia.*
[4] *MacTaggart Scott Australia Pty Ltd, South Australia, Australia.*
[5] *Defence Materials Technology Centre (DMTC), Melbourne, Australia*

* *aang@swin.edu.au.*

For maritime engineering components, such as hydraulic piston rods, continued exposure to seawater can lead to detrimental biofouling growth and corrosion. To enhance the component's long term durability, one of the solutions is to apply an engineered coating layer that offers high wear resistance as well as biofouling and corrosion protection. The thermal spray process is an established coating technology that can apply a wide range of materials onto a targeted surface. Coating materials are heated to or near their melting points, these molten or partially molten droplets are subsequently accelerated in a gas stream and projected against the surface to be coated. Amongst the various thermal spraying techniques, air plasma spraying (APS) and high velocity oxygen fuel spraying (HVOF) have been successfully used for the coating of hydraulic rods. Nevertheless, within the open literature, there is limited information on the maritime field testing performance data for such coatings, especially with regard to biofouling resistance.

The overall aim of the work is to provide critical information to help engineers to assess thermal spray coating survivability in real maritime environment and establish life-cycle maintenance solutions

To evaluate the suitability of thermal spray coatings for protecting marine hydraulic piston rods, a range of traditional and novel coatings with different chemical compositions have been deposited by either APS or HVOF thermal spray technology. The primary focus of this work is to characterise the coatings when exposed to the physical, chemical and biological conditions encountered in Australian marine sites. These coated samples have been distributed among 3 maritime field test sites around Australia.

This works presents preliminary results of biofouling rates, corrosion rates of these thermal spray coatings, as well as reporting any changes to the surface metrology. Another focus of the work is to measure appropriate properties of biofouled coatings; such as coating spalling resistance and adhesion strength when established biofouling products are being removed.

Acknowledgments: The authors would like to acknowledge the support of the Defence Materials Technology Centre (DMTC). The DMTC was established and is supported under the Australian Government's Defence Future Capability Technology Centres Program
.

PT S10-12

Identification of variables that are significant to the rate of change in a ship's powering penalty

J Travis HUNSUCKER*[1,3], Geir LUND[2], Jari OINAS[2], and Geoffrey SWAIN[1]

[1] Center for Corrosion and Biofouling Control, Florida Institute of Technology Melbourne, FL, USA
[2] Global Marine Technical Services, Miami, Royal Caribbean Cruises Ltd, FL, USA
[3] SHIPWRIGHT LLC, Port Everglades, FL, USA

**jhunsucker2008@my.fit.edu*

The decision as to when and where to clean the hull and propeller of most vessels is made reactively based on diver reports or proprietary software. With numerous ports prohibiting in-water hull cleaning, it becomes advantageous to know the factors that affect the approximate development rate of the powering penalty. This could allow the location and timing of the hull and/or prop cleaning to be optimized. Approximately five years worth of powering and operational schedule data were analyzed from four different ships of the same class in an attempt to better understand the influence of environmental factors on the powering performance. The data were reduced, in a manner similar to ISO 19030-1, to a key performance indicator (KPI). The rates of change of the KPI were correlated with multiple aspects that comprise the ship's operational schedule: modal speed, region of operation, duty cycle, bottom paint, time since cleaning and cleaning type etc... Environmental data from the Hybrid Coordinate Oceanographic Model (HYCOM) were also included in the analysis. P-value testing and ranking of correlation coefficients identified statistically significant variables and ranked their order of importance to the rates of change in KPI. The identification of the significant variables to the rate of change in a vessel's powering penalty will allow the cleaning frequency to be optimized based on the ship's operational schedule.

PT S11-1

Antifouling properties of nature-inspired synthetic compounds

Joana R. ALMEIDA*[1], Marta CORREIA DA SILVA*[1,2], Emilia SOUSA[1, 2], Madalena PINTO[1,2], Vitor VASCONCELOS[1,3†,] Isabel CUNHA[1†]

1 CIIMAR/CIMAR - Interdisciplinary Centre of Marine and Environmental Research, University of Porto, Portugal
2 Laboratory of Organic and Pharmaceutical Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Rua Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal
3 Department of Biology, Faculty of Sciences, University of Porto, Rua do Campo Alegre, P 4069-007, Porto, Portugal.

[†] These authors contributed equally to this work.

** jalmeida@ciimar.up.pt, m_correiadasilva@ff.up.pt*

The development of alternative environmentally friendly and non-toxic antifouling technologies is a challenge. Synthesis of nature-inspired compounds has been exploited to the development of antifouling agents, given the potential to guarantee commercial supplies [1]. This work aims to test a series of synthetic small molecules with chemical similarities with natural products with recognised AF properties (sulfated compounds) and also novel scaffolds (xanthones and thioxanthones), as potential environmentally friendly antifouling agents. The anti-settlement potential towards *Mytillus galloprovoincialis* plantigrades larvae, ecotoxicity to target and non-target species (*Artemia salina*) and biochemical modes of action by the modulation of selected enzymes, acetylcholinesterases (AChE) and phenoloxidase (PhOx) were evaluated. Synthetic small molecules, belonging to different chemical classes, were obtained by feasible syntheses, with high scale-up potential, and isolated with a purity higher than 95%, Antifouling activity was evaluated for thirty-five compounds using an *in vivo* anti-settlement test with *Mytilus galloprovincialis* plantigrades larvae at two top concentrations, 250 μM (sulphated compounds), 100μM (xanthones and thioxanthones) and 50 μM (for both groups of compounds). The compounds with the most promising AF activity were selected for further investigations concerning antifouling effectiveness *versus* toxicity, and general ecotoxicity to *Artemia salina* nauplii.
Nine of the tested compounds showed highly significant differences ($p \leq 0.001$, Dunnet's test) in the percentage of settled larvae against the control for the two concentrations tested. The assessment of effectiveness *versus* toxicity of these promise compounds showed EC50 values ranging from 3.53 to 22.59 μM, LC50 levels higher than 500 μM, and LC50/EC50 between 17.42 and 141.64. However, four of the selected compounds showed significant toxicity at 25 and 50μM to *A. salina* after 24 h of exposure. Also, potential biochemical modes of action were identified for some of the selected compounds.
In conclusion, five promising non-toxic antifouling compounds were found (R10S, XGLUS, AGS, 3,4-dOHX, and XP13), deserving further investigation as candidates for incorporation in paints. However, investigation of the mode of action is essential to consider the effectiveness of the antifouling activity [2].

Acknowledgements: This research was partially supported by the Strategic Funding UID/Multi/04423/2013 through national funds provided by FCT and ERDF, in the framework of the programme PT2020, by the projects PTDC/MAR-BIO/4694/2014 and PTDC/AAG-TEC/0739/2014, and by a postdoctoral scholarship to JRA (SFRH/BPD/87416/2012).

[1] M. Correia-da-Silva, E. Sousa, M.M.M. Pinto, Med. Res. Rev., 34 (2014) 223-279.
[2] J.R. Almeida, V. Vasconcelos, Biotech. Adv., 33 (2015) 343-357.

PT S11-2

Natural antifouling compounds: promising non-biocidal alternatives from cyanobacteria

Joana ALMEIDA*[1], Susana CRUZ[1], Micaela FREITAS[1], Marco PRETO[1], Isabel CUNHA[1†] and Vitor VASCONCELOS[1,2†]

[1] CIIMAR/CIMAR - Interdisciplinary Centre of Marine and Environmental Research, University of Porto, Portugal.
[2] Department of Biology, Faculty of Sciences, University of Porto, Portugal.

[†] These authors contributed equally to this work.

** jalmeida@ciimar.up.pt*

Considering the toxicity of the antifouling (AF) paints that continue to be used, natural environmentally friendly alternatives are being exploited to biofouling control [1]. Microorganisms, and particularly cyanobacteria, have been considered promising potential sources of non-toxic AF compounds, as they are able to produce a wide range of secondary metabolites with recognized bioactivity in a wide range of biological responses, including AF properties [2], and also have the advantage of ensuring product supplies renovation.
This study aims to screen several different strains of cyanobacteria for potential AF properties using anti-settlement bioassays with plantigrade larvae of the biofouling mussel *Mytilus galloprovincialis*. Twenty-five cyanobacteria strains were cultured and up-scaled, and recovered biomass was repeatedly extracted with warm (<40 °C) CH2Cl2/MeOH (2:1), evaporated and dissolved in DMSO. Plantigrade larvae were exposed for 15 hours to different cyanobacterial organic extracts in controlled conditions. Post-exposure settlement was determined by the production/lack of byssal threads by each test individual, determining the potential of each strain to inhibit mussel adhesion. Promising extracts were fractionated by a gradient of polarity to obtain less chemically complex fractions and new assays were performed testing each obtained fraction. *In vitro* phenoloxidase (PhOx) activity, involved in the synthesis of mussel byssus polyphenolic proteins was performed to search for possible mode of action related with adhesion of the extracts with AF activity.
Organic extracts from strains *Microcystis aeruginosa* LEGE05195, *Leptolyngbya* sp. LEGE07075, *Nostoc* sp. LEGE06077, and *Leptolyngbya* sp. LEGE07080 significantly inhibited the settlement of plantigrade larvae, when compared to DMSO control. Fractions and further subfractions of some of the extracts showed significant bioactivities indicating the presence of promise AF compounds. PhOx activity *in vitro* was not modulated by any of the promise cyanobacteria extracts, suggesting that the AF mode of action is not related with the processes of adhesive synthesis.
Future perspectives include the identification and chemical elucidation of new potent AF compounds or even brand new unknown compounds, and the incorporation in paints and other polymeric matrices to test their real potential in biofouling scenarios.

Acknowledgements: This research was supported by the Strategic Funding UID/Multi/04423/2013 through national funds provided by FCT and ERDF, in the framework of the programme PT2020 and by a postdoctoral scholarship to JRA (SFRH/BPD/87416/2012).

[1] J.R. Almeida, V. Vasconcelos, Biotech. Adv., 33 (2015) 343-357.
[2] L.T. Tan, B.P. Goh, A. Tripathi et al. Biofouling 26 (2010) 685-95.

PT S11-3

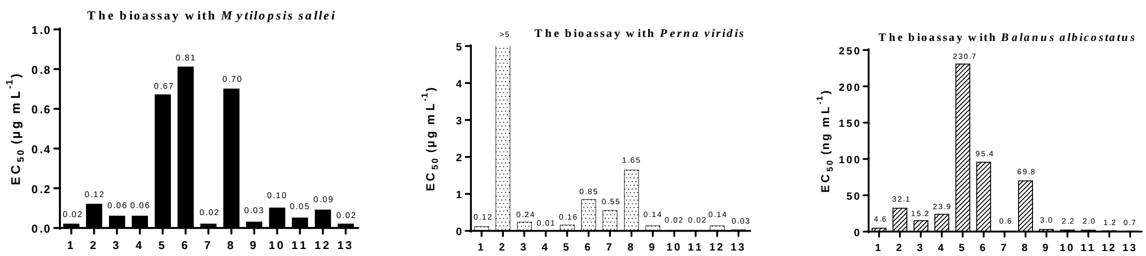
Cardiac glycosides and aglycones as potential green antifoulants

Hui LIU[1], Danqing FENG[1]*, Yingkun QIU[2], and Caihuan KE[1]

[1] *College of Ocean & Earth Sciences, Xiamen University, Xiamen, PR China.*
[2] *School of Pharmaceutical Sciences, Xiamen University, Xiamen, PR China.*

**dqfeng@xmu.edu.cn*

Cardiac glycosides are usually composed of a steroid nucleus and an unsaturated lactone (collectively referred to as an aglycone) and a sugar moiety. They are widely used in the treatment of heart failure and atrial arrhythmia [1]. Their antibacterial and anticancer activities have also been observed [2]. In this study, four cardiac glycosides and nine aglycones were investigated for their antifouling activity. Four compounds, odoroside A, digitoxigenin, oleandrin, and odoroside H, were isolated from the terrestrial plant *Nerium indicum* using bioassay-guided procedures during the present screening for novel environmentally friendly antifouling agents. Their antifouling activities were compared to nine commercial natural products which were also cardiac glycosides and aglycones (Fig. 1). As shown in Fig. 1, they exhibited high anti-settlement activities against the black striped mussel *Mytilopsis sallei* (all compounds EC_{50}<1 μg mL^{-1}), the green mussel *Perna viridis* (12 compounds EC_{50}<2 μg mL^{-1}) and the barnacle *Balanus albicostatus* larvae (all compounds EC_{50}<0.25 μg mL^{-1}). Analysis of structure–activity relationships suggested that the presence of sugar moiety at the C3 position had a significant influence on the expression of antifouling activity in cardiac glycosides. The acute toxicity of the tested compounds was examined against one non-target organism, the larvae of the brine shrimp *Artemia saline*. The 24 h LC_{50} values of these thirteen compounds were all over 9 μg mL^{-1}, with seven compounds of 24 h LC_{50} >100 μg mL^{-1}, indicating their potential as green antifoulants. The coating containing the cardiac glycosides and aglycone mixtures extracted from *N. indicum* exhibited antifouling activity in the field over a period of two months. Overall, this study indicates the significant antifouling activities of cardiac glycosides and aglycones for the first time. The wide distribution of cardiac glycosides and aglycones in terrestrial plants (such as *N. indicum*, which is abundant in resources) makes the supply of sufficient amounts needed for commercial application of them as antifoulants possible.



