10 INTERNATIONAL CONGRESS ON MARINE CORROSION AND FOULING

University of Melbourne
Australia
8-12 February 1999

JOHN A. LEWIS

10th International Congress on Marine Corrosion and Fouling

incorporating

2nd U.S./Pacific Rim Workshop on Emerging Non-Metallic Materials for the Marine Environment

BOOK OF ABSTRACTS

The University of Melbourne
Melbourne, Australia
8 - 12 February 1999

Sponsors

Appreciation is extended to the following organisations that have provided financial support to the Congress. Their support has ensured the success of the conference.

Comité International Permanent pour la Recherche sur la Préservation des Matériaux en Milieu Marin (COIPM)

CSIRO Centre for Research on Introduced Marine Pests, Australia

U.S. Office of Naval Research International Field Office, Europe

U.S. Office of Naval Research International Field Office, Asia

Defence Science and Technology Organisation, Australia

The Gordon and Breach Publishing Group

Department of State Development, Victoria

Hempel's Marine Paints A/S, Denmark

Jotun Paints, Australia & Norway

International Paint, Australia

Radiometer Pacific, Australia

Kansai Paint Co., Japan

Environment Australia

Congress Convenor

John A. Lewis
DSTO Aeronautical & Maritime Research Laboratory
GPO Box 4331
Melbourne 3001, Australia

Telephone: +61 (0) 3 9626 8418 Facsimile: +61 (0) 3 9626 8341
E-mail: john.lewis@dsto.defence.gov.au

Scientific Committee

Dr Iwona Beech	*University of Portsmouth, UK*
Dr Robert F. Brady, Jr	*Naval Research Laboratory, US*
Dr Maureen E. Callow	*University of Birmingham, UK*
Prof. Stephen de Mora	*University of Quebec, Canada*
Dr Robert Fletcher	*University of Portsmouth, UK*
Dr Paul Gatenholm	*Chalmers University of Technology, Sweden*
Dr Chad L. Hewitt	*CRIMP (CSIRO), Australia*
Prof. E.B. Gareth Jones	*BIOTEC, Thailand*
Dr Michael J. Keough	*University of Melbourne, Australia*
Dr Kyu-Hwa Lee	*Institute of Machinery & Materials, Korea*
Prof. Giulio Relini	*Universita di Genova, Italy*
Dr Peter Steinberg	*University of New South Wales, Australia*
Dr Geoffrey Swain	*Florida Institute of Technology, US*
Prof. Tadashi Matsunaga	*Tokyo University of Agriculture & Technology*
Dr Richard Wetherbee	*University of Melbourne, Australia*

Conference Managers

Michael Sullivan & Fiona Campbell
Venue and Conference Management
The University of Melbourne
Parkville 3052, Australia

Telephone: +61 (0) 3 9344 4490 Facsimile: +61 (0) 3 9344 6122
E-mail: m.sullivan@pb.unimelb.edu.au

Effects of CCA (copper-chrome-arsenic) preservative treatment on the settlement of barnacles and serpulid worms on wood

Ruth M. Albuquerque[1], Craig J. Brown[2,3], Simon M. Cragg[2] & Rod A. Eaton[2]
[1]formerly Forest Products Research Centre, Buckinghamshire Chilterns University College, now HLS Ltd., Huntingdon
[2]Institute of Marine Sciences, University of Portsmouth ([3]now CEFAS, Burnham Laboratory)

Biodeterioration due to marine wood-borers renders the use of non-durable timber without protection uneconomic. Pressure treatment with copper-chromium-arsenic (CCA) provides protection. Though this broad-spectrum biocide resists leaching, some effects on non-target organisms are anticipated. The settlement of non-target species of fouling invertebrates on treated wood surfaces was studied to quantify effects on the organisms most exposed to leachate. Settlement of calcareous fouling organisms was affected in an unexpected fashion – greater numbers settled on treated wood surfaces than on untreated wood. This was particularly evident in serpulid worms and acorn barnacles. This phenomenon was noted at coastal sites in Greece, Portugal, France, the UK and Sweden. Differences in settlement rate occur even in newly exposed wood. Intensity of barnacle settlement also varies across annual growth rings.

A new non-toxic concept in marine fouling control

Kjell Alm and Stephan Gyllenhammar
Sealcoat Almyra SA, PO Box 70327 – 16601 Glyfada Athens, Greece

In controlling hard surfaces immersed in seawater from biofouling there are two principal ways doing this. First and most commonly used is to alter the surface in a chemical way. This means that a leakage of toxic substances to the marine environment will occur. Second, and not so common, is to alter the surface in a physical way which is non-toxic to the marine environment. The Sealcoat fibrelock method belongs to the second alternative. It means that a dry and clean surface is first coated with an epoxy glue. After that, tiny synthetic fibres of different lengths and densities are applied on the surface with a newly developed technique that orientates the fibres and gives a desired fibrelock density. This gives a dense fibrelock fur like a velvet-surface.

The Sealcoat fibre-flock surface gives a good protection against hard fouling organisms like barnacles, mussels and tubeworms. There can be slight attachment of soft fouling organisms like hydroids, tunicates and seaweed by idle lying vessels, but as they are often loosely attached they will be washed away when ships are in traffic. Another advantage of the Sealcoat fibrelock antifouling method is the long-lasting effect of several years that will be very economic favourable for the shipping industry.

Idiosyncracies of low surface energy (foul release) anti-foulings: drag, roughness and maintenance

Colin D Anderson[1], R Townsin[1] and Maxim Candries[2]
[1]International Paint, Stoneygate Lane, Felling, Gateshead, Tyne & Wear, England NE10 0JY
[2]Dept of Marine Technology, Newcastle University, England, NE1 7RU

The successful commercial introduction of non-toxic, low surface energy (foul release) anti-fouling hull coatings requires the discussion of practical and theoretical issues raised by the characteristics of these environmentally compliant coatings.

Foul release coatings have quite different dry and wet tactile friction. The conventional Hull Roughness Analyser is unable to operate on these surfaces without some lubrication of the skid, and added grip for the drive wheel. The paper discusses consequences for paint surface roughness measurement.

From exploratory flat plane tests in the towing tank at the University of Newcastle-upon-Tyne, UK, it appears that the conventional correlation between ship paint roughness, characterised by Rt(50), and added drag ΔCf, no longer applies. The paper indicates that the roughness added drag of foul release coatings is less than indicated by the conventional roughness measure, Rt(50). The practical consequences are discussed.

Foul Release coatings are at their most effective as anti-foulants when under hydrodynamic shear, and exceptionally so on high speed craft, but fouling can occur when a ship is laid up for any period. This fouling is usually washed off by the ship getting underway. However if the lay up is for an extended period then underwater cleaning may be required. Such cleaning must not damage the coated surface or it will lose its efficacy. The paper describes an investigation into the use of a new underwater cleaning vehicle designed to clean foul release coatings without damaging them.

Copper leach rate methods ISO/DIS 15181-1,2. Round robin test results.

Santiago Arias
Pinturas Hempel, S.A. P.O.Box 8 Polinyà (Spain)
Article written on behalf of ISO/TC35/SC9/WG27

Eight different laboratories have participated in a round robin test organised to validate the copper leach rate draft test methods ISO/DIS 15181-1,2 for antifouling paints. Four different paints have been tested, representing the most commercially significant antifouling coating technologies currently in use. No significant differences observed in the leach rate data could be attributed to the analytical methods used (FAA, GFAA, ICP) or due to paint application. Inter-laboratory differences in copper leach rate were particularly obvious for non organotin paints. Organotin copolymer based paints showed a lower degree of variation. As a result, an organotin based paint has been chosen as the appropriate reference paint for the ISO test procedure.

Spatial and temporal trends in environmental concentrations of tributyltin and heavy metals around a naval facility in Cockburn Sound, Western Australia

Irene J. Baran & John A. Lewis
DSTO Aeronautical & Maritime Research Laboratory, GPO Box 4331, Melbourne 3001, Australia

HMAS Stirling, the RAN fleet base in Western Australia, is located in a large semi-enclosed embayment to the south of Perth. Tributyltin (TBT) concentrations were first measured in both sediments and mussels collected in the vicinity of the naval base in 1989 and the first DSTO survey was undertaken in 1991. Since 1993, we have collected and determined TBT concentrations in mussel tissue from a number of sites in the region at 6 monthly intervals. The period of study has encompassed the introduction of RAN initiatives to reduce the input of TBT from Navy sources and State regulations banning the use TBT use on small craft throughout Western Australia. An observed reduction in TBT levels over time can be attributed to these initiatives. During 1998 a more intensive sampling program was undertaken in the direct vicinity of the harbour to assess the spatial spread of contamination. Results suggest that the bay on which the base is located, Careening Bay, has limited water exchange with waters of Cockburn Sound. This reduces the rate of dilution, diminution and degradation of TBT in the water mass and results in greater accumulation of TBT in tissues of mussels within the bay.

Environmental impacts of antifouling biocide usage in Australia

G.E. Batley
Centre for Advanced Analytical Chemistry, CSIRO Energy Technology, PMB 7, Bangor NSW 2234, Australia

The usage of tributyltin (TBT)-containing antifoulants was restricted to boats over 25 m in length, in most Australian states, from around 1988. Prior to that, significant impacts had been identified on shellfish cultivation, particularly affecting the oyster industry. TBT was shown to have a synergistic effect on copper uptake by oysters, and because copper was often used in formulations in combination with TBT, many cultivated oysters exceeded the health limits for copper. Since the banning of TBT, and despite the replacement of TBT with antifoulants based on copper in association with common pesticides, oysters are no longer affected and oyster copper levels are in compliance.

Foreshore areas in Sydney Harbour, for example, have shown increased biodiversity as a consequence of the banning of TBT on small craft, although large vessels continue to be a source of TBT in harbours. Because of its long half-life in sediments, TBT is still detectable in most estuarine sediments. Sediment quality guidelines for TBT have recently been developed for Australia and these will be described.

Suitable alternatives to TBT are being researched, but in the interim, combined copper/pesticide formulations continue to be widely used. No adverse environmental consequences have been reported. Recommended home-made paint formulations incorporating veterinary tetracycline, were shown to have poor antifouling properties and to be environmentally undesirable.

Environmental risk assessment of marine antifoulants

Daniel Baur, Andrew Jacobson, Vincent J. Kramer, and Chris Nichols
Rohm and Haas Company, Philadelphia, PA, USA

The Environmental risk of marine antifouling compounds is a function of the environmental concentration (exposure) and the toxicity of the compound (hazard). This risk can be quantified using a risk quotient. For the biocidal active in marine antifouling paints a quotient often used involves a comparison of the predicted environmental concentration (PEC) to the predicted no effect concentration (PNEC). The PNEC is obtained from the toxicity data of the antifouling agent, generally the lowest concentration a chronic effect is observed times an appropriate margin of safety. The PEC, which is generally obtained from modeling results, allows for a prospective determination of the environmental concentration. The PEC:PNEC quotient for antifouling actives has been obtained for the industry standard, Tributyltin (TBT), and an environmentally preferable alternative, Sea-Nine® 211 Biocide (2-n-octyl-4,5-dichloro-1-isothiazolin-3-one). The results have been obtained using a series of validated models (e.g., EXAMS and Luttik-Johnson) and under a wide range of geographical and environmental conditions. In all cases examined, the predicted environmental concentration of Sea-Nine was less than the PNEC (PEC/PNEC <1). However for TBT, the predicted environmental concentration was generally greater than the predicted no effect concentration. Thus, from an environmental risk perspective, Sea-Nine is an environmentally preferable alternative to TBT.