] *Fig. 1 EC_{50} values of four cardiac glycosides and nine aglycones against settlement of* Mytilopsis sallei, Perna viridis *and* Balanus albicostatus. *1: Odoroside A; 2: Digitoxigenin; 3: Oleandrin; 4: Odoroside H; 5: Digoxigenin; 6: Convallatoxin; 7: Cinobufagin; 8: Resibufogenin; 9: Gamabufotalin; 10: Arenbufagin; 11: Telocinobufagin; 12: Bufotalin; 13: Bufalin.*

[1] P. Ioannis, E.P. Diamandis, *Nat. Rev. Drug. Discov.* **2008**, 7, 926-935.
[2] M.M. Huq, A. Jabbar, M.A. Rashid, C.M. Hasan, *Fitoterapia*. **1999**, 70, 5-9.

PT S11-4

Algae against algae: microalgae as source of novel antifouling compounds

Isabel FREIRE*, Maribel REYERO and Ana OTERO

Department of Microbiology and Parasitology – University of Santiago de Compostela, Spain.

**isabel.freire@usc.es*

Marine biofouling consists in the accumulation of micro- and macroorganisms on submerged surfaces and it is a major economic problem costing billions of dollars a year to the global economy. Microorganisms such as bacteria and microalgae play an important role in the early stages of biofouling. Current antifouling commercial products use highly toxic metallic or copper-based technologies that have a short half-life. One promising ecofriendly alternative technology to heavy metal-based antifouling paints could be based on the use of active compounds from the marine organisms. Corals, sponges, macroalgae, fungi, cyanobacteria and bacteria are candidates for the identification of molecules with antifouling active. In this sense, microalgae are eukaryotic photosynthetic microorganisms which produce a multitude of high-value compounds being especially interesting because their production has been already stablished at industrial level, being economically feasible ans sustainable in comparison to other marine organisms.
The aim of this work is the study of the presence of inhibitory activity of algal growth in the culture media of different microalgal strains. Ethyl acetate extracts obtained from the culture media from logarithmic, stationary and late stationary phase of eight microalgae were tested against four different species of microalgae: *Tetraselmis suecica*, *Nannochloropsis gaditana*, *Porphyridium cruentum* and *Nitzschia sp*. Assays were carried out 2-mL cell culture plates under conditions promoting algal attachment. None of the tested extracts showed activity against the four model microalgae used as target. Extracts from the *Chlorophyte Dunaliella salina*, and the *Cryptophytes Rhodomonas salina* and *Chroomonas placoidea* produced a reduction of biofilm formation between 20 to 60 % for *T. suecica* and *P. cruentum* biofilms. The *Nitzschia acicularis* extract obtained from logarithmic phase cultures was very active agains P. cruentum, with an inhibition 80 % of growth, but was inactive for the other 3 species tested. All extracts from *Tetraselmis chuii* and stationary phase extracts from *Phaeodactylum tricornutum* diminished *T. suecica, N. gaditana* and *P. cruentum* biofilms between 20 to 30 %. Finally, *Nannochloropsis gaditana* and *Porphyridium cruentum* extracts did not show any biofilm inhibitory activity.
Data confirm the presence of growth inhibitory activities against the four microalgal species tested in the culture media of several microalgal strains. Although further research is required in order to analyse the activity present in the biomass fraction, characterize the molecules responsible for the activity and to establish culture conditions driving to maximal production at both, laboratory and industrial scales, results indicate the feasibility of the algae-against algae approach for the control of microfouling processes.

Acknowledgements: This work has been supported from the European project BYEFOULING “Low-toxic cost efficient environment-friendly antifouling materials” (FP7-OCEAN-2013 612717).

PT S11-5

Antifouling properties of the brown alga *Taonia atomaria* (Woodward) J. Agardh from Tunisian coasts: field experiments

Leila KTARI*,[1], Mokhtar BAYOUDH [2], Wafa CHERIF[1,3], Cheima M'DALLEL[1] and Monia EL BOUR[1]

[1] *INSTM, National Institute of Marine Sciences and Technologies Tunis, Tunisia.*
[2] *ULT, Université Libre de Tunis, Tunis, Tunisia.*
[3] *FST, Faculté des Sciences de Tunis, Tunisia.*

* *leila.ktari@instm.rnrt.tn*

Dictyotales species are known to have a large array of bioactive secondary metabolites possessing a broad defensive action. In this work we present the antifouling activity of *Taonia atomaria*, a Dictyotacean alga collected from the northern coasts of Tunisia. The antifouling potential of crude extract prepared with dichloromethane has been evaluated *in vitro* on the basis of its antibacterial and algicidal activities. Positive results on laboratory assays led to test this algal extract on field experiments. Two experiments were performed. The first one was the "phytagel method" [1] and the second consisted in the incorporation of crude extract into marine varnish and coat it on steel plates. All experiments were performed in triplicates and positive and negative controls were considered. After 48 hours of immersion a bacterial inhibition was observed on steel plates coated with extract. However, this inhibition was no more obtained after an immersion of a week. Biofilm composition (bacteria and microalgae) was analyzed at 48h and one week. The field experiments were maintained for 28 days and macrofouling evolution was observed on a weekly interval.
Obtained results are encouraging since they confirm a positive inhibition of biofilm in its first stage forming. This study consolidates the possibility of use of algal natural substances to prevent marine fouling. Work is in progress to reinforce and develop these results.

[1] R.C. Pereira, A.G. Carvalho, B.A. Gama, R. Coutinho,. *Braz. J. Biol*. **2002**, 62, 311-320.

PT S11-6

Evaluation of bioactive properties of *Cystoseira foeniculacea L.* (Grev. Emend. Sauvageau) and *Halocnemum strobilaceum* (Pall.) Bieb 1819 extracts from Trapani saltworks (NW Sicily): antioxidant and antimicrofouling.

Vincenzo Alessandro LAUDICELLA[1], Rozenn TREPOS[2], Concetta Maria MESSINA[3], Andrea SANTULLI[1,3], Claire HELLIO[2].

[1]Consorzio Universitario della Provincia di Trapani, Istituto di Biologia marina, Via G. Barlotta 4, 91100 Trapani, Italy.
[2]Plateforme de Bioprospection BIODIMAR, laboratoire LEMAR, Université de Bretagne Occidentale, 29200 Brest, France.
[3]University of Palermo, Department of Earth and Marine Science DiSTeM, Marine Biochemistry and Ecotoxicology Laboratory, Via G. Barlotta 4, 91100Trapani, Italy.

concetta.messina@unipa.it and claire.hellio@univ-brest.fr

Nowadays the scientific research is witnessing a "throwback" in the natural product discovery, in order to highlight new molecules with bioactive properties and in the meantime being “green” and environmentally friendly. Thus, in this study we present the preliminary results on the evaluation of the bioactive properties of two aqueous extracts obtained from organisms developing in harsh and extreme condition as the ones faced in solar saltworks: a brown seaweed, *Cystoseira foeniculacea* (CYS) and an halophyte, *Halocnemum strobilaceum* (HAL). In order to characterize these two extracts we have evaluated their total polyphenol content, antioxidant activity and their antimicrobial and anti-microfouling properties.
The two extracts are characterized by a rich polyphenol content due to the extreme conditions faced in their natural environment (5.93 ± 0.45 mg GAE g^{-1} DW). The elevate polyphenol content grants to both extracts relevant antioxidant properties (EC_{50}DPPH between 1.9 – 7.6 mg ml^{-1}; EC_{50}REDPOW between 2.5 – 4.7 mg ml^{-1}).
The extracts also exhibited interesting antimicrobial and antimicrofouling properties, being able to inhibit the settling of fouling bacteria as *V. natriegens*, *V. proteolyticus*, *P. iirgensii*, *R. litoralis* and *H. aquamarina.* The MIC concentrations were comparable to the ones shown from commercial antifouling products as Sea Nine 211.
Further investigations are still on going in order to evaluate the antimicrobial properties against pathogenic bacteria strains and to characterize the chemical composition of these extracts. These results, although preliminary, give an idea of the wide range of applications in which the two extracts might be employed.

PT S11-7

Exploiting the chemodiversity of tropical microalgae for the discovery of natural antifoulants through the BIOPAINTROP project

Damien REVEILLON[1,*], Ahlem OTHMANI[1], Jean TURQUET[2], Alina TUNIN-LEY[2], Jean-François BRIAND[1], Gérald CULIOLI[1]

[1]MAPIEM EA 4323, Université de Toulon, 83957 La Garde Cedex, France
[2]Hydrô Réunion, 97490 Sainte Clotilde, La Réunion, France

** damien.reveillon@univ-tln.fr*

The BIOPAINTROP project aims to develop antifouling coatings based on molecules isolated from tropical marine resources (Reunion Island, Indian Ocean). In such rich and diversified ecosystems, marine microalgae have been proved to biosynthesize a wide range of bioactive molecules. Thus, these organisms which could be biotechnologically produced constitute a promising source of natural antifoulants.
A collection of 50 tropical microalgae, half of them isolated from natural tropical biofilms, belonging to 6 taxonomic groups was screened for their antifouling properties.
For each strain, algal cultures were lyophilized and the resulting biomass (500 mg/strain) was extracted by maceration in methanol (MeOH)/dichloromethane (1/1, v:v). The corresponding extracts were then fractionated by reversed-phase (C_{18}) solid phase extraction (SPE) in four fractions eluted with (i) water, (ii) water/MeOH (1/1, v:v), (iii) MeOH and then (iv) dichloromethane, respectively. The fractions obtained in sufficient amounts were assayed for their anti-adhesion properties and toxicity against three biofilm-forming marine bacterial strains isolated from the Bay of Toulon.
Fractions eluted with MeOH showed the highest anti-adhesion activity (*i.e.* 93% of all active fractions) and 17 microalgal fractions had EC_{50} values between 1 and 50 $\mu g.mL^{-1}$ against two or all the bacterial strains tested. Even though dinoflagellates fractions were the most active, they also showed an important toxicity (*i.e.* $IC_{50} < 50\ \mu g.mL^{-1}$) and may be not suitable as a source of environmentally friendly antifouling compounds.
Fractions from two microalgal strains, one diatom and one cyanobacteria, were then selected for further studies to confirm their promising antifouling potential.

Figure 1: PLS-DA score plot comparing the MeOH fractions of all the microalgal strains of the collection

Furthermore, the chemodiversity of the complete collection of tropical microalgae was evaluated through the untargeted metabolomic analysis of their MeOH fractions by Liquid-Chromatography-Mass Spectrometry (LC-MS). The results showed that clustering was mainly based on taxonomic groups; dinoflagellates fractions being the most scattered.

PT S11-8

Antifoulin potentials of marine macroalgae extracts from coast of La Paz bay, Mexico

Ilse SÁNCHEZ-LOZANO[1], Claudia J. HERNÁNDEZ-GUERRERO*[,1], Mauricio MUÑOZ-OCHOA[1], Bárbara ZONZÁLEZ-ACOSTA[1], Sergio MARTÍNEZ-DÍAZ and Claire HELLIO[2]

[1] Instituto Politécnico Nacional, Centro Interdisciplinario de Ciencias Marinas, La Paz, B.C.S. México.
[2] Universite de Bretagne Occidentale, Brest France.

**cguerrer@ipn.mx*

It is recognised that seaweeds are important sources of natural products, and some of this compounds have an important role in the defence against epibiosis[1]. Therefore several researches studying the potential of marine algae extracts help solving a serious problem such as biofouling and the severe consequences of the use of highly polluting agents. The goal of this work is to evaluated methanol and dichloromethane extracts of seaweeds *Codium fragile, Ulva lactuca, Sargassum horridum, Gracilaria vermiculophylla y Laurencia gardneri* from La Paz Bay, Mexico. The seaweeds extracts were tested in laboratory assays to assess whether or not these inhibit the growth of marine bacteria involved in the formation biofilms[2], inhibition of phenoloxidase activity[3] (at the concentrations of 0.1, 1, 10, 100 y 1000 µg mL^{-1}) and a toxicity assay on brine shrimp nauplii. The results (Table 1) in the antibacterial activity showed that dichloromethane extract of *L. gardneri* was active in all the bacteria strains tested (MIC ≤1 mg mL^{-1}). In the inhibition of enzyme activity, newly dichloromethane extract of *L. gardneri* and ethanol extract of *S. horridum* were the most active. The latter achieved 100% inhibition at a concentration of 100 µg mL^{-1}. The extracts were not toxic at the concentrations tested. These results indicated the presence of active substances in *L. gardneri and S. horridum* that could be used as no toxic antifouling agents.

Table 1: Antifouling activity of seaweeds extracts.

SEAWEEDS	FRACTIONS	INHIBITION OF PHENOLOXIDASE ACTIVITY		ANTIBACTERIAL ACTIVITY (MIC µg mL^{-1})		
		10 µg mL^{-1}	100 µg mL^{-1}	***Bacillus subtilis***	***Bacillus pumillus***	***Micrococcus sp.***
L. gardneri	EtOH	+	++	-	1	0.01
	CH_2Cl_2	+++	+++	1	1	0.01
S. horridum	EtOH	+++	+++	-	10	10
	CH_2Cl_2	+	+	-	-	-
C. fragile	EtOH	+	+	-	-	0.01
	CH_2Cl_2	+	+	-	-	0.01
U. lactuca	EtOH	++	++	-	-	50
	CH_2Cl_2	+	+	-	-	0.01
G. vermiculophyla	EtOH	+	+	-	-	10
	CH_2Cl_2	+	+	-	-	0.01

(- no inhibition, + 1-30% inhibition, ++31-59% inhibition, +++ for more than 60% inhibition).