Secreted proteoglycans as natural antifouling agents in marine invertebrates

Charlie D. Bavington[1], Rebecca Lever[2], Michelle M. Grundy[1], Clive P. Page[2] and J. Douglas McKenzie[1]
[1]The Scottish Association for Marine Science, PO Box 3, Oban Argyll, PA34 4AD, UK.
[2]Department of Pharmacology, King's College, University of London, Manresa Road, London, SW3 6LX, UK.

Marine invertebrates have efficient antifouling mechanisms to prevent epibiont surface colonisation. These antifouling mechanisms are poorly understood but may include the maintenance of a 'non-stick' surface and secretion of anti-adhesive compounds.

Mucus secretions collected from the starfish *Marthasterias glacialis* contained 210 ± 78 μg ml^{-1} (mean ± SEM, n=5) of proteoglycans. Chromatographic studies indicated that the PG was sensitive to digestion by chondroitinase ABC but not heparinases suggesting that the glucosaminoglycans were of the chondroitin sulphate or dermatan sulphate type. Radiolabelling studies with $^{35}SO_4$ confirmed that the PG is sulphated.

Adhesion of ^{3}H-thymidine labelled *Pseudomonas fluorescens* to tissue culture plastic was inhibited in a dose-dependent manner by PG from *M. glacialis*. Bacterial adhesion was inhibited by 64 ± 9% in the presence of 34 μg ml^{-1} mucus proteoglycans. Commercially available heparin had no effect on adhesion and 100 μg ml^{-1} dermatan sulphate increased adhesion by 58 ± 7%. Adhesion of radiolabelled human leukocytes to endothelial cells was inhibited by 68 ± 7% in the presence of 34 μg ml^{-1} mucus PG.

These results demonstrate that the PG present in mucus secretions of *M. glacialis* are potent antiadhesives which reduce both bacteria and cellular adhesion. Mucus is likely to provide a major contribution to antifouling by some invertebrates.

The effect of marine *Pseudomonas* NCIMB 2021 biofilm on AISI 316 stainless steel

I.B. Beech[1], V. Zinkevich[1], L. Hanjangsit[1], J. Smith[1], R. Gubner[1] and R. Avci[2].
[1]School of Pharmacy and Biomedical Sciences, University of Portsmouth, St. Michael's Building, White Swan Road, Portsmouth PO1 2DT, UK
[2]Department of Physics, Montana State University, Bozeman, Montana 59717, USA

Polished and as received AISI 316 stainless steel coupons were exposed for 30 days to a pure culture of marine *Pseudomonas* NCIMB 2021 in a continuous flow bioreactor. The development of biofilms and corrosion damage of steel were investigated using techniques of electron (SEM) and atomic force microscopy (AFM). Passive layers on polished and as-received coupons were characterised to evaluate the effect of biofilms on the composition of such layers. The latter was performed employing X-ray photoelectron spectroscopy (XPS) analysis.

SEM and AFM observations revealed that surfaces of polished steel were colonised to a greater extent than as-received specimens. Micropitting of steel occurred underneath the biofilm, regardless of surface finish. The thickness and composition of the passive layer differed markedly between as-received and polished surfaces. In the presence of a biofilm the layers became iron-depleted and enriched in carbon.

This communication further discusses the significance of the biofilm-influenced changes in the passive layer composition on the corrosion resistance of AISI 316 stainless steel in marine environments.

Influence of divalent cations and pH on adsorption of a bacterial adhesin to solid surface.

N. Bhosle[1], P.A. Suci[2], A.M. Baty[2], R.M. Weiner[3] and G.G. Geesey[2].
[1]Marine Corrosion and Material Research Division, National Institute of Oceanography, Dona Paula, Goa, India.
[2]Center for Biofilm Engineering and Department of Microbiology, Montana State University, Bozeman, MT, 59717
[3]Department of Microbiology, University of Maryland, College Park, MD, 20742.

Hyphomonas MHS-3 (MHS-3) elaborates a capsule, composed of polysaccharide and protein, which serves as the substratum holdfast for this prosthecate, marine, film-forming bacterium. A purified polysaccharide component (fr2ps) of the capsule binds with high affinity to germanium (Ge) oxide surfaces in artificial seawater. The effect of divalent cations and pH on adhesion to Ge was evaluated by attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FT-IR). The results indicate that divalent cations participate in the binding of fr2ps to Ge oxide and that the atomic size of the cation is important in the binding interaction. Hydrogen ion concentration exhibited little influence on the interaction between the fr2ps and the Ge oxide. The results suggest that this marine surface fouling bacterium has evolved an adhesin that utilizes Ca^{++} ion to mediate strong interactions with oxide surfaces. These interactions may promote interactions with oxides in the sediment environment where these bacteria exist.

Underwater evaluation and maintenance of antifouling coatings with remotely operated vehicles

Gerard S. Bohlander
Carderock Division, Naval Surface Warfare Center, 9500 MacArthur Blvd, Code 641, West Bethesda, Maryland 20817-5700

The U.S. Navy relies on antifouling coatings that contain cuprous oxide for repelling settling and attachment of marine fouling. It is sometimes necessary to conduct underwater hull cleanings to extend the life of the antifouling paints, due to the extended mission cycles of Navy ships. A new system is being developed which permits the removal of marine fouling while containing and recovering cuprous oxide that may be generated by the cleaning process. This system also performs maintenance scans of the hull, determining paint thickness and cathodic protection potentials. This system is now being ship tested to determine the best approach for capture and treatment of copper containing effluent. A spin-off of this program has been the development of a system for remote in-water inspection of the thickness of the underwater hull antifouling coatings. In order to avoid drydocking or to pre-plan the docking work package it is desirable to perform a comprehensive underwater survey of the hull prior to entering the drydock. This now can be performed with a Remotely Operated Vehicle, ROV. This paper describes the new cleaning system and the ongoing acquisition and evaluations of antifouling paint thickness data. Results from actual deployments are reported. This information was subsequently used to assist in planning the drydock maintenance package for the antifouling coatings for a U.S. Navy ship.

Controlling biofouling on ferry hulls with copper-nickel sheathing

Les Boulton[1], Carol Powell[2] and Bruce Hudson[3]
[1]Les Boulton & Associates Ltd, PO Box 101-261, North Shore Mail Centre, Auckland, New Zealand (Consultant to the Nickel Development Institute)
[2]Consultant to the Nickel Development Institute, Birmingham, U.K.
[3]Copper Mariner Ltd, Auckland, New Zealand

Marine biofouling is commonplace on immersed marine structures including the hulls of vessels which are in routine commercial operation, such as harbour ferries. Regular removal of biofouling is required on passenger ferries otherwise fuel consumption rises and the vessel is slowed in the water during service. The cost associated with removal of the biofouling can be very high if the ship is frequently dry-docked to remove biofouling and debris off the hull. This may involve slow mechanical scraping, high pressure water blasting and the employment of expensive manual labour, as well as long periods of unproductive downtime.

Copper-nickel alloys exhibit excellent corrosion resistance in sea water and in addition show a high natural resistance to biofouling. These alloys have proved their performance over many years in applications such as sea water piping, intake screens, water boxes and for cladding of offshore structures. More recently boat hulls have also been clad with 90-10 copper-nickel alloy for control of biofouling and corrosion resistance.

This paper describes recent trials and testing of 90-10 copper-nickel alloy sheathing on the hulls of two commercial ferries on the Waitemata Harbour, Auckland, New Zealand. One older ferry (MV *Koru*) is constructed of FRP-coated wood and the second newer ferry is a solid FRP hull catamaran (MV *Osprey*). The *Osprey* is a fast (20 knots) whereas the *Koru* is slow (9 knots) and it is kept in reserve most of the time. The *Osprey* has been in service for about 30,000 sea miles. The two ferries were sheathed with adhesive-bonded 90-10 copper-nickel panels (*Koru* four years ago and *Osprey* 2.5 years ago) and both vessels have been in commercial service since.

Results to date with the sheathing have been excellent, with a quick, easy underwater hull cleaning schedule in place (*Osprey*) and faster dry-docking turnaround times (*Koru*). The evidence presented will suggest that 90-10 copper-nickel sheathed ships' hulls require less frequent cleaning intervals. Drag is reduced, allowing improved fuel consumption and higher boat speeds on average. The biofouling results of a parallel testing programme in which panels of wood, steel and aluminium alloy were sheathed with 90-10 copper-nickel and immersed for four (?) years in a polluted, quiescent harbour environment will also be described.

The chemistry of nonstick surfaces and their application as fouling release coatings

Robert F. Brady, Jr.
Chemistry Division, Naval Research Laboratory, Washington, DC 20375-5342

For some twenty years the marine coatings industry has been intrigued by polymer surfaces with no inherent power to interact with other materials, especially with the biological polymers used by marine organisms to bind themselves to objects in the sea. Polymers with nonstick surfaces have been made from sundry materials, and their resistance to marine fouling in both static and dynamic tests has been evaluated in the world's oceans. The polymer surface property which has been most frequently correlated with bioadhesion is its critical surface tension (γ_c); in fact, a generalized relationship between γ_c and marine fouling was first formulated more than twenty years ago. However, resistance to fouling is also influenced by other bulk and surface properties of the polymer. This talk will review the distinct types of polymeric materials used in fouling resistant coatings, interpret the performance of the coatings in terms of their composition, and present alternative interpretations of the relationship between γ_c and biofouling. These understandings will then be used to develop requirements for improved polymers which refuse or resist strong bonds to other materials.

Organic corrosion inhibitors for coatings

Adalbert Braig, Sonia Megert and Simon Lord
Imaging and Coating Additives, Ciba Specialty Chemicals Inc., 4002 Basel, Switzerland

The market for anticorrosive paints has been characterized by major changes within the past decade. Changing performance requirements along with legislative activities (VOC regulations) are driving the industry towards environmentally more acceptable coating technologies (e.g. High-Solids, powder coatings, UV-curable systems, waterborne paints). Limitations impeding or banning the use of the most effective anticorrosive pigments such as chromates and red lead have challenged the industry to develop novel classes of anticorrosive pigments.

Alternative concepts to formulate environmentally more acceptable paints such as the usefulness of purely organic corrosion inhibitors for long-term protection were initially considered less promising However, organic corrosion inhibitors for coatings must be considered today as a realistic alternative to the existing, more traditional concepts in the area of corrosion protection. The chracteristics of organic inhibitors will be discussed along with mechanistic aspects. Exposure results will underline the efficiency of such inhibitors in a variety of applications.

Impacts of invasive species introduced through the shipping industry

Mary Sue Brancato and Debra MacLellan
Parametrix, Inc. 5808 Lake Washington Blvd. NE, Suite 200 Kirkland, Washington, USA 98033.

Invasive species—also called exotics, nonnative species, or non-indigenous species—have been introduced inadvertently into many marine waters by the shipping industry. These species are transported as fouling organisms on ship hulls and in the ballast water of transient ships. Ship fouling can result in the transport of organisms across oceans as well as between coastal ports. While most ship fouling is associated with invertebrates and plants, some evidence suggests that fish also accompany a heavily fouled vessel. The degree of fouling on ships, fishing vessels, and private boats has been reduced through the use of antifoulant paints. Prior to their use, about one-third of the introduced species in Australia are believed to have been transported via fouling organisms on the hulls of overseas shipping vessels. Some fouling still occurs today, especially in situations where antifouling paint cover is chipped, difficult to apply, or otherwise ineffective. Invasive species can have adverse ecological and economic impacts by causing declines in native species through habitat alteration or by out-competing native species, and thus, permanently reducing biological diversity. Mariculture and commercial and recreational fishing can also be adversely affected because the new invading species are predators, competitors, and parasites, and some cause or carry disease. Finally, some invasive species, such as toxic dinoflagellates and cholera-causing bacteria, can affect human health.