[1] B. da Gama, E. Plouguerné, R.C. Pereira, In: J.P. Jacquot, P. Gadal, N. Bourgougnon (Ed.), *Advances in Botanical Research, Elsevier*. **2014**. 71, 413–440.
[2] C. Hellio, R. Trepos, R.N. Aguila-Ramírez, C.J. Hernández-Guerrero, In: D.B. Stengal, S. Connan (eds), *Natural Products from Marine Algae: Methods and Protocols*, Methods in Molecular Biology. **2015**. 27, 421-435
[3] C. Hellio, N. Bourgougnon, Y. Le Gal, *Biofouling: The Journal of Bioadhesion and Biofilm Research*. **2000.** 16(2-4), 235-244.

PT S11-9

Bridging the gaps over a sea of biofouling – SP Technical Research Institute of Sweden aims to facilitate the antifouling innovation process for research groups

Mattias BERGLIN[1], Johan SVENSON[1,*], Emiliano PINORI[1]

[1]Department of Chemistry, Materials and Surfaces SP Technical Research Institute of Sweden, Box 857, SE-501 15 Borås, Sweden

** Johan.svenson@sp.se*

SP Technical Research Institute of Sweden is a leading international research institute. Our goal is to narrow the gap between innovation and commercial products and we strive to effectively resolve the challenges posed to our partners, and collaborators. To answer to the needs of the expanding global marine activities, SP devotes substantial resources to this prioritized area and we are particularly active within the field of antifouling.
SP addresses the fouling challenges encountered by sectors such as marine transport, aquaculture and also the rapidly expanding field of ocean energy. To be able to successfully address and assist the development of new, environmentally friendly, antifouling strategies SP offers the following services and support:

* Formulation optimization of active paint ingredients
* Dispersion of active paint ingredients in paint
* Formulation of ad-hoc paint
* Cytotoxicity bioassays
* Antifouling efficacy assays (Algae, bacteria, barnacles)
* Raft field testing of antifouling efficacy of materials, paints and coatings in several location reflecting different climates and environments
* Standardized release rate analysis from paint to sea water according to ISO 15181-1
* Regulatory advice for the registration of new antifouling products
* Contact with paint producers

In addition to the above mentioned services SP, also actively participate in the generation of grant proposals within the marine realm and has experience from leading large multidisciplinary international antifouling projects together with both academia and industry.
SP is willing to discuss problems and potential solutions with anyone that is faced with challenges related to marine fouling and the development of novel antifouling strategies.

PT S11-10

Synthesis of α,α-disubstituted amino acid isocyanide derivatives and antifouling activity: structure–activity relationship studies

Shuhei TAKASHIMA[1], Yasuyuki NOGATA[2], Erina YOSHIMURA[3], Kazuhiro CHIBA[1], and Yoshikazu KITANO*,[1]

[1]Laboratory of Bio-organic Chemistry, Tokyo University of Agriculture and Technology ,3-5-8 Saiwai-cho, Fuchu-shi, Tokyo 183-8509, Japan
[2]2Environmental Science Research Laboratory, Central Research Institute of Electric Power Industry, 1646 Abiko, Abiko-shi, Chiba 270-1194, Japan
[3] CERES, Inc., 1-4-5 midori, Abiko-shi, Chiba 270-1153, Japan

** kitayo@cc.tuat.ac.jp*

Benthic organisms such as barnacles, mussels, and hydroids often cause severe damage to hulls of ships, cooling systems of power stations, and fishing nets. Organotin compounds, such as tributyltin, were widely used in the 1960s to inhibit their adherence. Later, organotin compounds were found to be persistent and toxic to many marine organisms. Tin-based paints were officially banned by the International Maritime Organization in September 2008. Marine coatings based on copper, zinc, and various booster biocides have been widely used as alternative antifouling (AF) paints. However, these chemicals have a negative impact on the aquatic environment. Therefore, environmentally friendly, less toxic AF compounds need to be developed urgently. To develop promising AF compounds, detailed structure–activity relationship studies of natural AF-active compounds were performed, resulting in various artificial AF active isocyano compounds.[1]–[4] Recently, we focused on isocyanides derived from amino acids because they would eventually be biodegraded to the original nontoxic amino acids over the years. All the synthesized amino acid isocyanides showed antibarnacle activity against the cypris larvae of the barnacle *Balanus amphitrite*. Moreover, almost all the synthesized compounds showed significant toxicity at high concentrations. However, all the synthesized amino acid isocyanides were enantiomeric mixtures. Therefore, the structure of amino acid isocyanide derivatives was modified by introducing the same side chain at the α-position because α,α-disubstituted amino acid isocyanides were achiral. Herein, we report the AF activity of the newly synthesized amino acid isocyanides.

Isocyanoacetic acid benzyl ester (glycine isocyanide) was used as the scaffold of α,α-disubstituted amino acid isocyanide derivatives. Glycine isocyanide was prepared from glycine benzyl ester by the formylation of the amino group of glycine followed by the dehydration of the resulting formamide. α,α-Disubstituted amino acid isocyanides were synthesized from glycine isocyanide by the nucleophilic substitution of the α-position with alkyl halides or Michael addition with acrylic esters. The AF activity and toxicity of the synthesized disubstituted amino acid isocyanides were evaluated against the cypris larvae of the barnacle *B. amphitrite*. All the synthesized disubstituted amino acid-isocyanide derivatives showed AF activity. Moreover, a low mortality rate was observed at a high concentration in all the cases.

[1] Y. Kitano, T. Ito, T. Suzuki, Y. Nogata, K. Shinshima, E. Yoshimura, K. Chiba, M. Tada, I. Sakaguchi, *Perkin Trans. 1*, **2002**, *38*, 2251–2255.
[2] Y. Kitano, A. Yokoyama, Y. Nogata, K. Shinshima, E. Yoshimura, K. Chiba, M. Tada, I. Sakaguchi, *Biofouling,* **2003**, *20*, 187–192.
[3] Y. Kitano, Y. Nogata, K. Shinshima, E. Yoshimura, K. Chiba, M. Tada, I. Sakaguchi, *Biofouling,* **2004**, *20*, 93–100.
[4] Y. Kitano, C. Akima, E. Yoshimura and Y. Nogata, *Biofouling,* **2011**, *27*, 201–205.

PT S11-11

Seaweed mediated synthesis of Ag/Ti, Ag/Zn and Ti/Zn nanoparticles: potent antifouling property

V. SRI RAMKUMAR[1*], S. PRAKASH[2], R. RAMASUBBURAYAN[3], E. KANNAPIRAN[4], R. BABU RAJENDRAN[1]

[1]Department of Environmental Biotechnology, School of Environmental Sciences, Bharathidasan University, Tiruchirappalli – 620024, Tamil Nadu, India.
[2]Research Institute, SRM University, Kattankulathur – 603203, Tamil Nadu, India.
[3]Centre for Marine Science and Technology, Manonmaniam Sundaranar University, Rajakkamangalam – 629502, Tamil Nadu, India.
[4]Department of Zoology, Directorate of Distance Education, Alagappa University, Karaikudi – 630003, Tamil Nadu, India.

** avksri@gmail.com*

Biofouling is the major economic concern in marine installations. This is controlled by using biocides that shows detrimental effects on non targeted organisms. The present study is designed to synthesize seaweed mediated nanoparticles and explore its antifouling properties with minimal effects on unintentional organisms. Ag/Ti, Ag/Zn and Ti/Zn nanoparticles (NPs) are synthesized using the seaweed *Turbinaria conoides* collected from Gulf of Mannar, Southeast coast of India. Results of FT-IR spectrum showed occurrence of diverse functional groups in the seaweed extract, which could account for the reduction of metal ions to metallic NPs. Synthesized bimetal NPs were characterized by UV-Vis spectrophotometer, XRD, HRTEM, EDX and SAED pattern. HRTEM images showed attractive shapes and size ranging 10–60 nm. Crystalline nature of the NPs was evidenced by SAED pattern with bright circular spots corresponding to (111), (200), (220) and (311) Bragg’s reflection planes. The size of the NPs were further determined by DLS analysis. Stability of NPs were analyzed uisng zeta potential analyis and found to be stable at 22.5 (Ag/Ti), 26 (Ag/Zn) and 28 mV (Ti/Zn). Screening results inferred that, synthesized NPs exhibited wide spectral antagonistic activity (13–21 mm) on marine biofilm bacterial strains with least MIC and MBC values. CLSM images evidenced good antibiofilm activity by the NPs. It also showed promising antimicroalgal activity with MIC range of 5–35 µg/mL. Anticrustacean assay using *Artemia salina* larvae recorded LC_{50} value of 45 (Ag/Ti), 54.4 (Ag/Zn) and 60 µg/mL (Ti/Zn). Mollusc foot adherence assay using limpet *Patella vulgata* showed 6% fouling upon treatment with NPs and 90% regaining after transfer to fresh seawater. Furthermore, lower EC_{50} and higher LC_{50} values, therapeutic ratio (LC_{50}/EC_{50}) of >9 recorded by NPs against mussel *Perna indica* indicated its non-toxic nature and environmental compatibility with the antifouling coatings.

Keywords: Seaweed; *Turbinaria conoides*; Nanomaterials; Antifouling activity.

PT S11-12

Tropical microalgae isolated on Reunion island (France, Indian Ocean) as sources of antifouling molecules: the BIOPAINTROP project

Alexis BAZIRE[3], Yves BLACHE[2], Laurent BLÉRIOT[5], Christine BRESSY[2], Jean-François BRIAND[2], Dalyal COPIN[3], Gérald CULIOLI[2], Maxime DELBURY[6], Laurent DUFOSSÉ[4], Fabienne FAY[3], Isabelle GRONDIN[4], Isabelle LINOSSIER[3], Ludovic MANGRIE[5], Karine REHEL[3], Pierre SAULEAU[3], Thierry TAYE[6], Alina TUNIN-LEY[1], Jean TURQUET[1,*], Claudia ZEA OBANDO[3] and Mayalen ZUBIA[1]

[1] HYDRÔ Réunion, Sainte-Clotilde, Île de La Réunion, France.
[2] MAPIEM, Université de Toulon, France.
[3] LBCM, Université de Bretagne Sud, Lorient, France.
[4] LCSNSA, Université de La Réunion, Indian ocean, France.
[5] BIOALGOSTRAL, Sainte-Clotilde, Île de La Réunion, France.
[6] NAUTIX, Guidel, Bretagne, France.

* *jean.turquet@hydroreunion.re*

Biofoulings are associated to colonization of artificial submerged structures by aquatic organisms. This process induces adverse effects such as loss of hydrodynamism, weight increase of equipments… Numerous toxic compounds (copper, arsenic) have been used during decades to avoid biofouling of ships, until organostatic substances were developed. According to their toxicity for marine environment and fauna, due to their non-specificity and non-biodegradability, EU has banned them since 2008. For this reason, a new strategy, focusing on environmental friendly molecules is requested aiming to provide coatings that release progressively active natural compounds, non-toxic for environment. In tropical marine environment, deterrent molecules are recognized as one of the most efficient way for protection against predators or competition with other surfaces organisms (e.g corals, microalgae). Such active compounds are considered quite « infinite » (20,000 have been described to date), so of them for their antifouling activity. As a significant component of marine organisms, microalgae are a promising source of active natural substances, with biotechnological potential value. Growing microalgae is a worldwide project for various purposes actually *e.g*. biofuel. BIOPAINTROP project aims to develop antifouling coatings with active biomolecules originating tropical marine resources (microalgae) from Reunion Island. 2 main objectives have been designated: *(i)* identification of active molecules from tropical microalgae and *(ii)* incorporation of these compounds in adequate coatings to confirm the efficiency of these products in both temperate and tropical marine environment. To reach the targeted results, a pluridisciplinary group has been set up with 6 French teams with complementary expertises: *(i)* HYDRÔ based on Reunion island and specialized in tropical marine microalgae, *(ii)* 3 University laboratories: LCSNSA (Reunion) specialized in natural products valorisation, LBCM (Bretagne), specialized in marine biotechnologies; MAPIEM (Toulon) specialized in polymer materials engineering and marine biocompounds, *(iii)* Private partners: NAUTIX producing environmental friendly paints, expert in processing ecological and antifouling coatings; BIOALGOSTRAL a start-up from Reunion specialized in production/valorisation of microalgae biomass.

Acknowledgments*: BIOPAINTROP project funded by the French National Research Agency (ANR) – 2012/2017.*

PT S12-1

Synthesis and antifouling properties of non-metal acrylic boron polymers for marine antifouling application

Yakun LI[1], Suwen LI[1], Rongrong CHEN*,[1], Jun WANG[1], Lianhe LIU[1,2] and Kazunobu TAKAHASHI[1]

[1] Harbin Engineering University, Harbin, China.
[2] Qingdao Advanced Marine Material Technology Co., Ltd, Qingdao, China.

** Chenrongrong95@163.com.*

Marine antifouling coatings with environmental friendly resin matrix would reduce the hazard and ecological risk to the marine environment, as the polymer play an important contribution to the antifouling performance. Poly tributyltin methacrylate resin are gradually replaced by metal (copper and zinc) acrylic and other self-polishing resins since its forbiddance in 2008 because of high toxicity. However, the copper and other metal ions released from metal acrylic and other self-polishing resins are also toxic to marine environment [1, 2].
In this study, the non-metal acrylic boron polymers (ABP) were synthesized by acrylic acid polymer and pyridine-triphenylborane_(PTPB). In order to inspect the antifouling and eco-friendly properties of the developed acrylic boron polymers, the self-peeling rate measurement, algae settlement and algae growth rate assays were carried out. After immersed in seawater, the hydrolysis of the acrylic boron polymers could lead to a gradual self-peeling of the acrylic boron polymer surfaces, which was controlled by the content of the hydrolyzable boric group. As a result, the fouling organisms attached to the surfaces were peeled off. The diatom *Nitzschia closterium* was employed as model fouling to study its settlement and growth rate. The results showed that little or no algae cells attached on the surfaces of the acrylic boron polymers with higher content of hydrolyzable boric group, and the growth rate of algae solution containing blank substrates is almost the same as the one containing acrylic boron polymer. This study provides new insights into the development of the acrylic boron polymer with preferable algae resistance properties and environmental friendliness.

Acknowledgements: This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.

[1] M. Lejars, A. Margaillan, C. Bressy, *Chem. Rev.* **2012**, 112, 4347-4390.
[2] Y. Erik, K. Jenny, E. Britta, *Sci. Total Environ.* **2010**, 408, 2459-2466

PT S12-2

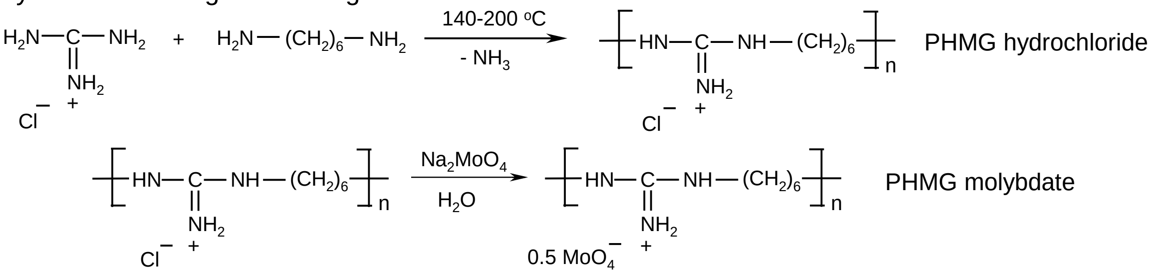
New antifouling coating containing polymeric biocide polyhexamethylene guanidine molybdate

Alexander PROTASOV[1], Jean-Francois BARDEAU[2], Irina MOROZOVSKAYA[1], Galina GURYANOVA[1], Larisa METELYTSIA[2], Larisa KALASHNIKOVA[3], Iryna KOPERNYK[3], Ludmila KIPNIS[1], Oksana TARASYUK[3], Olena MOSHYNETS[4], Sergiy ROGALSKY*[,3]

[1]Institute of Hydrobiology of NAS of Ukraine, Kyiv, Ukraine
[2]Institut des Molécules et Matériaux du Mans, Université du Maine, Le Mans, France
[3]Institute of Bioorganic Chemistry and Petrochemistry of NAS of Ukraine, Kyiv, Ukraine
[4]Institute of Molecular Biology and Genetics of NAS of Ukraine, Kyiv, Ukraine

** sergey.rogalsky@gmail.com*

New promising antifouling agent polyhexamethylene guanidine (PHMG) molybdate has been synthesized by anion metathesis between polymeric biocide PHMG hydrochloride and sodium molybdate according to following scheme:



The obtained cationic polymer has limited water solubility of 0.15 g/l. The ecotoxicity of PHMG molybdate was evaluated on *Daphnia magna* and *Danio rerio* (zebrafish) freshwater model organisms. The values of LD_{50} were found to be 0.7 mg/l for *D. magna* and 16 mg/l for *D. rerio* which indicates slight toxicity of PHMG molybdate. It should be noted that the known disinfectant PHMG hydrochloride, which is precursor for PHMG molybdate, showed similar acute toxicity (LD_{50} of 1.3 mg/l for *D. magna* and 11 mg/l for *D. rerio*). In order to study antifouling properties of PHMG molybdate it was dispersed in the industrial ship paint (XC-413, Ukraine) as solid pigment in the content of 5 wt%. The paint XC-413 is designed for the protection of underwater metallic constructions against corrosion and consists of the pigments suspension in the solution of vinyl chloride copolymers and coal varnish with addition of gelled organic dispersion of polyvinyl chloride in the mixture with bentonite clay. The painted steel panels were kept in the water of Kaniv reservoir (Dnipro River) for 228 days for the evaluation of the dynamics of fouling biomass.

Figure 1. Painted steel bars after 228 days exposure in Dnipro River: control coating (left) and coating containing 5 wt % of PHMG molybdate (right).

After 129 days exposure, Bryozoa dominated in biofouling of tested substrates forming 86% (649 g/m^2) of total biomass on control panel surfaces. Considerably lower Bryozoa fouling biomass (15 g/m^2) was detected for coatings containing PHMG molybdate. The Dreissenidae mollusks were found to form 88% (2182 g/m^2) of the fouling biomass on the control panel surfaces after 228 days exposure, whereas coatings containing PHMG molybdate showed much less biomass value of 23.6 g/m^2 (Figure 1).

PT S12-3

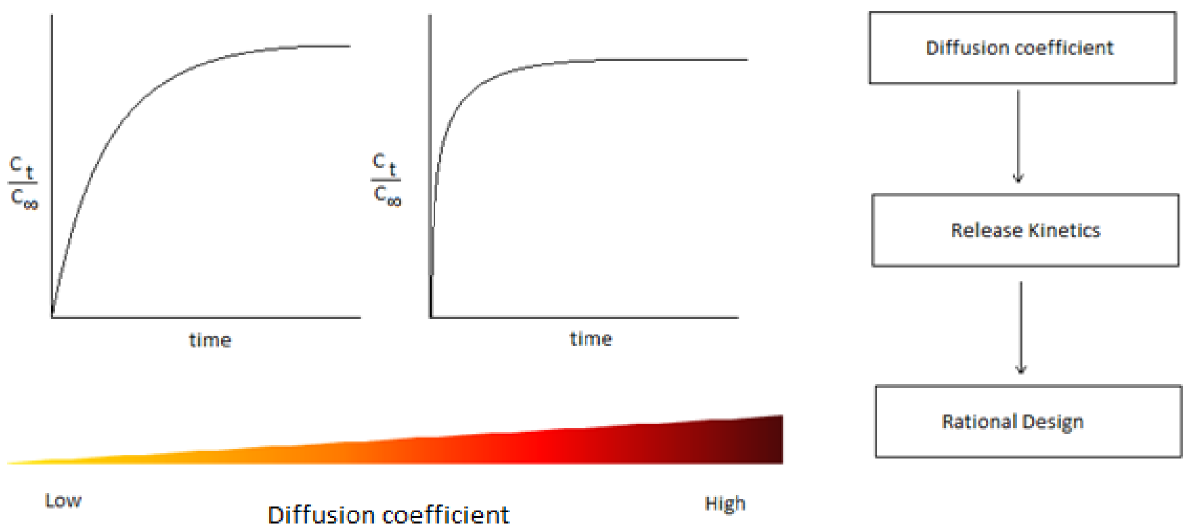
Diffusion of biocides in polymeric matricies: a tool for rational coating design

Alexander PAPIEZ[1] and Justin PERRY[2*]

[1]Department of Applied Sciences, Northumbria University, Newcastle Upon Tyne, United Kingdom, NE1 8STEmail: alexander.papiez@northumbria.ac.uk
[2]Department of Applied Sciences, Northumbria University, Newcastle Upon Tyne, United Kingdom, NE1 8ST

** justin.perry@northumbria.ac.uk*

The post Tributyltin (TBT) area has reignited the search for environmentally benign anti-fouling solutions. In order to achieve long-term hull protection coatings must exhibit a sustained minimum level of biocide release under normal conditions. Often this problem is addressed through the optimization of matrix polymer properties coupled with observation of the biocide release performance of the resulting coating.
In order to develop tools to aid in the rational development of anti-fouling products we have investigated the physical chemistry of biocide release. Our interest has focused on the mobility of biocides in a polymer matrix described by the diffusion coefficient derived from Fick's second law. Flame photometry, LC-MS and NMR spectroscopy allow accurate study of both metal ions ubiquitous in sea water and biocidal analytes. By fitting experimental data to the relevant solutions of Fick's law, diffusion coefficients may be estimated and used to describe the mobility of biocidal species.
By applying this methodology to a range of biocide/matrix systems, our understanding of the fundamental mechanisms of biocide release will be advanced; this will be a great asset in the quest for improved anti-fouling technologies.



PT S12-4

Grafting antifoulant groups into silicone based polyurethane：combination of antifouling and fouling release properties

Qingyi XIE, Chunfeng MA, Guangzhao ZHANG*

Faculty of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, P. R. China

* *msgzzhang@scut.edu.cn*

Silicone has been widely applied to prepare fouling release coatings due to its low surface energy and low elastic modulus. However, it has poor mechanical performance and limited efficacy against slime, especially in static conditions. We have synthesized polyurethane with polydimethylsiloxane (PDMS) soft segment and antifoulant (N-(2,4,6-trichlorophenyl) maleimide) pedant groups via a thiol-ene click reaction and a condensation reaction. Our study shows that the polymer coating has low surface energy (~25 mJ/m^2) and a stably high water contact angle (~100 °). When the antifoulant content is higher than 14 wt% in bulk, sufficient antifoulant can migrate onto the coating surface. Biological tests demonstrate that such polymer surface can effectively inhibit the adherence colonization of microorganisms such as bacteria, diatom and barnacle cyprids. After immersion in marine for 110 days, the polymer exhibits excellent anti-biofouling performance endowed by the combination of antifouling and fouling release abilities.

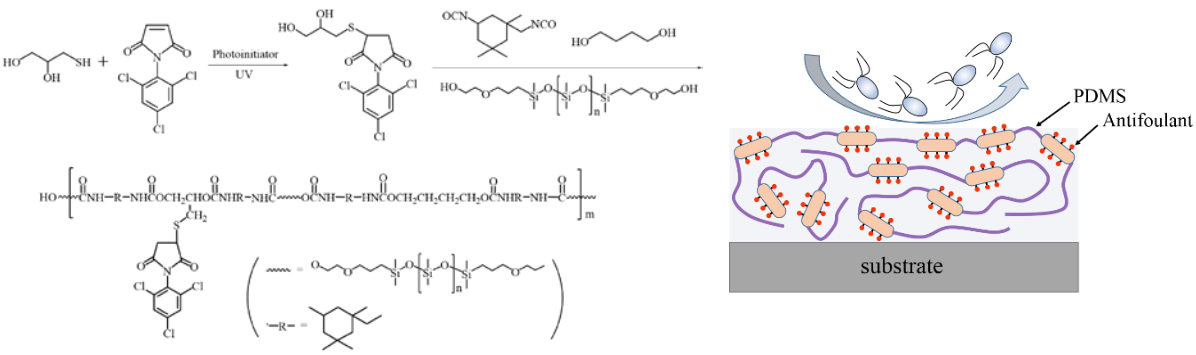


Fig. 1: Synthesis route and antifouling mechanism of PDMS based polyurethane with chemically attached antifoulants

[1] Lejars, M.; Margaillan, A.; Bressy, C. *Chem. Rev*. **2012**, *112*, 4347-4390.
[2] Ma, J. L.; Ma, C. F.; Yang, Y.; Xu, W. T.; Zhang, G. Z. *Ind. Eng. Chem. Res*. **2014**, *53*, 12753-12759.
[3] Xie, Q. Y.; Ma, C. F.; Liu, C.; Ma, J. L.; Zhang, G. Z. *ACS Appl. Mater. Interfaces* **2015**, *7* (38), 21030-21037.

PT S12-5

Contrasting biofouling in steam condenser: MATChING Approach

Rob ONDERWATER [1], G. WEGRIA[1], Sophie PEETERBROECK[1] Mireille POELMAN[1], and Danila CUMBO* [2]

[1] Materia Nova ASBL, Av Copernic 1, 7000 Mons Belgium.
[2] Enel Engineering and Research, Pisa, Italy.