Cellular and molecular approaches to primary adhesion in *Enteromorpha*

James A Callow, Michele S Stanley and Maureen E Callow
School of Biological Sciences, The University of Birmingham, Birmingham B15 2TT, UK.

Novel solutions to non-toxic control of fouling organisms depend on a greater understanding of the mechanisms involved in the adhesion process. The major fouling macroalga, *Enteromorpha*, initiates attachment through motile spores which secrete a glycoprotein adhesive from vesicles contained in the anterior region of the spore. This paper describes a combined cell biological and immunological approach to characterise adhesive processes and to identify the adhesive molecules. Monoclonal antibodies have been raised to settled spores displaying the adhesive on their surfaces. Candidate antibodies towards the adhesive have then been selected by ELISA, Western Blotting, immunofluorescence and immunogold microscopy, in combination with functional inhibition assays. The antibodies then serve as molecular probes to biochemically identify and characterise the corresponding adhesive materials as described more fully in the accompanying poster (Stanley, Callow and Callow). The relationship between spore adhesive and cell wall proteoglycans is discussed.

Algal biofilms and biofouling: problems and perspectives

Maureen E Callow
School of Biological Sciences, The University of Birmingham, Birmingham B15 2TT, UK

Fouling of man-made structures structures by algae is a major problem throughout the world. The green alga *Enteromorpha* (grass) is the most widespread and troublesome on ships' hulls. The current generation of non-tin antifouling coatings is fairly ineffective in controlling this alga, and its control remains a major objective of fouling research. The success of *Enteromorpha* as a fouling organism is due, in part, to the production of enormous numbers of motile spores which colonize new substrata. Colonisation depends on a number of processes, involving substratum location, settlement, temporary and permanent adhesion. The various stages involved in the transition from motile to adhered spores will be illustrated by a video. Spores respond to a number of environmental 'cues' which may be important in attracting them to a particular location. Data will be presented which indicate that fatty acids act as chemoattractants. The role of chemical and topographical cues in moderating spore settlement will be discussed.

The relative contributions of introduction vectors to the Port Phillip Bay biota.

Marnie L. Campbell and Chad L. Hewitt
CSIRO, Centre for Research on Introduced Marine Pests, GPO Box 1538, Hobart Tasmania 7001, Australia.

Since British discovery of Port Phillip Bay, 197 years ago, at least 172 exotic, cryptogenic and possibly introduced species have become established within the bay. Recent bay-wide biological surveys, literature reviews and museum searches by numerous organisations (CRIMP, DSTO, MAFRI, Marine Science and Ecology, Museum of Victoria, University of Melbourne and Auckland University) have confirmed this. The vectors for these introductions are varied, with hull fouling & boring being the predominant (58.8%) method of translocation. This dominance began with historical fouling on wooden vessels and has continued through to modern times. Exotic organisms capable of being translocated via hull fouling include the bryozoan *Watersipora subtorquata* and possibly the recently arrived algae *Undaria pinnatifida*. Mariculture (23.2%), semi-dry and dry ballast (3.1%), ballast water (14.5%) and intentional introductions (0.4%) have also participated in translocating exotic species to this region. Mariculture is directly responsible for the introduction of *Crassostrea gigas* and can be implicated in the introduction of corophids such as *Corophium acherusicum* and hydrozoa such as *Bougainvillea ramosa*. Semi-dry and dry ballast may also be responsible for introductions of the crustacea *Carcinus maenas* and *Caprella* species. Ballast water is responsible for translocating species such as the echinoderm *Asterias amurensis*, the fish *Acanthogobius flavimanus* and the polychaete *Sabella spallanzanii*. The role of ballast water has increased in recent years, however hull fouling and mariculture still significantly contribute to introductions.

The structure and function of an international, independent marine coatings board for assessing the risks of alternative antifouling products and technologies

Michael A. Champ[1], Thomas J. Fox[2], Harold E. Guard[3], R. James Maguire[4], Keith H. Pannell[5], Peter F. Seligman[6] and Geoffrey W. Swain[7]

[1]Advanced Technology Research Projects Corporation (ATRP Corp.), Arlington, Virginia
[2]Center for Advanced Ship Repair and Maintenance (CASRM), Norfolk, Virginia
[3]Biomolecular & Biosystems S&T Division, Office of Naval Research, Arlington, Virginia
[4]National Water Research Institute, Environment Canada, Burlington, Ontario, Canada
[5]Department of Chemistry, University of Texas at El Paso, Texas
[6]Environmental Sciences Division, SPAWARSYSCEN, San Diego, California
[7]Florida Institute of Technology, Melbourne, Florida

Tributyltin (TBT) antifoulant coatings have been estimated to save ship owners over two billion dollars annually in fuel avoidance and shipyard costs. Nevertheless, the International Maritime Organization has recently recommended a global ban on the use of TBT by 1 January 2003. In the U.S., TBT has been a regulated chemical for over 30 years, and the recently proposed global ban confirms how difficult it is to regulate low release rate toxic additives (biocides) in antifouling boat bottom paints that impact non-target organisms at levels near limits of detection. The economic and environmental consequences and global impact of this regulatory action is far reaching, it could double the costs of antifouling. The time period for implementing the ban is generous from a regulatory perspective, but its impact will be significant in the antifouling $ 500 million annual marketplace, placing the ultimate users of antifouling coatings at undefined financial risk. The implementation of the ban requires a shift to alternatives in a marketplace that usually requires a minimum of 3-5 years of product testing for acceptance. In this time period, both the marketplace and the regulatory authorities will need to evaluate and "accept" available alternatives by assessing a wide range of environmental, technical, economic and public health risks. In the US, there are currently few new technology alternatives "approved" (i.e., a silicone paint and a self-polishing co-polymer copper coatings with a zinc Omadine co-biocide) and it is known that prospective alternatives do not meet EPA VOC requirements, and long term effects on the environment are unproven. In the 5-year phase out period, it is likely that the marine transport industry will be forced to return to older copper-based antifoulants as an interim measure. The problem is how to screen alternatives to meet the deadline without accepting an alternative which in the future may exhibit unanticipated environmental or public health risks.

The global regulatory process needs a new approach to assist in the phase out of TBT and characterization and evaluation of alternative antifouling products, coatings, technologies and systems (etc.). This approach would center around the development of an independent – international Marine Coatings Board (MCB) funded from the future fuel savings by ship owners which would promote the development and comparative evaluation (standardized testing) of antifoulant alternatives to the banned TBT. Proposed examples include: paint efficacy, longevity, release rates, degradation rates, persistence, bioavailability, biologically relevant exposure concentrations, toxicity (acute and chronic) to target and non target organisms, deformities and immune system expression to name a few.

The purpose of the MCB is to complement national regulatory activities by integrating the data and information requirements of national regulatory bodies together with those of ship owners and operators, coating manufacturers, harbor authorities, and others into standardized assessment protocols that can evaluate and rank available alternatives. International Working Group Meetings of the MCB would review and select available technologies for testing and evaluation. Alternatives would be identified and evaluated in international intercalibrated demonstration experiments utilizing scientific and regulatory criteria and standardized protocols developed by the MCB. The MCB could directly and indirectly oversee the standardized testing and evaluation of the most promising candidates. These would be bid out by RFP (Request For Proposals) to ship R&D groups; industry or academic R&D laboratories across the world to conduct closely monitored standardized

comparative assessments providing data and information for environmental, economic and human health risk assessments. The MCB data and information would complement and support national regulatory efforts and would be available to anyone, anytime, anywhere on the Internet. This would allow the regulatory process and the forces of the marketplace to work together to develop the most suitable alternatives in the shortest time period

Physico-chemical model for prediction of seawater metal corrosion

B.B.Chernov and S.A.Ponomarenko
Far-Eastern State Marine Academy, Vladivostok, Russia

The paper discusses the processes of corrosion products' film growth on the metallic surfaces and corrosion reagents film transport in relation to metal corrosion behavior prediction in natural seawater. Proposed by the authors common physical-chemical approach to this processes enables to interrelate the thickness of corrosion failure metal K with exposure time t as follows:

$$K - \frac{P}{V_p}\left(1 - \frac{V_p}{V_o}\right)\left(1 - \exp\left(-\frac{V_p K}{P}\right)\right) = V_p t,$$

where coefficient P characterizes the protection properties of corrosion products, V_o and V_p - initial and steady corrosion rates, consequently. Data base application of metal corrosion in different ocean regions has allowed to estimate the coefficients depending on physical-chemical seawater parameters: temperature, dissolved oxygen concentration, hydrostatic pressure, flow rate of seawater etc. The approach described seems to have been applied for the first time to numerically define the effect of seawater environment variations on metals' corrosion. The data obtained has been used to chart the corrosion activity of seawater for mild steel, copper, aluminum and their alloys.

Recent marine wood preservation research in Australia

Laurie J. Cookson and Damian K. Scown
CSIRO Forestry and Forest Products, Private Bag 10, Clayton South MDC, Vic. 3169, Australia

Marine wood preservation research over the last 15 years in Australia has tackled two main problems for the industry. The first was to demonstrate that existing commercial treatments could give reliable performance in the sea, in the face of erratic performance and inadequate specifications. The key solution was to study the biology of marine borers. Collating and identifying marine borers from different areas around Australia, and examining their preservative tolerances, enabled the Australian coastline to be divided into seven major hazard zones. Piling options can now be specified that will give more than 20 years service life in each zone. More recent difficulties for the industry are questions about the fate of the copper-chromium-arsenic (CCA) and creosote commonly used to protect wood in the sea. Current research focuses on the CCA levels found in barnacles growing on treated piles. Alternative chemicals and methods of protection that seem intrinsically more appealing environmentally are also being examined. Recent research areas are the natural durability of timber in the sea, new generation wood preservatives that are arsenic and chromium free, and potentially active agents extracted from marine organisms.

Experimental evaluation of the effects of recruitment and competition on the succession and stability of the fouling community at Cabo Frio Island, Rio de Janeiro, Brazil.

Ricardo Coutinho
Instituto de Estudos do Mar Almirante Paulo Moreira, CEP 28930-000, Arraial do Cabo, Rio de Janeiro, Brasil.

The present study was designed to examined the hypothesis that the succession and stability of the fouling community at Cabo Frio island, Rio de Janeiro, Brazil, are controlling by the recruitment and competition of the dominant species. Manipulation experiments in panels were done in a *Sargassum furcatum* bed during two years. We observed a seasonal change in composition and abundance of species, with oportunists species ocorring in 3-4 months and later sucessional species after this period. "Stability" was reach after six months. *Mycale microsigmatosa* and *Schizoporella errata* dominated the community with 9-47% and 10-63% of cover area respectively. Our results, showed that the "equilibrium" after a disturbance occurs in about 6 months depending on the reprodutive structure present in the water and the competitive ability of species.

Factors influencing a vessel's degree of fouling.

Ashley D.M. Coutts[1], Malcolm Haddon[1] and Chad L. Hewitt[2]
[1]Australian Maritime College, P.O. Box 21 Beaconsfield, Tasmania.
[2]Centre for Research on Introduced Marine Pests (CRIMP), CSIRO Marine Laboratories, P.O. Box 1538, Hobart, Tasmania.

Twenty-one vessels of international and domestic origin greater than 10,000 tonnes (gross) were surveyed between October 1996 and August 1997 at Bell Bay and Long Reach, northern Tasmania, Australia. Photographs and samples were systematically collected from all vessels at three depths (waterline, middle and bottom) at three positions along the hull (bow, middle and stern). Questionnaires were used to obtain each vessel's particulars and voyage memos since their last dry dock. Physical data collected included average voyage speed, age of antifouling paint, and average voyage duration between ports. Each vessel was assigned an "index of fouling" according to the combined frequency of occurrence on each vessel of 15 higher taxonomic groups (Maxillopoda, Malacostraca, Ostracoda, Rotifera, Nematoda, Annelida, Mollusca, Ectoprocta, Cnidaria, Chordata, Chlorophyta, Phaeophyta, Cyanophyta, Rhodophyta and Bacillariophyta). A linear relationship between the index of fouling and the three main factors, average voyage speed, age of antifouling paint, and average voyage duration was found to be highly significant accounting for 60% of variation in the available data (Adj. $r^2 = 0.603$, $F = 11.127$, df = 3, 17, $P < 0.001$). After an outlier was removed the proportion of variation accounted for rose to 72% (Adj. $r^2 = 0.722$, $F = 17.465$, df = 3, 16, $P = 0.006$). Of the three factors the most influential was the age of antifouling paint.

Biox: on-line monitoring of biofilm and chlorination

Pierangela Cristiani[1], Alfonso Mollica[2], Giovanna Ventura[2] and Elena Lai[2]
[1]ENEL S.p.A. RESEARCH Department, Environmental, Via Reggio Emilia 39, 20090 Segrate, (MI) Italy,
[2]Consiglio Nazionale delle Ricerche - Istituto per la Corrosione Marina dei Metalli, Via De Marini 6, 16149 Genova, Italy

To improve the chlorination treatments of steam condenser cooling sea water, ENEL has recently patented an innovative electrochemical system BIOX which monitors on-line the biofilm growth and the concentration of effective T.R.O. (total residual oxidant) diffusing toward the sensor surface, during the chlorination treatments. The system is already installed in some ENEL power stations. The results point out that this new device will be useful to optimise the biocide treatments in the most different conditions.

Neurotransmitter antagonists as antifouling agents against cyprids of *Balanus improvisus.*

Mia Dahlström[1], Lena Mårtensson[2], Per Jonsson[3] and Hans Elwing[1].
[1]Department of Cell and Molecular Biology, Interface Biophysics, Göteborg University
[2]Department of Zoophysiology, Göteborg University
[3]Tjärnö Marine Biological Laboratory, Göteborg University, Sweden.

Okano *et. al*, demonstrated that cement production from isolated cement glands from *Megabalanus rosa*, was induced by norepinephrine (Okano K et. al *J Exp Biol* ,1996, 199, 2131-2137). Consequently, we thought it worthwhile to investigate if receptor antagonists to norepinephrine will inhibit settling of cyprids due to insufficient cement production. Cyprids, obtained from laboratory-cultured adult *Balanus improvisus*, were transferred to tissue culture petridishes of polystyrene. Phentolamine, an unspecific adrenergic receptor antagonist, was added and results of the assay were registered after eigth days. Significant inhibition of settling was found in a concentration intreval of 1 - 100 μM of phentolamine. At 33-100 μM, phentolamine appeared to be toxic to the cyprids. Some juveniles settled at low concentrations of phentolamine detached from the surface indicating insufficient cement production. Other effects of phentolamine on settling behaviour and physiology can not be excluded. Yamamoto *et al* also studied the effect of pentolamine on larval settling of *B. amphitrite*. (Yamamoto H et. al *Biofouling*, 1998, 13, 69-82) Their results differed from ours in that minimal settling inhibition occurred at concentrations about 100 times higher compared to our experiments.

Bacterial behaviour influenced by physicochemical modifications to polymer coatings exposed to the marine environment

Helen M Dalton, Kevin C Marshall and Paul E March
School of Microbiology and Immunology, The University of New South Wales, Sydney NSW 2052

Primary colonizers of surfaces in the marine environment modify and enrich surfaces rendering them more amenable to subsequent attachment by bacteria, microalgae, fungi and protozoa which can then have an influential effect on colonization by invertebrates as well as ultimate performance. Coatings developed for aquatic environments are significantly modified by microbial biofilms. This microbial interaction leads to coverage of surfaces masking surface properties, increased leaching of additives within the polymer matrix and degradation by biological products of the polymer and their additives. These coatings are then vulnerable to penetration of the polymer matrix by microbial elements. Any or all of this damage may lead to mechanical instability and enhance subsequent biofouling.

Utilizing the surface-responsive shift in morphology of a marine bacterium in a controlled marine environment, a biological assay of temporal changes in surface hydrophobicity is being utilized both to determine heterogeneities in substratum hydrophobicity at the μm level and to monitor the fate of coatings when immersed in a marine environment. It is probably unrealistic to successfully design coatings that completely escape biofouling so the goal of developing minimally adhesive coatings that attenuate fouling is being actively pursued. Laboratory contrived as well as natural marine microbial biofilm formation is being monitored to evaluate this characteristic of coatings.

Applications of marine bacteria as surface-sensitive bioprobes that can detect changes in surface characteristics will contribute to design, selection and evaluation of coatings developed for use in the marine environment.

Cost analysis of TBT self-polishing copolymer paints and tin-free alternatives for use on deep-sea vessels.

Nimmi Damodaran[1], John Toll[2], Mike Pendleton[1], Conrad Mulligan[1], David DeForest[2], Michael Kluck[2], John Felmy[1] and Mary Sue Brancato[2]

[1]Princeton Economic Research, Inc., 1700 Rockville Pike Suite 550, Rockville, Maryland, USA 20852

[2]Parametrix, Inc., 5808 Lake Washington Blvd. NE Suite 200, Kirkland, Washington, USA 98033.

We conducted a comparative analysis of the costs of tributyltin (TBT) self-polishing copolymer (SPC) antifouling paints and their alternatives, to better understand the economic impact of restricting the use of TBT on deep-sea vessels. Costs evaluated include antifouling paint costs, dry-docking rates, clean hull fuel consumption, and fuel consumption penalties as a result of hull fouling. TBT SPC paints offer significant cost savings to ship owners and operators, because their five-year dry-docking interval reduces dry-docking costs and revenues lost during dry-docking, assuming a 30-month dry-docking interval for tin-free antifouling paints. As a conservative estimate, we assumed no fuel penalty in comparing TBT SPCs and tin-free SPCs. Tin-free SPCs are 95 to 146% more expensive, and copper ablatives are 156 to 401% more expensive than TBT SPCs. This is due to higher dry-docking costs, revenues lost, paint costs, and, in the case of copper ablatives, fuel costs. We have conservatively assumed that TBT and tin-free SPCs provide the same fuel efficiency, so the environmental risks or benefits of switching from a TBT SPC to a tin-free SPC would have to do primarily with the pesticidal impacts on non-target organisms. What data are available suggest that tin-free antifouling paints do pose risks to the environment. None of the tin-free alternative paints have been shown to be as safe as or safer for the environment over the long term than TBT SPC paints for use on deep-sea vessels.

Tributyltin in the marine environment...NO WORRIES?

Stephen de Mora

Département d'océanographie, Université du Québec à Rimouski, Rimouski, Québec G5L 8W9 CANADA

Tributyltin (TBT) has the reputation of being an excellent antifoulant and a notorious pollutant. This dichotomy of perspective has long coloured the debate on the use (and continued use) of TBT in the marine environment. This presentation will provide a brief case history of TBT as a marine pollutant and outline why concerns for the future endure. Firstly, numerous studies have illustrated the potency of TBT as a broad spectrum pesticide that can affect non-target organisms. Of notable concern has been the masculinization of female gastropods (imposex) and the deformation of oyster shells. Legislative response was swift, global, and effective, although considered unwarranted in some circles due to the paucity of scientific evidence. The efficacy of such legislation will be briefly considered. Secondly, concerns for the marine environment continue despite limitations on the use of TBT, Recent investigations have attested to the longevity of TBT in sediments and the instigation of imposex at remote locations (i.e. TBT derived from oceanic shipping). Ongoing studies document the occurrence of TBT in higher trophic levels and have broadened our understanding of the ecotoxicological effects, including the role as an endocrine disrupter. Finally, the evolution of future laws will be considered. The 42nd session of IMO-MEPC recently enunciated the aim to develop a global, legally binding instrument to ban TBT usage. One legacy of the TBT story has been to instil prudence about introducing alternatives to TBT antifoulants into the marine environment.

Use of a novel leach-test method for the evaluation of antifouling paints

Jane Dormon
Hempel's Marine Paints A/S, Lundtoftevej 150, Lyngby DK-2800, Denmark

Testing of the efficiency of antifouling paints has traditionally been conducted by toxicity testing (of one form or another) on samples of the biologically active agent alone. For this study, it was considered that a more realistic approach would be to test instead, the actual antifouling coating. In this case, a suitable substrate would be coated with the coating to be tested, and toxicity testing would be conducted on the leachate, i.e., soaked panels would leach the included biologically active agent into the surrounding water. Samples of the water could be collected and tested against various target and non-target organisms. The advantages of this method are: (a) it should give a more accurate feeling for the antifouling properties of the paint system, than that acquired by testing the biologically active agents alone, (b) by comparing the toxicity test results from newly developed antifouling coatings, with results from coatings of known performance (i.e., older, well understood systems), it could be possible to predict the antifouling potential of the "new" coating, and, (c) by testing paints that have been immersed over different periods of time (and comparing them with coatings of known "life expectancy"), it may be possible to predict the life expectancy of the antifouling coating. Important factors to consider in these tests are: surface area to volume ratio; duration of "soak period"; interaction of paint components; interpretation of results.

The following test method attempts to address all of these issues and produce a reasonably quick (by comparison with raft testing) method for the evaluation of the antifouling performance of A/F coatings

Effects of seawater immersion on the surface properties of some silicone and fluorosilicone coating materials

Francis Fernández Estarlich[1,2], Sue A. Lewey[2], Thomas G. Nevell[1], Adrian A. Thorpe[1], John Tsibouklis[1], and Andrew C. Upton[2].
[1]Centre for Chemistry, School of Pharmacy and Biomedical Sciences, University of Portsmouth, St. Michael's Building, White Swan Rd., Portsmouth, PO1 2DT, U.K.
[2]Maritime Faculty, Southampton Institute, East Park Terrace, Southampton, SO14 0YN, U.K.

Liquid-surface interactions for some commercial silicone elastomers and synthesised fluorosilicone elastomers have been studied from measurements of contact angles of submerged air bubbles, using double distilled water, artificial seawater, filtered sterilised seawater and seawater, over periods of up to 6 weeks. Well-characterised surfaces including poly(methyl methacrylate) (pmma), and paraffin wax have been used for comparison. Bacterial settlement in seawater has been monitored by optical microscopy and scanning electron microscopy and some materials have been tested in sea exposure trials.

Immersion in distilled water or sterile artificial seawater had no effect on pmma but progressively reduced the contact angles of all silicones by up to 70°. Changes were slow, and considerable differences between the silicones were maintained over at least three weeks. Greater and more rapid changes were however observed in non-sterilised seawater and after 7-14 days most surfaces showed similar contact angles (25°-32°). Absorption of water by the silicones is shown, consistently with previous work; the process is considerably affected by dissolved salts. In filtered and non-filtered seawater, however, it appears that the early stages of biofilm formation, occurring over 7 days, determined the contact angle observed. In marine antifouling trials, some silicone elastomers performed well while most fluorosilicones showed some resistance to fouling. Observations of microbial settlement will be reported together with more detailed surface energy determinations.

Assessing the impact of anti-fouling compounds in the marine environment. Lessons to be learned from the use and misuse of biological indicators of TBT contamination.