**danila.cumbo@enel.com*

The 33% of the heat transfer losses in a CuNi condenser can be attributed to water-side deposits and biofouling. Trying to mitigate this phenomenon is not an easy task for Power Plant owners in today's restrictive and regulated discharge environment that limits the common practices of adding chemicals to cooling water systems to control fouling, deposits, and corrosion. To contrast biofouling formation, six different technology approaches will be developed and investigated in the frame a collaborative Project which has recently been selected for funding by the European Commision under the H2020 funding program. The acronym of the project is MATChING which stands for "Materials and Technologies for performance improvement of Cooling Systems in Power Plants". These six approaches include the use of 1) enzyme-based anti-fouling coatings; 2)coatings with ultra-smooth surfaces allowing fouling –release; 3) Coatings with embedded nano-paticles (like oxides of zinc, magnesium, copper or titanium) with antibacterial properties; 4)optimization of existing commercial coatings (like those based on silicon rubber or poliethilen glycol) through reduction of their thickness; 5) coatings with surface functionalization through the addition of antibatteric peptoids and finally 6) the use of tailored alloys with biocide properties (introduction of alloying elements to stainless steel). All these technologies will be first produced, evaluated and characterized in the laboratories of project partners with deep expertise in material science (DTI, MATERIA NOVA, IONICS, AIMEN). A selection of these materials and coatings will be then tested in a facility belonging to EDF (PERICLES) and the most promising solutions will be demonstrated in a pilot condenser that will be produced by INTEGASA and will be installed in one of the Endesa Power Plant for long test run.
The use of coatings to contrast the biofouling is only one of the technological solutions that the project envisages to reach its goal that is the reduction of cooling water demand in the energy sector. Other solutions comprise: the use of membrane based technologies for the recovery and reuse of municipal, process and blow down waters in power stations; the use of advanced materials and coatings to promote drop-wise condensation in steam condenser; the development of advanced hybrid cooling towers for geothermal high temperature power plants, and hybrid cooled binary cycles for low temperature geothermal fields, combining dry/wet cooling, and closed loop groundwater cooling. The partnership is composed of 4 Utilities (ENEL, EGP, ENDESA, EDF), 5 Technology Providers (SPIG, INTEGASA, AQUASTILL; PATHEMA, IONICS), 6 Research institute (VITO, LABORELEC, CNR ITM, DTI, AIMEN, MATERIANOVA) and 1 Service provider (DNV GL).

PT S13-1

Self-structuring surfaces with polydimethylsiloxane-thiole-acrylate coatings

A. BRINKMANN*[,1], V. STENZEL[1], S. BUCHBACH[1], B. DAEHNE[2], W. BREMSER[3]

[1] Fraunhofer Institute for Manufacturing Technology and Advanced Materials, Bremen, Germany.
[2] LimnoMar, Laboratory for Aquatic and Marine Research, Norderney, Germany
[3]University of Paderborn, Paderborn, Germany

* *andreas.brinkmann@ifam.fraunhofer.de*

Hydrophobic and hydrophilic surfaces are able to protect objects from biofouling depending on material compositions and the existing fouling organisms. Amphiphilic surfaces with hydrophobic and hydrophilic local areas, called “domains” [1], are well known and could be used as fouling release systems. The presented new domain structured coating material is based on thiole-acrylate resins in combination with polydimethylsiloxane-copolymers. A special characteristic of this material is a hybrid curing reaction. The curing can be initiated by UV radiation or with a catalyst. Depending on the curing conditions different forms of domains in the nano or micro meter scale could be observed *fig.1*. Samples with different domain size, domain surface concentrations and domain geometry could be manufactured. Appropriate samples were tested on Norderney in the North Sea and on different kinds of ships. After 5 months exposure some of the samples show a high potential for an application as an fouling release system *fig.2*.

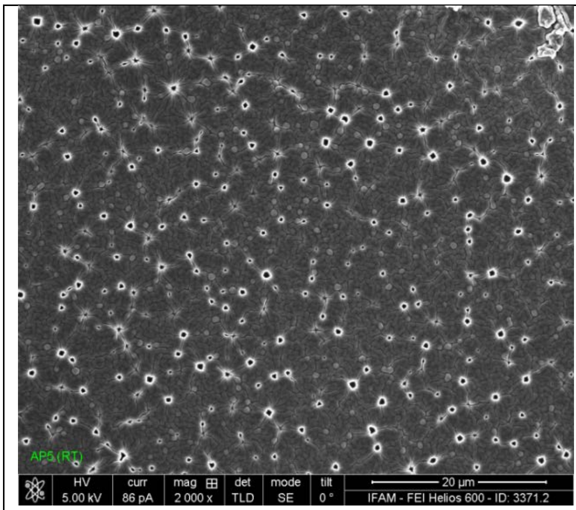


Fig. 1: SEM picture of a self-structured coating surface

Fig. 2 : Sample after 5 month North Sea exposing

Acknowledgements: The work presented in this study has been funded by the German Federal Ministry for Economic Affairs and Energy, R&D Project FoulProtect (Grant Agreement No. 03SX370)

[1] Claudia M. Grozea and Gilbert C. Walker, Approaches in designing non-toxic polymer surfaces to deter marine biofouling, The Royal Society of Chemistry Soft Matter, **2009**, 5, 4088–4100

PT S13-2

A new sensitive self-polishing coating

Clément DEZANET*[,1,2], Christine BRESSY[1], Anne-Cécile LASNE[2], Christian FAVENNEC[2], and Yves BLACHE[1]

[1] *MAPIEM, Toulon, France.*
[2] *DCNS, Lorient, France.*

* *Clement.dezanet@univ-tln.fr*

All seawater submerged surfaces are quickly colonized by a marine biofilm and subsequently, by vegetal and animal species (Fig. 1).

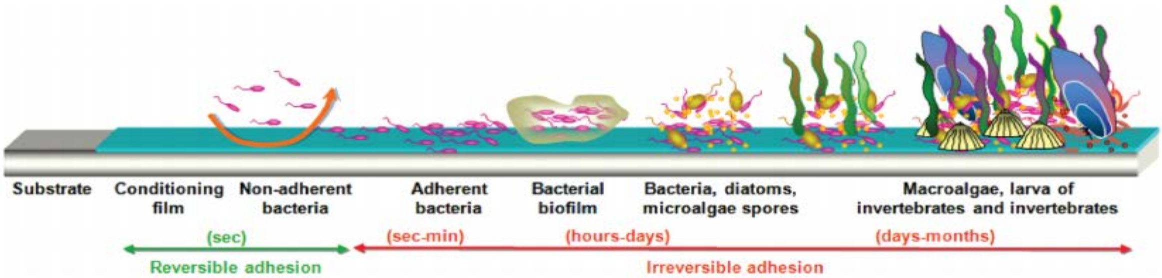


Fig 1: Time line evolution of marine biofouling [1]

A few seconds after immersion, macromolecules (proteins, etc.) adhere to the surface to form the conditioning film. Within hours, bacteria settle and after days, larvae and algae colonize the conditioned surface. This undesirable effect of colonization creates a lot of problems, especially in the marine industry. The biofouling increases the frictional resistance on the ship hulls due to an increase of the roughness, resulting in an increase of fuel consumption [2]. Many solutions have been developed to inhibit the settlement of animal and vegetal organisms. Fouling Release Coatings (FRCs) are known to decrease the adhesion strength of some marine macroorganisms on surfaces due to their low surface energy and low elastic modulus [1] but are efficient only at high speed (> 5 knots). On the other hand, Self-Polishing Copolymer (SPC) coatings are efficient under static condition. The antifouling efficacy of SPC coatings relies on both the release of synthetic biocides into the marine environment and the controlled erosion of the surface [3]. As the biocidal legislation is more and more restrictive, it's necessary to develop new alternatives of coatings. In our laboratory, Andjouh et al.[4] have recently developed bio-inspired polymers based on bromotyramine derivatives. In addition, Nguema et al.[5] have developed new electroactive polymers expected to reduce the biofilm colonization. In association with DCNS, we currently develop a new self-polishing coating sensitive to molecules secreted by marine bacterial biofilms, the erosion being therefore initiated by specific extracellular polymeric substance. This new coating should be efficient under static conditions, no released of biocides and a long life efficiency (as SPC and FRCs), so it's very interesting for the naval industry and unmoving structures (hydroelectric plant, oil platform, etc.).

[1] M. Lejars, A. Margaillan, C. Bressy, *Chem. Rev.*, **2012**; 112, 4347−4390.
[2] M. P. Schultz, J. A. Bendick, E. R. Holm, W. M. Hertel, *Biofouling*. **2011**, 27, 87-98.
[3] D. M. Yebra, S. Kiil, K. Dam-Johansen, C. Weinell, *Prog. Org. Coat.*, **2005**, 53, 256–275.
[4] S. Andjouh, Y. Blache, *Bioorg. Med. Chem. Lett.*, **2015**, 25, 5762–5766.
[5] R. W. Nguema Edzang, M. Lejars, H. Brisset, J.-M. Raimundo, C. Bressy, *RSC Adv*. **2015**, 5, 77019-77026.

PT S13-3

Tethered liquid surfaces as high performance anti-fouling coatings

Deniz DOGAN[1], Wolfgang BREMSER[1], Bernd DAEHNE[2]

[1] *University of Paderborn (Coatings, Materials & Polymers), Paderborn, Germany*
[2] LimnoMar*, Norderney, Germany*

** ddogan@mail.uni-paderborn.de*

Micro phase-separated siloxane-polyurethane coating systems have a great deal of potential for anti-fouling applications. The advantages of this system in the ship industry compared to polydimethylsiloxane (PDMS) elastomer coatings is, that the surface is mechanically stable [1].
We present an epoxy-amine coating, which is modified with PDMS, can be cured at low temperatures and is easily applicable on ships. The corresponding coating surface exhibits a highly ordered self-patterning of PDMS rich domains, covering the epoxy-Amin matrix (fig. 1). Phase separated PDMS is immobilized through a covalent bond to the epoxy matrix. Our current studies focus on correlation between domain size distribution and the fouling rate of the coating. Furthermore we have tested the influence of hydrophilic polyamines and other hydrophilic additives on the fouling rate. For example the Epoxy-PDMS-system, which was cured with hydrophobic polyamine and addition of hydrophilic polyisocyanate showed an excellent fouling rate of 89 after 57 days North-Sea-exposure (fig. 2).

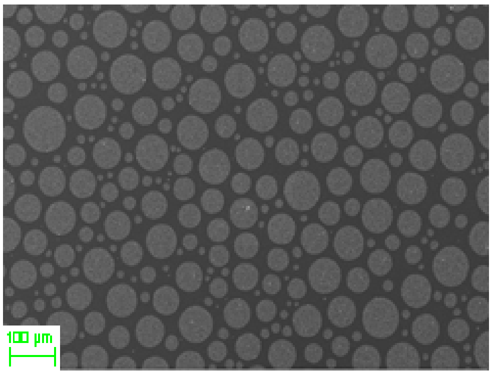


Fig. 3: highly ordered surface pattern SEM-picture of surface structuring epoxy-PDMS-coating

Fig. 4: sample with excellent anti-fouling property

Acknowledgements: The work presented in this study has been funded by the German Federal Ministry for Economic Affairs and Energy, R&D Project FoulProtect (Grant Agreement No. 03SX370)

[1] P. Majumdar, D. C. Webster, *Polymer* **2007**, *48*, 7499–7509.

PT S13-4

Development of novel test platform for textured antifouling surfaces

Sandra KWIATKOWSKA[1,3], Rohit MISHRA[2], Alan BARRETT[1,3], Ivan MAGUIRE[1,3], Jens DUCRÉE[2] and Fiona REGAN[1,3*]

[1]*School of Chemical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland*
[2]*School of Physical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland*
[3]*DCU Water Institute*

**Fiona.Regan@dcu.ie*

Over the recent past, research into novel antifouling methods for marine surfaces has gained significant attention. Minimisation of microbial colonisation requires combined methodology of material design, including tailored surface chemistry, regulation of bulk material characteristics, and thoroughly considered surface topography. A number of studies have been demonstrated already, that microbial adhesion can be influenced by topographic cues [1][2]. Therefore evaluation of an efficient anti-fouling surface requires extensive analysis of biological responses to surface topography.A physical biomimetic approach provides promising, non-toxic methods, mainly through imitating topographical patterns of a marine organism's surface [3].

In the current work, different micro-structured PDMS (poly dimethylsiloxane elastomer) surfaces structured with for example densely and loosely packed circles or triangles, were tested to evaluate settlement time and adhesion strength of the diatom *Psammodictyon*. These textured surfaces were compared with the flat surface as control. Photolithography was used as a technique of fabricating surface textures. Pattern - etched silicon wafers were employed as a negative template for production of textured PDMS elastomer. Small areas of textured and flat PDMS were then exposed to cultured diatoms. After a required incubation time, diatoms were examined by SEM. It was assumed, that a pitch smaller than the average diatom body (10 x 5 x 10 µm) between micro structures aids antifouling, and any wider pitch between features aids biofouling. SEM results confirmed both assumptions. Overall, flat surfaces and surfaces containing loosely packed features, showed no difference, both were covered by large numbers of single cells, double, triple and clusters of diatoms, while surfaces containing densely packed circles demonstrated significant reduction of cells, showing only a few single cells. Furthermore, cells found on surfaces containing triangles, were found to rest against feature walls. Obtained results display that increased micro structure pitch allows diatoms to respond to micro texture by using them as anchoring spots. This search provides important information for future development of materials using surface textures as a mean of antifouling technology.

Included in this experiment is the study of centrifugal hydrodynamic forces, to determine the forces needed to detach diatoms from textured surfaces integrated into centrifugal microfluidic chambers. A major advantage of this method is that the quantification of forces is done in a hydrodynamic environment where the only forces exerted on a particle on a surface are the buoyancy force and the centrifugal force that are easily quantifiable depending on the density of the fluid and the particle and the distance of the particle from the axis of rotation. The method involves microfluidic assembly, diatom introduction, incubation, and testing will be described.