Stewart M. Evans and Geoff J. Nicholson
Dove Marine Laboratory, Cullercoats, Tyne and Wear, NE30 4PZ, UK.

Two biological indicators of TBT contamination, abnormal shell growth in oysters and imposex in whelks, have provided valuable information on the impact and extent of TBT pollution in the marine environment. They have also been used successfully in monitoring changes in contamination during the past decade or so. However, they have generated misleading information when they have been used as: (i) actual measures of ambient concentrations of TBT; (ii) indicators of breeding performance; and (iii) predictors of the survivorship of species. One reason is that responses such as imposex are not, as has often been assumed, specific to TBT. Imposex can, for example, be caused by phenyltins, nonylphenol and other agents. There may also be 'natural' causes and imposex in whelks and shell chambering in oysters have been reported in populations which have had no history of exposure to TBT. Other reasons are that insufficient attention has been given to the sensitivity of the different developmental stages to TBT, longevity and habits of indicator species. It will be argued that, while biological indicators should play key roles in assessing the impacts of pollutants, more rigorous protocols are needed.

Enhanced oxidation of tributyltin contaminated washdown waters

Lyn Fletcher[1] and Heri Bustamante[2]
[1]Maritime Platforms Division, DSTO, GPO Box 4331, Melbourne Vic 3001, Australia
[2]Australian Water Technologies E S & T, 51 Hermitage Rd, West Ryde NSW 2114, Australia

During the washdown of ship hulls painted with tribuytltin (TBT) antifouling paints, large quantities of toxic TBT contaminated wastewater are produced. New regulations are being introduced limiting the amount of TBT that can be discharged. Hence the need to develop processes to destroy TBT in wastewater.

Enhanced oxidation techniques that produce hydroxyl radicals have been demonstrated to be capable of degrading TBT in water. The oxidation process occurs via sequential dealkylation until inorganic tin is finally produced. Of the enhanced oxidation techniques tested, UV/oxidation provided the fastest reaction rates. TBT is normally present in dockyard wastewater as both dissolved TBT and associated with insoluble paint particles. However when treating dockyard wastes, high variability in reaction rates was observed. UV/oxidation relies on light penetrating the sample and turbidity was assessed as being a major influence on final reaction rates. Consequently, highly efficient and cost effective pretreatment to remove solids is required for this treatment process to be successful. DSTO is currently collaborating with AWT to produce a complete treatment process for dockyard washdown wastewaters.

Rapid assessment of the crevice corrosion resistance of stainless steel alloys in sea water

Neil Gage and Brian T. Moore, DSTO Aeronautical & Maritime Research Laboratory, GPO Box 4331, Melbourne, Vic 3001

In the last two decades there have been significant improvements in stainless steel alloy compositions for marine applications. Many of these alloys are reported to have markedly better corrosion resistance, particularly with respect to crevice and pitting corrosion characteristics, than the still commonly used austenitic grade 316L. Duplex stainless steel alloys are of particular interest because of their greater yield strength (double austenitic grades), thereby enabling gauge reductions with subsequent weight and cost savings.

The DSTO, on behalf of the Australian Defence Forces (ADF), has refined a technique designed to enable a rapid assessment of the crevice corrosion resistance of stainless steel alloys in seawater. Potentially, there is a broad range of applications for candidate alloys including periscope housings, seawater holding tanks, pumps and fittings. This study examined a new modified cyclic polarization technique specially designed to determine crevice corrosion susceptibility. Two ASTM standard tests involving ferric chloride immersion and a long-term field trial in tropical seawater were also employed for comparison. Test alloys included: the austenitic grades 316L and 254SMO, duplex grades 2304, 2205, Ferralium 255 and 2507 and the nickel alloy Inconel 625 as a reference because of its high corrosion resistance.

Inconel 625 and duplex 2507 proved to be the most corrosion-resistant alloys with austenitic 254SMO and duplex alloy, Ferralium 255, slightly inferior. Duplex 2205 was the next best performed alloy while of the two lowest grade materials examined, duplex 2304 was shown to be marginally more resistant than austenitic 316L.

The effects of seaweed natural products on biofouling

Bernardo A.P.Gama[1], Ana G.V. Valle[1], Ricardo Coutinho[2] and Renato C. Pereira[1]
[1]Departamento de Biologia Marinha, Universidade Federal Fluminense, C.P. 100.644 CEP 24001-970, Niterói, Rio de Janeiro – Brazil
[2]Instituto de Estudos do Mar Almirante Paulo Moreira, CEP 28930-000, Arraial do Cabo, Rio de Janeiro – Brazil

Antifouling is one possible ecological function of marine natural products found in some sea weeds. To investigate the hypothesis that seaweeds possess chemicals that influence fouling settlement, crude organic extracts from the seaweeds *Stypopodium zonale, Dictyota menstrualis* (Phaeophyta) and *Laurencia obtusa* (Rhodophyta) were incorporated at natural, volumetric concentrations into hard, stable gels (phytagel[tm]) that served as substrata for fouling settlement in the field. Treated and control gels were randomly interspersed and submerged at 1 m depth for seven weeks (from July, 9 to August, 28, 1997) at Cabo Frio Island (Arraial do Cabo, RJ, Brazil). Settlement of invertebrates and algae on gels was weekly measured by a non-destructive point-sampling technique. Some replicate gels were removed after 5, 6 and 7 weeks and the amount of extract retained was measured. Fouling organisms settled significantly more on plates treated with *L. obtusa* extracts. Fouling on gels treated with *D. mentrualis* extract was not significantly different from fouling on control gels. We calculated a diffusion rate of extracts of 18.2% per week. Our findings suggest that the antifouling properties of *L. obtusa* crude extract act both reducing growth and development of settled fouling and inhibiting settlement of some foulers (*i. E.* reducing species richness). This field assay seemed to provide a ecologically relevant method for assaying the antifouling properties of extracts of marine organisms.

Toxic free (silicone based) fouling release systems

Eric Garcin[1], Corinne Dallies[2] and André Sage[2]
[1]Rhodia Chimie, 25 quai Paul Doumer , F-92408 COURBEVOIE Cedex, France
[2]Rhodia Chimie, 55 avenue des Frères Perret BP 22, F-69191 SAINT FONS Cedex, France

Concerns about toxicity of antifouling systems and the (partial) ban of tributyltin has led to the development of alternate formulations. Silicone polymers are an ecological solution since the systems are toxic free (without any biocide). The intrinsic low surface tension of silicone binders allow the formulated paints to have a very low adhesion power, thus preventing the foulings from sticking on the surface and making the coatings 'selfcleaning'.
In our presentation we will cover the basics of silicone chemistry, followed by a full study of the development of silicones based fouling release systems, including laboratory physical characterisation and fouling measurements. A tentative correlation between these properties will be proposed. Application results on test panels under rafts, and on boats which have sailed in the various seas around the world will be shown.

Antifouling from nature: Laboratory test with algae and sponges.

S. Geraci[1], M. Faimali[1], L. Piovetti[2] and G. Cimino[3]
[1]C.N.R. Istituto per la Corrosione Marina dei Metalli, Genova, Italy
[2]Université de Toulon et du Var- UFR Sciences et Tecniques, Toulon, France.
[3]C.N.R. Istituto per le Molecole di Interesse Biologico.Arco Felice, Napoli, Italy

The crude extracts of three species of Mediterranean sponges, *Reniera sarai*, *Cacospongia mollior* and *Rasfaliona* sp. And of seven species of marine algae, 5 belonging to brown, 1 to red and 1 to green algae, were submitted to laboratory screening to assess their antifouling performance by settlement inhibition tests carried out with the cyprids of *Balanus amphitrite*. In order to assess the effects of these crude extracts against non-target species, toxicity tests on *Balanus amphitrite* nauplius II, as a representative of zooplanktonic organisms, have also been carried out. Settlement test results of these crude extracts suggest that the search for natural antifouling is promising, specially if considering the antifouling effect magnification by purification of these extracts and the possible discovery of new molecules or functional groups.

The importance of ship hull fouling as a vector of species introductions into the North Sea

S. Gollasch
Institute for Marine Sciences, Duesternbrooker Weg 20, 20146 Kiel, Germany

During the last decades ballast water discharges have increased throughout the world in most of the major ports. Discharge volumes are considerable high in some cases and the probability of successful establishment of self-sustaining populations of exotic species is expected to increase with greater volumes of discharged ballast water and reduced ship transit times. Ships have been recognized as a major vector for the introduction of non-indigenous and harmful organisms.

A joint research project between the Institute for marine Sciences, Kiel and the University of Ham-burg commissioned by the German Environment Protection Agency (Berlin) was launched in 1992 to investigate species introductions by international ships traffic. The ballast water, tanks sediment and hull fouling of nearly 200 vessels have been sampled. Found species ranged from microalgae to 15 cm long fishes. Of the 404 species identified, approx. 60 % were classified as non-indigenous species to German waters. Non-indigenous species were recorded in 37 ballast water (37,8%), 30 sediment (56,6%) and 126 hull samples (97,5%).

Furthermore an assessment was undertaken to identify the risk of unintentional future species introductions. The potential for establishment was classified into 3 categories according to matching climatic and salinity conditions in the area of origin compared with those in the port of destination. Ballast water is estimated as an important vector for future introductions of non-indigenous species in our waters, but most of the species with the highest potential for establishment were recorded in hull samples and not in ballast water or sediment samples.

A recent (1998) summary of non-indigenous species in coastal waters of the North Sea revealed about 80 exotic species occurring in self-sustaining populations. The number is lower compared to other enclosed seas or bays as e.g. the Chesapeake Bay (116 introduced species) and the San Francisco Bay (212 introduced species). The majority of introduced species in the North Sea are invertebrates; predominantly crustaceans, polychaetes and molluscs. Most of these species have been introduced by ships and mariculture activities. Ships are assumed to be the most important vector (approx. 45 introductions). Hull fouling seems to be a more important vector (27 species) compared to ballast water (18 species). Even a new species to science (a turbellarian) was found in hull samples of one ship.

It was concluded that each vessel from overseas is a potential carrier of non- indigenous organisms in sufficient numbers to establish a founder population in the North Sea. Since even a single introduced non-indigenous species may cause severe damage, it is necessary to develop preventive measures for un- intentional species introductions. These measures should not focus on ballast water mediated introductions alone, but should in the same way take into account introductions by hull fouling of ships.

Fluoropolymer films: surface energy characteristics and marine anti-fouling performance

Paul Graham[2], Ian Joint[1], Thomas G. Nevell[2], Roger A. Pullin[2,3], Maureen Stone[2] and John Tsibouklis[2]

[1]Plymouth Marine Laboratory, Prospect Place, The Hoe, Plymouth, PL1 3DH, U.K.

[2]Centre for Chemistry, School of Pharmacy and Biomedical Sciences, University of Portsmouth, St. Michael's Building, White Swan Rd., Portsmouth, PO1 2DT, U.K.

[3]Maritime Faculty, Southampton Institute, East Park Terrace, Southampton, SO14 0YN, U.K.

In response to the short-comings associated with established materials for anti-fouling protection (including silicones) and the environmental contamination caused by paints/coatings containing copper or alkyl tin compounds, attention has been turned to the possible effectiveness of coherent films of low-surface-energy materials.

Some perfluoroitaconates, perfluoroacrylates and perfluoromethacrylates have been synthesised and characterised. Surface energy is reduced by incorporating the side-chain -$(CH_2)_2$-$(CF_2)_n$-F, with values < 6 mJ m^{-2} for $n>10$. The surfaces of such materials strongly repel most liquids.

Studies (optical, scanning electron and atomic force microscopy) with sulphate-reducing bacteria, *Pseudomonas* and *Bacillus megaterium* showed greatly reduced settlement on these polymers. *Enteromorpha spp.* were also reluctant to settle (relative to control materials). In both cases, however, attached bacteria or settled zoospores were observed mainly on areas with surface imperfections. The results indicate the importance of surface integrity combined with low surface energy for potential anti-fouling coatings.

Structural and Chemical Characterisation of Echinoderm Non-Fouling Surfaces.

Michelle M. Grundy[1], Dimitris Giantzudis[1], Charlie D. Bavington[1], Neville V. Richardson[2] and J. Douglas McKenzie[1]

[1]The Scottish Association for Marine Science, Dunstaffnage Marine Laboratory, PO Box 3, Oban PA34 4AD, United Kingdom.

[2]School of Chemistry, University of St. Andrews, Purdie Building, St. Andrews, Fife KY16 9ST, United Kingdom

Echinoderms have surfaces, free from microfouling organisms, despite having an enormous surface area. The major mechanism preventing fouling may be a non-stick surface coat or modified glycocalyx. However, the nature of these surfaces and the mechanisms by which adhesion is prevented, is poorly understood.

By means of immunohistochemistry, electron microscopy (EM), atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR), the surface cuticles of a variety of echinoderm surfaces have been investigated.

The cuticle of starfish and sea urchin tubefeet and sea cucumber body wall were found to stain positively for anti-collagen type I and anti-chondroitin sulphate. FTIR spectroscopy experiments confirmed that the echinoderm cuticle was predominantly proteoglycan in nature and that its composition could be manipulated with enzymic treatments, in order to elucidate which chemical components contributed towards its anti-adhesive properties. The EM and AFM studies have provided valuable, high resolution, information about the structural arrangement of the echinoderm cuticle.

The use of a customised bioreactor to study biocorrosion of sheet steel piling in tidal waters

Rolf Gubner and Iwona B. Beech
University of Portsmouth, School of Pharmacy and Biomedical Sciences, St. Michael's Building, White Swan Rd, Portsmouth PO1 2DT, UK

In marine environments, accelerated corrosion at, or just below the low-water level of steel structures, such as sheet steel piling, is of current interest to civil engineers in the UK. European steel producers and the University of Portsmouth studied the cause of this phenomenon in a European Coal and Steel Commission sponsored project. As part of laboratory-based corrosion assessments, a four-vessel bioreactor system was designed to reproduce tidal water movement. The electrochemistry on the sheet steel piling was simulated by electrically connecting a series of piling grade carbon steel coupons and positioning at different immersion depths in the bioreactor vessels. On-line corrosion rate monitoring was performed by applying linear-polarisation resistance, open circuit potential and zero-resistance ammetry measurements. Parameters, such as biofilm development, changing nutrient concentrations and exposure time of test specimens to air were investigated to determine their influence on the corrosion behaviour of steel piling grade carbon steel. It was demonstrated that the water-retaining capabilities of biofilms significantly increased the corrosion rates just below the low-water line. Furthermore, changes in the nutrient concentrations always resulted in an increase of the corrosion rates over a period of up to one week. An extended exposure time of specimens to air led to increased corrosion rates at the high-water level and a decrease in the corrosion rates at the low-water level.

The effect of extracellular polymeric substances on the attachment of *Pseudomonas* NCIMB 2021 to AISI 304 and 316 stainless steels

Rolf Gubner and Iwona B. Beech
University of Portsmouth, School of Pharmacy and Biomedical Sciences, St. Michael's Building, White Swan Rd, Portsmouth PO1 2DT, UK

The importance of extracellular polymeric substances (EPS) in bacterial attachment, biofilm development, and deterioration of steel is a subject of continuing discussion. Our investigation aimed to determine the effect of treating AISI 304 and 316 stainless steel surfaces with three different types of exopolymers (planktonic, capsular and biofilm) on the initial attachment of marine *Pseudomonas* NCIMB 2021 species to steel. Exopolymers were produced by *Pseudomonas* NCIMB 2021 in a continuous flow bioreactor. Chemical analysis demonstrated that the EPS varied in their carbohydrate and protein content and composition.

The adhesion studies revealed that the type and concentration of exopolymer forming a conditioning layer on the steel surface had a statistically significant influence on the attachment of cells to steel. In view of these results, the role of free surface energy in cell attachment is currently under investigation, to establish which is the key mechanism influencing irreversible bacterial adhesion to pre-conditioned steel. The latter takes into account chemical interactions between EPS and cells and alterations of the surface energy of steel due to the deposition of EPS.

Macrofouling processes: a developmental and evolutionary perspective.
Michael G. Hadfield, E. Carpizo-Ituarte, E.Holm, B. Nedved and C. Unabia
Kewalo Marine Laboratory, University of Hawaii, 41 Ahui St., Honolulu, HI 96813, USA

The marine world of 10,000 years ago was not characterized by ships, barges, docks, floats, and pilings. Thus we should attempt to imagine the habitat in that pre–maritime– human marine environment where they evolved in order to understand the biology of recruitment of common fouling species. Most of the invertebrate species typical of the fouling community are never found elsewhere. Most exist only on substrata where tidal exposure does not occur, especially in tropical and sub–tropical waters. In the pre–maritime–human environment this habitat must have been restricted to natural floating materials, mainly the drift logs, most abundant in bays and estuaries. Unlike larvae of species inhabiting other marine substrata, those of fouling–community invertebrates almost universally settle in response to non–specific biofilms, a habit we assume evolved long ago for settlement on floating marine material. Because of this commonality, we may be able to understand recruitment processes in this entire community of organisms if we can determine the nature of the processes in one or two typical species. We have been intensively studying the interactions between marine–biofilm bacteria and larval settlement in the ubiquitous warm–water, fouling polychaete worm *Hydroides elegans*. Larvae of *H. elegans* settle very rapidly in response to unispecies films from many, but not all, marine–biofilm bacterial species tested. The cellular–molecular mechanisms by which they detect chemical characteristics of biofilm bacteria are different from those used in typical chemoreception by most animals. Settlement in competent larvae is "primed" for a very rapid response. Metamorphosis occurs without *de novo* gene transcription and translation, and thus larvae attach to a surface biofilm within 15 min, complete primary–tube construction and metamorphosis in a matter of hours, and begin feeding in less than 10 hrs. Rapid settlement and metamorphosis in response to biofilms, traits that have great selective advantage to species living on substrates as ephemeral as floating logs, are typical of most fouling–community species.

Designing an environmentally safe marine antifoulant
John C. Harrington, Andrew Jacobson, Lorna S. Mazza and Gary Willingham
Rohm and Haas Company, Philadelphia, PA, USA

In the 1980's when tin-based antifoulants came under regulatory scrutiny, Rohm and Haas Company began to examine the isothiazolones as an environmentally preferable alternative to tin-based compounds. Our search generally followed the paradigm that environmental risk is a function of toxicity and exposure. We realized that it would be extremely difficult to design a marine antifoulant that was toxic to fouling organisms (e.g., tube worms and barnacles) but non-toxic to their closely related non-target organisms (e.g., mussels and oysters). Instead, we looked for compounds that would have reduced exposure—a short environmental half-life and/or partition rapidly into a matrix of limited bioavailability. The results of this investigation yielded Sea-Nine® 211 Biocide (2-n-octyl-4,5-dichloro-1-isothiazolin-3-one), a very efficacious compound. Unlike TBT, Sea-Nine degrades very rapidly in the environment with a half-life of less than 1 hour. Degradation involves cleavage of the isothiazolone ring and subsequent oxidation to metabolites with minimal toxicity to aquatic organisms. Sea-Nine and its metabolites rapidly and tightly adsorb to sediment and do not desorb when the sediment is disturbed. In contrast to TBT, there is minimal bioconcentration of Sea-Nine by aquatic organisms. The environmentally preferable characteristics of Sea-Nine were recognized by the receipt of the Presidential Green Chemistry Award in 1996.

Marine biological invasions: patterns and processes at regional scales.

Chad L. Hewitt and Marnie L. Campbell
CSIRO, Centre for Research on Introduced Marine Pests, GPO Box 1538, Hobart Tasmania 7001, Australia.

The patterns of marine invasions are determined by multiple factors: the frequency and availability of trade routes linking source and recipient regions; the relative susceptibility of recipient biota and communities; and the relative 'invasiveness' of source biota. These patterns are slowly emerging as more studies elucidate the numbers and types of species found in novel environments. Based upon these survey studies both within Australia and around the world, the link between historical geography of the environment and the relative contributions of various vectors becomes apparent. Wooden hull fouling and boring and dry and semi-dry ballast have historically contributed the greatest numbers and diversity of species to various regions. Ballast water has recently become a transport vector which has received a great deal of attention, yet despite numerous taxa identified in the ballast tanks, few actual introductions can be directly linked to ballast water inoculations. The regional susceptibility to invasions by species transported from the various vectors is presented with an analysis at the level of the bioregion by specific habitat and timing. The rates of invasions at the regional and local (port) scales are contrasted illustrating a consistent trend for an exponential increase in invasions through time, but also demonstrate the influence of local scale phenomena which alter the signal.

Preventing biofouling in finfish aquaculture: novel coatings and polymers

Stephen Hodson[1], Rocky de Nys[2], Peter Steinberg[2], Gregor Christie[3], and Peter Rothlisberg[4]
[1]University of Tasmania, School of Aquaculture and the Cooperative Research Centre for Aquaculture, P.O. Box 1214, Launceston, Tasmania, 7250 Australia.
[2]Centre for Marine Biofouling & Bio-Innovation, University of New South Wales, Sydney, NSW, 2052, Australia.
[3]CSIRO Manufacturing Science and Technology, Normanby Road, Clayton, Vic., 3169.
[4]CSIRO Division of Marine Research, PO Box 120, Cleveland, Qld, 4163, Australia.

One of the major problems facing aquaculture in Australia is the fast rate at which immersed surfaces (nets, floats, lines, shells etc) become fouled. Biofouling of fish cages leads to reduction of water transfer, which reduces the supply of dissolved oxygen and removal of waste products. There is also evidence that fouling communities act as a reservoir for pathogenic microorganisms. Australia's CRC for Aquaculture is developing antifouling polymers and coatings that release biodegradable antifouling compounds. The polymers can be extruded as filaments to be woven into netting, or as flat sheets for other applications. The coatings can be applied to fish cage netting and other mariculture equipment. Both coatings and polymers have shown broad-spectrum efficacy in field trials at mariculture farms. We will present results of recent field trials, and discuss new developments in production of these materials.

Assessing the environmental effects of anti-foulants

Jack Holland
Risk Assessment and Policy Section, Environment Australia, PO Box E305, Kingston, ACT 2604

The Risk Assessment and Policy Section of Environment Australia undertakes the assessments of the potential environmental impact of agricultural and veterinary chemicals for the National Registration Authority as part of the process for national registration of these substances. This process, including Environment Australia's role, will be clarified during the presentation.

The approach taken to undertaking environmental hazard/risk assessments will also be outlined, with particular reference to the assessment of anti-fouling substances, which are defined as agricultural chemicals by the relevant Commonwealth legislation. These compounds present a rather different exposure and hazard/risk profile from the mainstream chemicals and the presentation will be illustrated by using examples gained from experience in assessing such substances, as well as from the open literature.

The need for a proper evaluation of all new chemical anti-foulants, including a close examination of the leaching rate and the fate of the chemical in the marine environment once released, in addition to the chemical's specificity and toxicity to a wide range of aquatic organisms, will be stressed.