[1] J Xu, W Zhao, S Peng, Z Zeng, X Zhang, X Wu, Q Xue. *Appl Surf Sci* **2014**;311, 703-8.
[2] L Xu, Siedlecki CA. *Acta Biomaterialia* **2012**, 8(1), 72-81.
[3] M. Salta *Journal of Ocean Technology* **2014**;9(4), 29-35.

PT S13-5

Liquid adhesion test bench with reclining ramp

Valentin GATE*,[1], Carole LAVAULT*,[2], Sylvain FOURNIER[2], Daniel TUROVER[1], Yves LAVAULT[2]

[1] SILSEF, Archamps, France / [2] AII SAS, Cran-Gevrier, France.

** valentin.gate@silsef.com; carole.lavault@aii-industrie.com*

Developed in partnership with SILSEF and AII Companies R&D teams, the described test bench offers a solution for dynamic liquid adhesion measurements on a wide range of materials. SILSEF develops and produce functional micro and nano-patterns on the industrial scale on a wide range of materials (glass, metal, polymers, semiconductors, thin films, …) in order to add value on surfaces by the modification of their natural properties (for example hydrophilic or hydrophobic properties). To testify the performances of its process, specifically developed for each customer, a tool giving additional measurable and reproducible evidences with a dynamic drop angle measurement was mandatory. AII brought its skills to develop a test bench composed of a motorized and instrumented reclining ramp with twelve optical sensor channels and a dedicated software to adjust test settings and collect results.

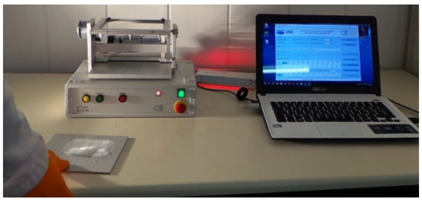


Fig.1: Sample positioning on the removable upper plate

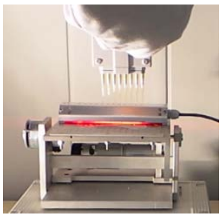


Fig.2: Calibrated liquid volume deposit through optical sensors holder

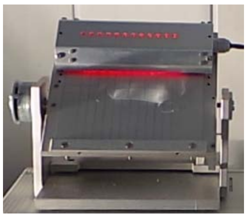


Fig.3: Ramp is tilted up to 90° with a constant speed (15s to 140s)

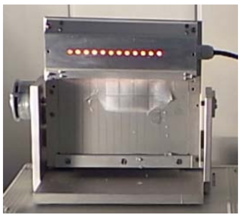
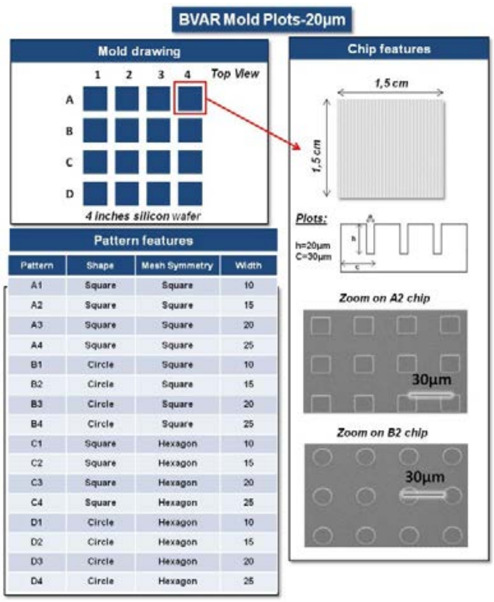


Fig.4: Critical tilt angle detection with an adjustable threshold



Pattern	Shape	Mesh Symmetry	Width
A1	Square	Square	10
A2	Square	Square	15
A3	Square	Square	20
A4	Square	Square	25
B1	Circle	Square	10
B2	Circle	Square	15
B3	Circle	Square	20
B4	Circle	Square	25
C1	Square	Hexagon	10
C2	Square	Hexagon	15
C3	Square	Hexagon	20
C4	Square	Hexagon	25
D1	Circle	Hexagon	10
D2	Circle	Hexagon	15
D3	Circle	Hexagon	20
D4	Circle	Hexagon	25

Fig.5: Micro-pattern shape description

Collected curves represent reflected light intensity of optical sensors in function of reclining ramp angle (0.5° angular resolution) with 4 different patterns.
A suddenly increase or decrease of light intensity is observed at the critical tilt angle, above which the drop rolls off. This tool can be provided with a range of accessories (video camera, cover, and gutter).

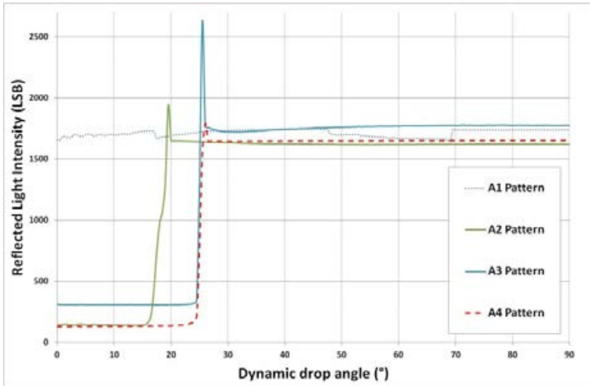


Fig.6: Repellency curve saved on 4 different patterns

This bench provides additional information to contact angle measurement with a dynamic drop angle measurement for a wide range of research and industrial applications, especially in biofilm formation detection with the ability to evaluate residual liquid during and after drop rolls off. Further developments can be considered according to specific needs.

[1] Callies M, Quéré D, “On water repellency” in the Royal Society of Chemistry, **2005**.

PT S13-6

Phase separation mechanisms in polydimethylsiloxane copolymer containing UV-curable polyurethane coatings

Simon RUTHMANN*,[1], Wolfgang BREMSER[1]

[1] *University of Paderborn (CMP: Coatings, Materials & Polymers), Paderborn, Germany*

* *ruthmann@mail.uni-paderborn.de*

Polydimethylsiloxane (PDMS) based environmentally friendly antifouling coatings have been subject of recent studies since the use of heavy metals will be further restricted in the future [1]. If PDMS is not covalently bound to the coating-matrix, it will be released after undefined duration. We investigate PDMS block copolymers which are more durable towards mechanical shear stress. The degree of bonding has been extensively studied by means of ^{1}H-NMR-spektroscopy. We have observed a diversity in formed surface structures by increasing the amount of bound PDMS. These polydimethylsiloxane domains differ in size, distribution and topography. For the preparation of coatings with the best possible antifouling performance it is important to understand the underlying phase separation mechanisms that lead to one surface structure or the other. Thus control over certain polydimethylsiloxane domains is gained. Therefore we developed a UV-curable polyurethane coating that was cross-linked after different amounts of time. Our studies lead to the conclusion that various system parameters are capable of accelerating or slowing the separation down. The corresponding samples will be field tested soon. Imaging methods like confocal laser scanning microscopy have been applied to study the surfaces. A characteristic surface structure and its topography are shown in figure 1.

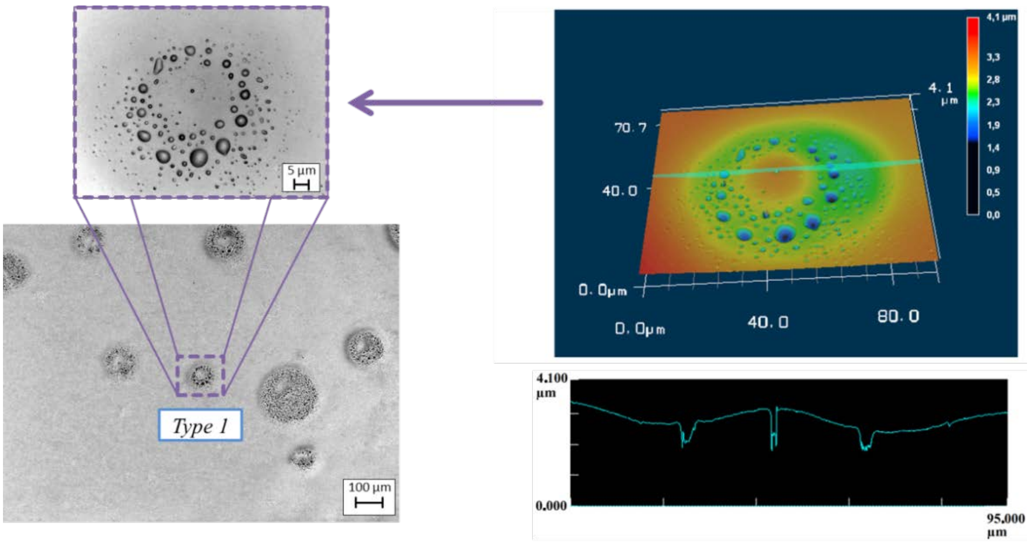


Fig. 1: Characteristic surface structure of PDMS block copolymers after short phase separation.

Acknowledgements: The work presented in this study has been funded by the German Federal Ministry for Economic Affairs and Energy, R&D Project FoulProtect (Grant Agreement No. 03SX370)

[1] B.T. Watermann et al. *Chemosphere* **2005**, 60, 1530–1541.

PT S13-7

The use of the sea anemone *Aiptasiomorpha minuta* as a possible agent to control biofouling on oysters during culture

Cyril Glenn Perez SATUITO*[1], Satoshi OHASHI[2], and Hitoshi KITAMURA[1]

[1] *Grad. School of Fish. Sci. and Environ. Stud., Nagasaki University, Nagasaki, Japan.*
[2] *South Pref, Area, Fisheries Extension Station, Nagasaki Prefectural Office, Shimabara, Japan.*

* *satuito@nagasaki-u.ac.jp*

Oyster cultures in Isahaya Bay, Nagasaki, Japan, usually become heavily fouled with barnacles and tunicates during the summer season. These biofoulers compete with oysters for food and space, and often cause mass oyster mortality that consequently lead to poor harvest. In this paper, the authors investigated the sea anemone *Aiptasiomorpha minuta* on the following: 1) its growth and survival at different temperatures and salinities in order to determine optimum conditions for mass culture, and 2) its mitigating effect on barnacle fouling when artificially attached on cultured oysters. The purpose was to evaluate the possibility of using *A. minuta* as an agent to control biofouling on oysters during aquaculture.
A. minuta were cultured at different temperatures (20, 25, 28 and 30°C) and salinities (8, 11, 15, 20 and 33) for 10 days on a diet of *Artemia salina* nauplii (200 nauplii/*A. minuta*) and their population growth and survival were observed daily. *A. minuta* were also attached to several PVC plates (10 x 10 cm) and were cultured in 500L tanks for 14 days. During culture, *A. minuta* were given *A. salina* nauplii daily after the seawater was renewed. Mass cultured *A. minuta* were then removed from the PVC plates and were let to attach to spat collectors, which were scallop shells with oyster spats (average shell length = 25 mm) attached to them. These spats were then employed in a field experiment conducted in Isahaya Bay, Japan, from August to October, 2013. Spat collectors without *A. minuta* attached to them were used as the control. The abundance of barnacles on the spat collectors and the growth and survival of cultured oysters were measured in the middle and end of experiments.
In the laboratory, *A. minuta* showed the highest increase in number when cultured at 28°C but did not grow at 20°C. High population growths were also observed when *A. minuta* were cultured at salinities of 15 and 20 but high mortalities were observed at salinities of 11 and below. When cultured in a 500 L tank, *A. minuta* increased in number by almost 4 times, and the yield after 14 days was about 4,900 individuals. The field experiment revealed that after suspending the spat collectors in the sea for 2 months, those with *A. minuta* attached to them had less barnacle fouling than their control counterpart. A clear inverse correlation was observed between *A. minuta* and barnacles, with more *A. minuta* attached to the spat collectors resulting in less barnacles. After 2 months of culture in the sea, no difference in survival rate was observed between the group with *A. minuta* attached to them and the control. However, shell growth of oysters in the group with *A. minuta* was significantly higher than the control. Thus, the sea anemone *A. minuta* can be used as a possible agent for mitigating barnacle biofouling on oysters during aquaculture.

Joint workshop

JW-1

Mussel adhesion test as a tool to assess new antifouling coating

Jérôme DELROISSE [1*], Mélanie DEMEULDRE [1], Elise HENNEBERT [1], Juan Antonio ALDUNCIN [2], Sylvain DESPREZ [3], Marios MICHAILIDIS [4], Rob ONDERWATER [3], Laura SANCHEZ [2], Dmitry SHCHUKIN [4], Patrick FLAMMANG [1]

[1] Biology of Marine Organisms and Biomimetics, University of Mons, Mons, Belgium.
[2] Biomaterials Unit, Cidetec, Donostia-San Sebastian, Spain.
[3] MateriaNova, Ghislenghien, Belgium.

[4] Stephenson Institute for Renewable Energy, University of Liverpool, Liverpool, United Kingdom.