Bacteria immobilised in hydrogel: a new concept to prevent development of biofouling communities

Carola Holmstrøm[1,2], Peter Steinberg[2,3], Victor Christov[4] and Staffan Kjelleberg[1,2]
[1]School of Microbiology and Immunology, [2]Centre for Marine Biofouling and Bio-Innovation, [3]School of Biological Sciences, The University of New South Wales, Sydney 2052, Australia
[4]CSIRO Manufacturing Science and Technology, Normanby Road, Clayton, Vic 3039, Australia

A marine bacterium, *Pseudoalteromonas tunicata*, producing antifouling components and an *Escherischea coli* strain were used in this study to develop a method for the immobilisation of bacteria into a hydrogel. Different types of matrices immobilised with *P. tunicata* cells were screened using settlement of barnacle larvae as the bioassay. A polyvinylalcohol (PVOH) gel was demonstrated to constitute the optimal matrix because it allowed for an outflux of active biological components and remained stable in seawater. The (PVOH) gels immobilized with *P. tunicata* were inhibitory against barnacle larvae for two weeks. The presence of active bacterial cells in the matrix was tested by using the CTC-staining method and green fluorescent protein (GFP) tagged bacteria. The results suggest that no active *P. tunicata* cells could be detected in the gels after the immobilised gels lost their inhibitory activity against the larvae. To develop methods to increase the life-span of the immobilised gels, an *E. coli* strain was selected based on its cell size, stress resistance and the fact that a plasmid for expression of GFP could be transferred and maintained into the cells. Immobilised *E. coli* cells were normally found to be active in the PVOH gels for 2 months. However, the life-span of the immobilised gels were increased to more than 2 months by the incorporation of small particles together with the bacterial cells.

Investigation of the adsorption behavior of a mussel adhesive protein including kinetics of enzymatic cross-binding reactions

Fredrik Höök[1,2], Camilla Fant[1] and Hans Elwing[1]
[1]Department of Molecular and Cellbiology, Interface Biophysics, Göteborg University, Medicinaregatan 9C, SE-413 90 Göteborg, Sweden
[2]Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

We have studied adsorption and tyrosinase-induced crosslinking kinetics of *Mytilus edulis* foot protein-1 (Mefp-1) to/at a hydrophobic CH_3-terminated gold surface. This was done by combined use of Surface Plasmon Resonance (SPR), which measures the bound mass *excluding* bound water, and an extended version of the Quartz Crystal Microbalance (QCM-*D*) technique, which measures adsorbed mass *including* bound water and simultaneously the energy dissipation (*D*) (related to rigidity/viscoelastic properties) of the adlayer. According to SPR, the adsorbed mass of Mefp-1 was six times lower than that measured by QCM, which indicates adlayer of Mefp-1 binds (trap) a substantial amount of water. This was further supported by a huge increase in *D* upon adsorption, which suggests an extended very flexible adlayer. Upon exposure of preadsorbed Mefp-1 to tyrosinase, *D* decreased (increased rigidity) by a factor of 3, accompanied by an decrease in mass according to QCM. This is in accordance with crosslinking within and dehydration of the adlayer(s). In contrast, the SPR-data shows that addition of tyrosinase to preadsorbed Mefp-1 resulted in an increased mass of the protein layer(s), which suggests that binding of tyrosinase to preadsorbed Mefp-1 also occurs during the crosslinking reaction. Hence, these results provide unique information about surface binding and crosslinking mechanisms of Mefp-1, and open up a possibility for better understanding of marine bioadhesion in general, and for inventions of surfaces that will inhibit crosslinking of bioadhesives and hopefully also bioadhesion.

Antifouling paints and the global regulatory debate - an industry under scrutiny

Julian E Hunter
International Coatings, Akzo-Nobel, Stoney-gate Lane, Felling, Gateshead, Tyne and Wear, UK NE10 OJY

In recent years antifouling coatings containing biocides have taken centre stage with the world's regulatory authorities. Debate about the use of TBT continues at the global level at the International Maritime Organisation, although focus is now on agreeing a date for a mandatory TBT ban, enforceable throughout the world. With the inevitable demise of TBT comes more scrutiny of TBT-free biocides used in antifouling paints as concern is expressed that a ban of TBT should not simply be replaced by a different environmental problem arising from the us of alternatives.

This paper summarises the current status of current and evolving regulations affecting antifouling paints around the world, the antifouling debate at IMO-MEPC, a view on it's outcome and options going forward for the antifouling industry. The need for environmental risk assessment in evaluation of the potential environmental impact of existing and new biocidal antifouling products is also discussed.

Determination of realistic leach rates for environmental risk assessment

A.H. Jacobson[1], T.A. McGuckin[1], C. Nichols[1], G.L. Willingham[1] S. Arias[2], H.S. Elbro[2] and E.B. Kjaer[2]
[1]Rohm and Haas Company, Philadelphia, PA
[2]Hempel's Marine Paints A/S.

Risk assessments generally follow the paradigm, risk is a function of both exposure and hazard. The hazard component is obtained from toxicity testing data. The exposure component is a measure of the environmental concentration which depends upon inputs to the environment, environmental partitioning, and degradation rates. This paper examines various approaches to the estimation of environmental input values and discusses their relative validity.

Field methods utilizing static panels, ship patches, or field-monitoring devices may come close to real-world values. However, these methods are expensive, and time-consuming.
Several laboratory methods for leach rate determination have been developed (e.g., ASTM 5108-90 Organotin leaching rate method). The original purpose of such methodology was to compare the relative leach rate values for different paint formulations, and while these methods are useful for optimizing and comparing paint formulations, they were not designed to predict real-world leach rates. Moreover, it is evident that considerable work is still required to establish the precision of these methods.

A third possibility is to carry out a mass balance analysis. This is based on the assumption that all the biocide applied leaches out during the lifetime of the paint.

Mass balance analysis appears to give values which are more representative of realistic environmental load.

Disruption of the settlement of macrofouling organisms by pulse copper pollution events

Emma L. Johnston and Michael J. Keough
Department of Zoology, University of Melbourne Parkville VIC 3052

The impact of toxicants on marine fouling organisms is usually predicted from laboratory-based, constant-exposure, single species tests. However, toxicant releases into the marine environment are likely to vary in strength, duration and frequency. Toxicity may be modified by species interactions, indirect effects and fluctuating environmental conditions. As such, it becomes important to complement laboratory studies with investigations of the effects of the timing and frequency of pulse pollution events on the settlement of macrofouling assemblages.

I have used a field toxicant dosing system to investigate the impact of pulse copper pollution events on the settlement and development of assemblages of marine sessile organisms. Results of these tests show that the timing, frequency and location of pollution events can change the nature of the pollutant impact. Disruption of settlement was detectable in short term (2 week) and longer term (16 week) experiments and varied between sites. In the short term experiments, repeated simulation of the same pollution event at the same site but at different times had different deterrent effects on settlement. Settlement of the Serpulid polychaete *Hydroides elegans* in Port Shelter, Hong Kong, was greatly disrupted by pulse pollution events, yet recovery of the population occurred within weeks. Serpulid polychaetes in Port Phillip Bay were insensitive to pulse pollution events whilst adults of the ascidian *Ciona intestinalis* were susceptible. The rate at which indirect effects of pollution events became detectable also varied between sites depending on how quickly settlement space became a limiting resource.

Underwater hull cleaning into the 21st Century

David F. Jones
UMC International Plc, Warrior Close, Chandlers Ford, SO53 4TE, UK.

The imminent demise of TBT anti-fouling paints has already resulted in a dramatic upturn in the demand for underwater hull cleaning as ship owners opt for less effective tin-free alternatives. The future may lie with a new generation of biocide-free, low surface energy anti-fouling coatings which rely solely on their surface texture for their anti-fouling properties. However, conventional underwater hull cleaning methods scratch their surface and destroy their anti-fouling properties. This paper describes a novel machine which has been developed to provide back-up cleaning for these coatings and goes on further by describing two proposals for fully automatic systems. The author concludes by reviewing the financial implications of underwater cleaning as an adjunct to anti-fouling paints and as a stand alone means of fouling control.

Bacterial decay of wood in the marine environment

E.B. Gareth Jones, S.T. Moss and Venkatasamy
BIOTEC, National Centre for Genetic Engineering and Biotechnology, 73/1 Rama 6 Road, Bangkok 10400, Thailand
School of Biological Sciences, University of Portsmouth, King Henry 1st Street, Portsmouth, Hants., England

Wood in the marine environment is subject to attack by four groups of organisms: Molluscan, and Crustacean borers which are the most aggressive, and microorganisms that include the fungi and bacteria. Fungi have the ability to penetrate deeply into the wood while bacteria generally degrade the surface layers of the wood. However under certain conditions, in wood under anoxic conditions or preservative treated wood, bacteria can cause greater damage than fungi, as the latter are unable to grow under such conditions.

Bacterial decay of wood has received less attention than that devoted to the fungi and this can be accounted for by the difficulty in the study of bacterial activity. A number of decay patterns have been reported from narrow erosion, cavitation, to tunneling of the wood (Daniel, Nilsson and Singh, 1987). Tunneling is when bacteria preferentially decay the S2 layer of wood cell walls forming tunnels with chambers and chamber cross walls, which we have called tunneling type 1 (Mousouras, Jones, Venkatasamy and Moss, 1986). A second type of tunneling is caused by rod-shaped bacteria which burrow through the wood cell wall layers and form tunnels without the formation of chambers and chamber cross walls. This talk will focus on this second type of bacterial wood decay pattern with observations at the scanning and transmission electron microscope level.

Temporal trends in environmental concentrations of tributyltin and population status of sensitive species.

Jan Jonker[1], Joop Blok[1], James Keithly[2] and Mary Sue Brancato[2].
[1]Elf Atochem Vlissingen B.V., Haven 9850 Vlissingen-Oost, Vlissingen, Netherlands, NL4380.
[2]Parametrix, Inc., 5808 Lake Washington Blvd. NE, Suite 200, Kirkland, Washington, USA 98033.

Concern over release of tributyltin (TBT) in aquatic environments and impacts on non-target organisms arose in the early 1980s and led to the passage of regulations limiting use to commercial ships in many places around the world. Because commercial ships spend a great deal of time at sea, TBT use was prohibited on small craft. Monitoring programs in Europe, Japan and the United States have shown significant decreases in TBT in areas such as marinas that are used by small boats, and in areas such as commercial harbours and shipyards used by large vessels. The data from the U.S. monitoring programs show an average decrease of TBT concentrations of 67% in surface waters, 62% in sediments, and 39% in bivalve tissues. Monitoring in Japan since the late 80s demonstrated a similar rapid decline. Currently most water column samples are below the detection limit (3 ng/L). Surface water concentrations in the U.S. and Japan, where monitoring continues, are currently generally below the U.S. EPA marine chronic criterion and concentrations and effects have always been very localized. These programs show that generally low concentrations of TBT are present in the water column, that concentrations of TBT have decreased since regulation, and that TBT concentrations continue to decline. Based on current TBT concentrations, there are potential risks to <2% of aquatic species. In addition, populations of certain snails (*Nucella*), crustaceans, and oysters (*Crassostrea gigas*) sensitive to TBT and used as bio-indicators have shown both a historically localized response to TBT and population recoveries since regulation of TBT.

The roles and responsibilities of the International Maritime Organization's Marine Environment Protection Committee

Michael H. Julian
Australian Maritime Safety Authority, GPO Box 2181, Canberra City, ACT 2601, Australia.

The International Maritime Organization is a specialist agency of the United Nations responsible for the oversight and international regulation of maritime safety and marine environment protection. The Marine Environment Protection Committee (MEPC) is empowered to consider any matter within the scope of the Organization concerned with the prevention and control of pollution from ships. MEPC 'operates' two key international conventions; MARPOL 73/78 and OPRC'90; these conventions provide, through international agreement, a wide range of regulations and codes with the objective of protecting the marine environment from pollution by shipping.