** jerome.delroisse@umons.ac.be*

The BYEFOULING project focus on the design and the development of low toxic and environmentally friendly antifouling coatings for maritime applications. As a member of the BYEFOULING consortium, UMONS performs tests on new promising coatings developed by other consortium collaborators. Those tests involve some of the main macrofoulers of worldwide fouling communities, including the blue mussel *Mytilus edulis* (Mollusca, Bivalvia). Mussels produce a proteinaceous adhesive structure, the so-called byssus, for attachment to surfaces in the marine environment. This byssus consists of an array of adhesive plaques, each connected to a thread which is rooted to living tissue inside the animal. Here, we detail the methodological approach used in the attachment assays performed on adult mussels. After being placed in contact with the coatings of interest, byssal threads that anchor mussels to hard substrates are sectioned at their proximal end. Attachment force measurements of individual byssus thread are performed using an electronic dynamometer. Various information are collected including the number of adhesives plaques/byssus threads, the surface area of the adhesive plaques, the force needed to detach/break the plaque/thread and the mode of material failure (plaque detachment vs thread rupture). In order to correct for a size effect of individuals, scaled force measurement are reported. Adhesion strength is also expressed as tenacity (N m^{-2}) –i.e. ratio force/surface area. The mussel adhesion assay has been performed on different sets of coatings differing chemically (presence of biocide or surface functionalization) or physically (surface roughness). Attachment strength data are compared to controls and literature data.

Acknowledgements: This research is supported by the EU FP7 collaborative project “BYEFOULING - Low-toxic cost-efficient environment-friendly antifouling materials”, under Grant Agreement no. 612717.

JW-2

Evaluation of the influence of innovative antifouling solutions on the environmental impact of maritime transportation

Sophie DROPSIT[1*], Vasileios MARKAKIS[2], Aikaterini - Flora A. TROMPETA[2], Costas A. CHARITIDIS[2], Olivier TALON[1]

[1] Materia Nova, Mons, Belgium
[2] Research Unit of Advanced, Composite, Nano-Materials & Nanotechnology, School of Chemical Engineering, National Technical University of Athens, Zographos, Athens, Greece

** Sophie.dropsit@materianova.be*

Engineered structures such as ships are under constant attack from marine environment.
Engineered structures such as ships are under constant attack from marine environment. These structures need to be protected from the influence of saltwater, biological attack or temperature fluctuations [1]. A surface roughened by algae and barnacles may increase the ship's fuel consumption up to 40% [1] and consequently increase greenhouse gas emissions, as well as add strain on the structure and hinder manoeuvrability. Furthermore, marine organisms attached to a hull may be transported from sea to sea, invading the habitat of native species and change the biodiversity and ecology of sensitive marine areas.
In FP7 BYEFOULING project (www.sintef.no/Projectweb/BYEFOULING), antifouling coatings with enhanced performance are designed and developed. Our approach is to tackle the different stages of the biofouling process using innovative antifouling agents, covering surface-structured materials, protein adsorption inhibitors, quorum sensing inhibitors, natural biocides and microorganisms with antifouling properties. Encapsulation of the innovative compounds in smart nanostructured materials will be implemented to optimize coating performance and cost all along their life cycle.
LCA methodology is used to evaluate the environmental impact of the to-be-developed antifouling coatings and select the environmental friendlier. All production stages will be evaluated, taking into account processes, raw materials and energy consumptions. It is also crucial for the analysis to include the induced effects of the antifouling coatings on fuel consumption and direct air emissions. End-of-life strategies will be also included so as to decide the optimal waste management after usage period. Finally, LCA modelling will enable a comparison between the new antifouling coatings and the traditional ones, in order to promote the benefits in terms of environmental impact of maritime transportation.

Acknowledgements: This research is supported by the EU FP7 Programme/ THEME [OCEAN 2013.3] within the collaborative project "BYEFOULING - Low-toxic, cost-efficient, environment-friendly antifouling materials" (www.byefouling-eu.com) under Grant Agreement no. 612717.

[1] L.D. Chambers, K.R. Stokes F.C. Walsh and R.J.K. Wood, *Surf. Coating Tech.* **2006,** 201, 3642-3652.

JW-3

Picking the winners: choosing the most promising candidate coatings from a diverse selection

Andrew GUERIN*[1], Anthony CLARE[1]

[1] *Newcastle University, Newcastle upon Tyne, UK.*

* *andrew.guerin@newcastle.ac.uk*

One of the goals of the SEAFRONT project is to develop a small number of coatings with antifouling performance that equals or exceeds that of existing technologies. Antifouling performance of candidate coatings is therefore tested, in the laboratory and in the field, using standard assays, which can also be applied to existing commercial antifouling coatings. The main interest of individual coating producers may be to understand the relative performance of a range of coatings that they provide for testing, in order to help them fine-tune their coating formulations. In addition, large projects like SEAFRONT need to compare the performance of many different prototypes, tested weeks or months apart, so that the best technologies can be selected for further development and testing.
Testing using consistent assay methodologies is an important part of this process, as long as all coatings are amenable to the standard assays. The inherent variability resulting from the use of live organisms for testing also means that results cannot always be simply compared between assays conducted weeks apart. Inclusion of consistent reference surfaces can help. Further complications for decision-making arise when multiple assays (using different biofouling species) give opposing results.
This presentation will briefly explore these issues and discuss methods for selecting the best among varied coatings.

JW-4

Flow-based method for characterization of microfouling on marine surfaces

Gunhild HAGESKAL[1]*, Kjell D. JOSEFSEN[1], Martin AXELSSON[2] and Håvard SLETTA[1]

[1] *SINTEF Materials and Chemistry, Trondheim, Norway.*
[2] *JOTUN A/S, Sandefjord, Norway.*

* *gunhild.hageskal@sintef.no*

Introduction: IBIDI flow-system (Integrated BioDiagnostics, Germany) is a lab-scale system with defined flow conditions in a growth-chamber slide (µ-slide) designed for studies of biofilm formation. We have adapted and tested this system for studies of microfouling in seawater using so-called sticky-slides that can be attached to test surfaces (Fig. 1). Suitable flow parameters (flow-rate, share stress, growth area, medium, etc.) were established using standard µ-slides (plastic surface), that were monitored for real-time microfouling by EVOS FL Auto Imaging system (Life Technologies™).

Materials and Methods: Sticky-slides were attached to test surfaces treated with antifouling paint (SeaForce®) supplied by JOTUN. Seawater from the Trondheim fjord, Norway, was added a small amount of nutrients and inoculated into three parallel units. The degree of microfouling in the µ-slide was monitored daily under microscope until substantial microfouling was observed. This slide also functioned as a positive control. After one week, the degree of microbial colonization in the growth chambers was quantified by staining techniques (MTT-assay [1], Crystal violet assay [2]).

Results: Results from the CV assay are presented in Table 1. The degree of microfouling in the three parallel growth chambers was nearly similar, and significantly lower than in the control (µ-slide).

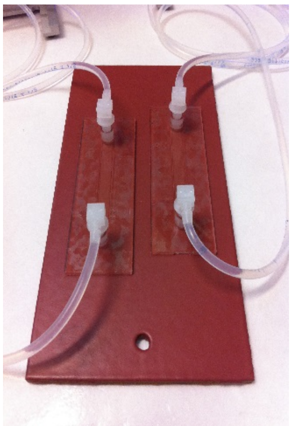


Fig. 1: Sticky-slides attached to test-surface.

Table 1. Microfouling quantified by crystal violet assay as absorbance at 540 nm after staining of three parallel seawater samples compared to one positive control after 1 week of flow.

Sample	Control (µ-slide)	sticky-slide 1	sticky-slide 2	sticky-slide 3
OD_{540}	1,85	0,423	0,441	0,441
Average ± st. deviation		0,44 ± 0,01 (2 %)		

Discussion: In natural water environments, attachment of microorganisms to surfaces often occurs under flow conditions. The method is thus an alternative to static microfouling analyses such as microtiter plate assays. The system mimics the first formation of microfouling under natural conditions, and the test organisms are a mixture of actual seawater organisms, as opposed to static systems where lab-strains often are used. The preliminary results indicates that this flow-based method is applicable for studies of the first layer of microfouling on marine surfaces. Further testing will be performed, including additional test-surfaces in the BYEFOULING project.

[1] S.K. Kairo, J. Bedwell, P.C. Tyler, A. Carter, M.J. Corbel. *Vaccine* **1999**, 17, 2423-2428.
[2] B. Pitts, M.A. Hamilton, N. Zelver, P.S. Stewart, *J. Microbiol. Met.* **2003**, 54, 269-276.

JW-5

Almost there! Or are we?

Dan ISAKSSON

I-Tech AB, Mölndal, Sweden.

dan.isaksson@i-tech.se

The experiences of going from academia to industry with Selektope will be briefly presented. A lot of the learnings during this process has been related to the somewhat naive approach that we had in the beginning of the development process. Understanding or at least be aware of the challenges in the industrial development is a key to reasonable expectations. This and how some of the pitfalls may be avoided by being part of larger research program such as Seafront will be discussed. The benefits of cooperating with the various partners within the program in order to try and understand the bigger picture such as challenges and time lines in various parts of the product development process will also be discussed. The presentation will sum up part of what I-Tech has contributed with and what we have learned from the Seafront program so far.

JW-6

Smallmatek – nanocontainers technology: a case study from academia to industry

Roberto MARTINS, Nuno NOGUEIRA, Frederico MAIA, Mário FERREIRA, Mikhail ZHELUDKEVICH and João TEDIM*

Smallmatek - Small Materials and Technologies, Lda, Rua Canhas, 3810-075 Aveiro, Portugal.

* *joao.tedim@smallmatek.pt*

In the frame of EU-FP7 project MUST (NMP3-LA-2008-214261), a research group from the University of Aveiro developed a set of nanostructured materials for controlled release of corrosion inhibitors for application in self-healing, protective coatings used in automotive, maritime and aeronautical industries. The promising lab tests obtained led to an increasing interest by different paint companies as well as end users. However, a gap between academia and industry existed: there was no intermediate agent in the value chain capable of scaling up and producing materials for testing, as well as a specialized team dedicated to market-driven product development. For that reason a group of researchers from the University of Aveiro founded, in 2010, a *start-up* company (Smallmatek Lda - SMT).
Nowadays, SMT employs around 10 people dedicated to the development and production of eco-friendly nano- and microcontainers able to store, transport and release, in a controlled way, different active compounds such as corrosion inhibitors, biocides, dyes, pH indicators, among others, which work as multifunctional additives to be incorporated in 'smart' functional coatings (Figure 1).
Smallmatek is involved in several R&D international projects, such as BYEFOULING (FP7/OCEAN/2013/612717), with the aim to develop new materials and products. Smallmatek is currently focused on the introduction of its own technology in the market after the current maturation phase together with some important players in the coatings sector.

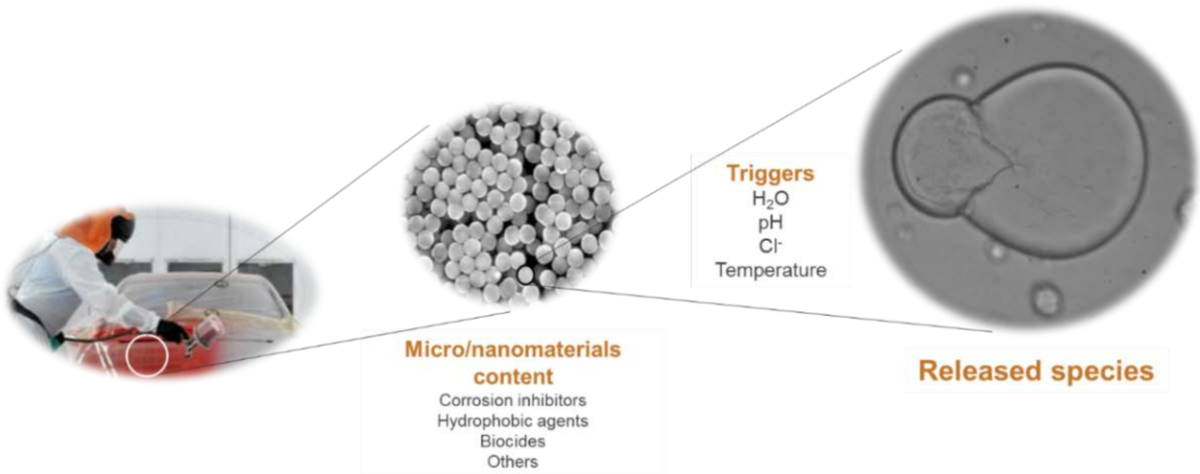


Fig. 1: Scheme of active compounds release from microcontainers when incorporated in a paint formulation.

JW-7

From discovery to market: the valley of death in anti-fouling research

Ana OTERO*

Departamento de Microbiología y Parasitología, Facultad de Biología, Edificio CIBUS; Universidade de Santiago de Compostela

** anamaria.otero@usc.es*

Ignited by governmental policies and increasing regulatory restrictions in the use of traditional anti-fouling compounds, the research effort in the area of novel anti-fouling strategies has greatly increased in the last decade. While 100-150 research papers were published per year in this area between 2000 and 2005, this number has increased to almost 800 publications on anti-fouling strategies in 2015. Regarding patents, the number has increased form 846 patents published in the period 2006-2010, to 1709 in the period 2011-2015. Despite all the efforts and advances, the research in this area still faces important problems. Regarding novel biocides or fouling-inhibitors of biological origin, important problems encountered at the basic research level are identifying sustainable biological sources and the use of reliable screening methodologies that will provide an adequate assessment of the activity in the more complex natural environment. Once an active compound is identified, the only way to ensure the survival through the long and often sterile processes of patenting and registering the new compound is the cooperation between research groups and the industrial sector in order to facilitate the pathway of the promising new technologies to the market.

JW-8

Performance of functionalized POSS derivatives applied to smart anti-fouling concepts

Monika PILZ*[1], Nicolas RIVAL[1], and Eirin LANGSETH[1], Tania P. TEIXEIRA[2], Séverine B. LARROZE[2], Rob C.A. ONDERWATER[3], Yehuda BENAYAHU[4]

[1]SINTEF Materials and Chemistry, Materials and Nanotechnology Department, Nano and Hybrid Materials Group, Oslo, Norway.
[2]AquaBioTech Group, Naggar Street, Mosta, Malta.
[3]MateriaNova, Ghislenghien-Mons, Belgium.
[4]Tel Aviv University, Department of Zoology, George S. Wise Faculty of Life Sciences, Tel Aviv, Israel.

** monika.pilz@sintef.no*

Several approaches with nanosized structures are under development and functionalized derivatives based on polyhedral oligomeric silsesquioxanes (POSS) are among the promising ones contributing to enhance anti-fouling performance. Those hyper-branched hybrid nanostructures ($[O_{3/2}Si(CH_2)_3NX_2]_{n,\ n=8,10,12}$ derive from a cost-efficient two-step production (www.funzionano.com), including a sol-gel process followed by functionalization. This synthesis route has the strategic advantage to yield in a variety of chemical surface functionalities appropriate to tune response efficiency to prevent micro- and macro-fouling (Fig. 1).

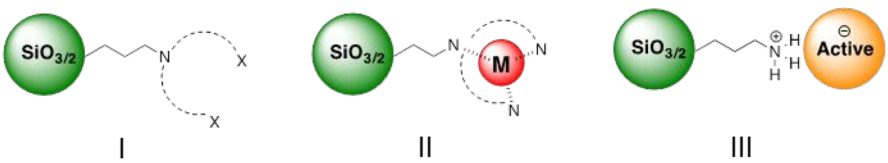


Fig. 1: Scheme of promising units for strategic anti-fouling concepts based on POSS nanostructure.

Different structural features of POSS derivatives (I, II, and III) as carriers for active species have been synthesized at SINTEF Materials and Chemistry and their anti-fouling activity screened by partners. Resistance to micro- and macro-fouling conditions as well as encouraging results from mesocosm and ecotoxicity studies will be reported. The release of active compounds from POSS complexes by environmental stimuli (e.g. artificial seawater) has been investigated in the laboratory.
Preliminary results from the first 6-months field exposure of modified self-polishing coatings in the Mediterrian Sea along the coast of Malta has been obtained and their resistance to bio-fouling in marine environment assessed.

Acknowledgements: This research is supported by the EU FP7 Programme / THEME [OCEAN 2013.3] within the collaborative project “BYEFOULING - Low-toxic cost-efficient environment-friendly antifouling materials” (www.byefouling-eu.com) under Grant Agreement no. 612717, coordinated by Christian SIMON, SINTEF Materials and Chemistry.

JW-9

Improved surface properties of antifouling coatings by incorporation of carbon nanotubes

Aikaterini-Flora TROMPETA, Ioannis KARTSONAKIS, Vasileios MARKAKIS, Elias KOUMOULOS, Costas CHARITIDIS*

Research Unit of Advanced, Composite, Nano-Materials & Nanotechnology, School of Chemical Engineering, National Technical University of Athens, Zographos, Athens, Greece

** charitidis@chemeng.ntua.gr*

Carbon nanotubes (CNTs) seem to be promising fillers in antifouling coatings [1-2]. The surface properties of the coatings can be modified on exposure to water with the addition of CNTs. The most profound effect recorded in literature, was the significant reduction of adhesion strength of adult barnacles growing on a silicone elastomer containing a small amount (0.05%) of multi-walled (MWCNTs) [3] and the improvement of the fouling-release properties of the coating [4]. PDMS filled with MWCNTs has been proved to be more hydrophobic, with an average contact angle of 95º [5-6]. For this reason, in BYEFOULING project, MWCNTS with different surface functionalisation have been synthesised and incorporated in a commercial antifouling paint, to improve its surface properties. Synthesis of MWCNTs has been accomplished using Thermal Chemical Vapour Deposition (T-CVD). The main advantage of CVD method for the growth of CNTs, is the large amount of material that is possible to be obtained, so this method is the first candidate for industrial applications. As grown, MWCNTs have highly hydrophobic surfaces, and are not dispersible in aqueous and organic solutions. Surface functionalization is required to make MWCNTs active. In order to increase the compatibility with the coating matrix, MWCNTs were functionalised and acyl-amino groups were grafted on their sidewalls, after their carboxylation. By this way, the dispersability of MWCNTs was enhanced and a uniform dispersion was obtained in the coatings matrix. For the addition of the functionalized MWCNTs in the commercial paint, a high shear mixer was employed, representing the industrial method for the production of paints. After the mixture, the coating was applied with a roller applicator on pre-coated PVC panels. Contact angle measurements were conducted in order to determine the hydrophobicity/hydrophilicity of the antifouling coatings containing different types of MWCNTs (pristine & functionalised with the different functional groups). The results showed that the antifouling paints with the acyl-amino functionalised MWCNTs, depicted higher contact angles, both before and after the exposure in artificial ocean water.

Acknowledgements: This research is supported by the EU FP7 Programme/ THEME [OCEAN 2013.3] within the collaborative project "BYEFOULING - Low-toxic, cost-efficient, environment-friendly antifouling materials" (www.byefouling-eu.com) under Grant Agreement no. 612717

[1] M.F.L. De Volder, S.H. Tawfick, R.H. Baughman and A.J. Hart, *Science*, **2013**, 339, 535-539.
[2] W. Turchyn, **2011**, Literature Seminar.
[3] A. Beigbeder, P. Degee, S.L. Conlan, R.J. Mutton, A.S. Clare, M.E. Pettitt, M.E. Callow, J.A. Callow and P. Dubois, *Biofouling*, **2008**, 24, 291-302.
[4] A. Beigbeder, R. Mincheva, M.E Pettitt, M.E Callow, J.A Callow, M. Claes, P. Dubois, *J. Nanosci. Nanotechnol.*, **2010**, 10, 2972-2978.
[5] C.M. Grozea and G.C. Walker, *Soft. Matter.,* **2009**, 5, 4088-4100.
[6] E.P. Koumoulos, A. Darivaki, and C.A. Charitidis, in 10th Pan-Hellenic Conference on Chemical Engineering, Patra, Greece, 2015.

JW-10

Exposure assessment of biocides and contaminants from antifouling paints and ballast water treatment installations

Bert van HATTUM*,[1], Jos VAN GILS[1], Arjen MARKUS[1] and Arthur BAART[1]

[1] *Deltares, Delft, Netherlands.*

* *bert.vanhattum@deltares.nl*

Antifouling compounds are applied in marine paints to prevent the growth of organisms on the hull of ships. This affects traveling speeds, fuel consumption, emissions of greenhouse gases, and spreading of unwanted species. Ballast water treatment installations are applied on ships to reduce the transport and spreading of invasive species via ballast water. Antifouling paints and ballast water treatment installations may be sources of direct inputs of contaminants into the marine environment. Against the background of the requirements of the EU legislation for biocidal products (BPD Directive 98/8/EC; BPR EU Regulation No. 528/2012), and the conventions on antifouling (2001) and ballastwater (2004) of the IMO (International Maritime Organization), there is need for reliable modeling and assessment tools for the prediction of exposure and risks of new antifoulants and pollutants from ballast water treatment systems. MAMPEC and MAMPEC-BW are exposure assessment models for antifouling compounds and ballast water. The models were developed by IVM (VU University Amsterdam) and Deltares with funding from industry (Antifouling Working Group of the European Paint Makers Association, CEPE) and others (EC-DG XI, IMO/GESAMP). In 1999 the first version of MAMPEC was released. The model has since been improved with regular updates. The upcoming release (version 3.1, 2016) is compatible with Windows 7-10, with menus and help in different languages (English, Japanese, Chinese, Spanish). It includes some important new features (extended emission scenarios, multiple run options, analysis of chemical fate processes, new export options). MAMPEC features an integrated 2D hydrodynamical and chemical fate model, based on the Delft3D-WAQ and Silthar model.

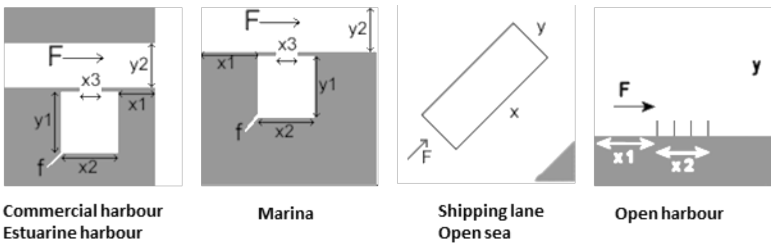


Fig. 1: Prototype environments in MAMPEC

The exposure assessment model is recognized and used by regulatory authorities and applicants in EU, USA and other OECD countries for antifouling substances and by the IMO and GESAMP for ballast water discharges. Sandardised emission and environmental scenarios for ballastwater were proposed in cooperation with the Technical University of Hamburg-Harburg for the German authorities (UBA). New applications of MAMPEC are expected for antifouling paints on marine constructions and holding nets applied in aquaculture. Examples and results of applications and validation exercises will be presented. The model, support and documentation are freely available at: https://www.deltares.nl/en/software/mampec/ [1].

[1] B. Van Hattum, J. Van Gils, H. Elzinga, A. Baart **2014**, MAMPEC 3.0 Handbook - Technical Documentation. Report nr. R-14/33. Institute for Environmental Studies, Vrije Universiteit, Amsterdam.

JW-11

The Antifouling Challenges for Marine Energy Developers

Cecilia ZAMBRANO*, [1], Ted ROSENDAHL[1], Arne QUAPPEN[1]

[1] *Minesto, Portaferry, United Kingdom.*

* *cecilia.zambrano@minesto.com.*

Economic growth, higher electricity prices, climate change and security of energy supply stress the global need for renewable energy. The oceans form one of the least explored, and at the same time, largest renewable energy source on earth. While most tidal stream developers focus on horizontal axis turbines, Minesto is developing a tidal energy power plant, called Deep Green, which converts the low-velocity ocean and tidal currents' kinetic energy to electricity. Deep Green consists of a kite, flying under water in figures of eight. Although this novel method of harnessing tidal energy is different in many ways from conventional turbine designs, Minesto, like most conventional turbine developers, has chosen composite materials for the device structure. For all tidal energy developers corrosion is a permanent threat that can be mitigated by using an effective composite coating. Skin friction affects the lift to drag ratio and thus efficiency of the device, therefore coatings must provide low skin friction and minimize fouling. While similar conditions apply for ship coatings, the operating conditions and consequences of coating failure are unique for tidal energy converters. The SEAFRONT project enable marine energy converter developers and coatings providers to understand the relevant processes to develop fouling control solutions.

Fig. 1: Minesto's Deep Green ¼ scale device.

Index

Last Name	First Name	Organization	Page
SAGHIR	Rehana	Lonza	
SAHA	Mahasweta	Geomar	13, 78
SAINTE-CATHERINE	Marie-Christine	DGA	
SAKHRI	Ahcène	Algerian navy	133
SALES	Muriel	DGA Techniques aéronautiques	
SALTA	Maria	University of Portsmouth	6
SALTERS	Bart	Philips	93, 115
SALVIN	Paule	Université des Antilles	136
SANCHEZ BADIA	Antoni	Pinturas Hempel SAU	
SANCHEZ LOZANO	Ilse	CICIMAR IPN	
SANTIAGO	Marta	PINTURAS HEMPEL SAU	
SANTOS	Olga	Alfa Laval	
SANTOS	Benjamin	CTC	
SATHE	Priyanka	Sultan Qaboos University	16, 113
SATUITO	Cyril Glenn	Nagasaki University	31, 183, 229
SCHULTZ	Michael	U.S. Naval Academy	117
SCHWANEMANN	Torsten	Umweltbundesamt Deutschland	
SCOFANO	Anna Maria	Petrobras	
SEEWALD	Oliver	University Paderborn	27
SEIM	Marit	Jotun A/S	
SETZER	Sascha	Federal Environment Agency Germany	
SHIBATA	Kiyoshi	Chiba Institute of Technology	123
SIMOES	Cristina	Biomimetx	
SIMON	Christian	SINTEF	
SO	Christopher	Naval Research Lab	55, 56, 57
SOARES REIS DE OLIVEIRA	Dinis	Chalmers University of Technology	
SOREAU	Sylvie	EDF R&D	
SPYRIDONAKOS	Spyridon	Vitex-Yannidis Bro SA	
STEINBERG	Peter	Sydney Institute of Marine Science	2
STEPHENS	Abraham	Florida Institute of Technology	54, 170
STORMS	Scott	Naval Surface Warfare Center - Philadelphia Division	18, 191
STUCHLIK	Adam	Jotun A/S	
STUEBING	Dorothea	Fraunhofer - IFAM	
STUHR	Susan	Ruhr-University Bochum	103