One of the MEPC's high priorities during the next biennium (2000/2001) is the holding of a Diplomatic Conference to adopt an international agreement banning the use of organotin compounds which act as biocides in anti-fouling paint systems on ships.

Variation in adhesion strength of hard fouling organisms to fouling-release coatings
Christopher J Kavanagh, Michael P Schultz, and Geoffrey W Swain
Florida Institute of Technology, 150 West University Blvd, Melbourne FL 32901, USA

This paper compares the adhesion strengths of phylogenetically diverse hard-fouling species settled on silicone fouling-release surfaces. Experimental sets of silicone coatings were exposed in the Indian River lagoon, Florida in 1997 and 1998. Measurements of the shear strength of adhesion of barnacles, oysters and tubeworms were made bimonthly. Interspecific comparisons of adhesion strengths to the same fouling-release coating were made when several species were present coincidentally. Periodic settlement of balanoid barnacles (*Balanus eburneus*) over the duration of study allowed for an examination of changes in adhesion strength over time. An episode of settlement by another barnacle, *Balanus improvisus*, allowed an intrageneric comparison of barnacle adhesion strength.

Settlement of invertebrate larvae in the field: complex cues & complex behaviour
Michael J. Keough
University of Melbourne, Parkville, Victoria, Australia

Larvae of fouling organisms settling in the field encounter a wide range of potential cues. Some cues, such as those presented by biofilms, are complex and dynamic, so the cues associated with a particular surface may change at short time intervals. Just as cues change, so too can larval responses to those cues – larvae age, and they may deplete their energy reserves with increasing time in the plankton and become less selective. Individual larvae may also differ in their response to a given stimulus. The local hydrodynamic environment can also affect the ability of larvae to respond to stimuli. The combination of these processes means that settlement is unlikely to be highly predictable. Even if we know the distribution of potential cues (or deterrents), we may not be able to predict the subsequent colonization of surfaces with much accuracy, except under unusual circumstances, such as extremely high settlement rates of individual fouling species.

Biofouling and antifouling methods used in cooling water systems of marine power stations in France.

Michel Khalanski
EDF, DER, Département Environnement, BP 49 78401 Chatou Cédex, France.

Electricité de France (EDF) operates fossil fuel and nuclear power stations located on the coasts of the English Channel, the North Sea and the Mediterranean Sea. Marine power stations are equipped with once-through cooling systems using sea water. The cooling water requirements for each site range from 90 m^3/s to 246 m^3/s.
Two types of biological problems are encountered in operation of these cooling systems:
- clogging of water intake structures by drifting organisms; in particular sea weeds and sea gooseberries (*Pleurobrachia pileus*),
- development of micro-biofouling producing slime in heat exchangers, and of macro-biofouling species.

This paper presents an overview on the EDF action programme against biofouling in marine power stations, comprising three parts:
- long-term survey of biofouling in ccoling water systems.
- studies on the biological cycle of the major biofouling species, modelling the growth of mussels,
- use of selected antifouling methods based on efficiency, cost and environmental acceptability.

Regulation of antifouling coatings in Australia

Ian Kirkegaard
Office of the Environment Protection Authority, South Australia

In 1990, the Council of Ministers for the Environment for Australia and New Zealand (now ANZECC) resolved to introduce consistent controls on TBT paints, with review in 1995. That review, and other action, was taken up in the strategy 'Working together to reduce impacts from shipping operations' which sought to co-ordinate management of all environmental impacts from shipping.

Through a condensed history of those actions, the paper discusses the challenges of seeking uniformity of action within a political federation of states, and with a neighbouring country. It also looks at TBT as a 'hot' public concern, but which lies within larger but less focussed environmental issues.

The more recent ANZECC strategy has concentrated on practical, 'no regrets' actions that can be taken now to minimise impacts of fouling and anti-fouling on the environment of Australia and New Zealand. It has benefited from consultation with the public and with particular vested interests.

Volatile substances from adult extracts induce larval settlement of the barnacle *Balanus amphitrite*

Hitoshi Kitamura and Noriaki Hirata
Faculty of Fisheries, Nagasaki University, Nagasaki 852-8521, Japan

Chemical basis for the gregariousness of the barnacle *Balanus amphitrite* consists of several kinds of cues for larval settlement. Glycoproteins isolated from adult barnacles termed as SIPC (MW>200kDa) as well as sugar chain structures were reported to play important roles in inducing larval settlement (Matsumura *et al.*, 1997). On the other hand, peptide pheromone and synthetic peptides also enhanced larval settlement (Rittschoff). From these evidence, amino acid related compounds are thought to be the chemical cue. We isolated from conspecific adults volatile substances which induced larval settlement. Crude extract from crushed adult barnacles were distilled for 30 minutes to separate volatile substances. Both distilled and the remaining fraction showed high settlement inducing activity. An active factor was also extracted by n-pentane from distilled fraction. GC-MS and GC analysis of the pentane extract revealed benzene compounds as a chemical cue. The commercially available substance also showed high inductive activity at 100 pg/liter.

Signal mediated bacterial colonization

Staffan Kjelleberg
School of Microbiology and Immunology, University of New South Wales, Sydney, NSW 2052, Australia

It has recently been demonstrated that extracellular signals such as acylated honoserine lactones (AHLs) can mediate both the formation of complex bacterial biofilms as well as bacterial swarming or surface motility which allows for rapid colonisation of surfaces. Because, complex bacterial biofilms reminiscent of multicellular structures appear to be a common form of biofilms, and a high proportion of marine bacteria has been found to exhibit surface motility, signalling is likely to be fundamental to the ecology of surface colonisation by bacteria.

The recent discovery that furanones, produced by the Australian red alga *Delisea pulchra*, have structural similarities with AHLs and deter fouling by bacteria on the surface of the plant, led to the hypothesis that furanones successfully prevent colonisation of a diverse range of marine bacteria by serving as specific antagonists of AHLs.

Laboratory experiments on the means by which furanones inhibit swarming revealed the specific competition between furanones and AHLs and the specific down regulation of the genes that mediate expression of the swarming phenotype. Further studies of the effect of furanones on swarming of bacteria from the surface of *D. pulchra* also demonstrated the inhibition of swarming by natural concentrations of furanones.

In comparison with the information that is available on signal driven biofilm formation and surface motility, very little information exists on the role of signals or the role of signal antagonists in attachment of bacteria to surfaces. Both laboratory and field experiments and demonstrated a structure function dependent specific down regulation of bacterial attachment by the addition of furanones, suggesting that signals are important also in mediating the initial stages of bacterial surface colonisation.

Such findings have general implications for the role that signals may play in bacterial colonisation. Rather than being dependent on a certain population density, which is the traditional model for biofilm formation, regulation of attachment requires a different model in which signal based regulation occurs in a signal cell.

Environmental risk assessment of Irgarol® 1051 antifouling biocide

Brigitta König[1†], Peter Dollenmeier[1], Stephan Klotz[1], Dick Balcomb[2] and Simon Lord[2]
[1]Ciba Speciality Chemicals Inc., Additives Division, CH-4002 Basel, Switzerland
[2]Ciba Speciality Chemicals Corporation, USA
[†]Author for correspondence

Irgarol® 1051 biocide, hereafter referred to in this abstract as the algaecide, is highly effective for use in antifoulant paints. It specifically prevents the growth of algae and other photosynthetic organisms on boat hulls, a key step in inhibiting the fouling process. Due to the mode of activity, toxicity to algae is very high, whereas the toxicity to crustaceans, fish or other animals is comparatively low.

The environmental fate of the algaecide was recently investigated in a microcosm study by determining degradation rate and metabolism in a simulated coastal marine environment. The results of the study showed a half-life of 24 days for disappearance of the algaecide. A primary metabolite appeared concurrently for the first month, then declined with approximately the same half-life as the algaecide. Neither the algaecide nor the metabolite accumulated in the sediment. Toxicity of microcosm water to algae declined in parallel with the concentrations of the algaecide, indicating that once degradation takes place, no residual toxicity is left in the microcosm.

To address the question of possible environmental accumulation, a monitoring study was performed in the Stockholm archipelago, an area of high boat density. Samples of water and sediment were taken over the full yachting season at varying distances from a very large marina. The results show detectable algaecide concentrations only within highly exposed marinas and only during the main boating season. In late autumn, all algaecide levels at all sites returned to the detection limit. Sediment levels were also close to the detection limit, indicating that there is no evidence of accumulation of the algaecide from year to year, neither in water, nor in sediment.

Irgarol® is a registered trade name of Ciba Specialty Chemicals, Inc. for 2-(tert-butylamino)-4-(cyclopropylamino)-6-(methylthio)-1,3,5-triazine

Hydrodynamic evaluation of the performance of foul release antifouling coatings

Brett S. Kovach and Geoffrey W. Swain
Ocean Engineering Program, Florida Institute of Technology, 150 West University Blvd., Melbourne, Florida 32901, USA

International restrictions on the use of biocides in antifouling paints have directed special attention towards the development of nontoxic foul release coatings. These coatings provide a minimally adhesive surface that will become fouled under static conditions but when subjected to an external flow, hydrodynamic forces can remove the fouling. A method to evaluate the performance of foul release coatings has been developed that measures the drag forces on communities of fouling to determine the free stream velocities required for fouling removal. Visual evidence of foul removal is also recorded. Measurements are made on fouled static immersion test panels using a floating element skin friction meter contained within an instrumented foil that is dragged from the side of a 7m powerboat at predetermined speeds. During testing the shear force, flow velocity, and video of the foul release are recorded simultaneously. Two commercially available and one experimental foul release coating were tested and their performance was compared to that of a copper self-polishing system.

Analytical characterization of natural marine biofilms

M.E. Lai[1†], V. Scotto[1] and A. Bergel[2]
[1] ICMM - CNR Istituto per la Corrosione Marina dei Metalli, Via De Marini 6, 16149 Genova, Italy
[2]Laboratoire de Génie Chimique, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse, France
[†]Present address: Laboratoire de Génie Chimique,Toulouse, France

The authors, interested to single out what bioproducts in marine biofilm could be associated to the high corrosion rates characterizing the behaviour of s.s. in the sea, have studied the structure and composition of natural biofilms by using analytical methods. The paper summarizes the main results of the study in which a particular attention has been given to the structure of the extracellular polymeric matrixes recently recognized as "key " factor for explaining the biocorrosion mechanisms.

The organisms succession in the colonization of the materials immersed in natural seawater, the incidence of the detritus and of the EsoPolymeric Substances (EPS) on biomasses, the evolution in time of the physiological activities in biofilm, the carbohydrate monomers contributing to the building up of the EPS matrixes together with the oxidoreductase enzymes entrapped in the slime are here evaluated and described. The EPS fraction, which in weight corresponds to the 30% of the intracellular carbohydrates, shows a protein content waving in between 5%-30% of the carbohydrate amount and a percentage distribution of single carbohydrate monomers, which is substantially indifferent to seawater temperature and season. The EPS matrixes , meanly formed by exose, (65-70%)- pentose (15-20%), , chetose (0-2%) - uronic acids (10-20%), predominantly glucuronic and galacturonic acids but lacking of reducing sugars , entrapped oxidoreductase enzymes as SOD, catalase and peroxidase which in mature biofilms reach mean activities of about 250 mU/cm^2 - $50mU/cm^2$ and 0,5 mU/cm^2 respectively.

These data refer to biofilms grown in Mediterranean Sea in very different environmental conditions and will be used in lab to simulate the natural corrosive environments that biofilms create at s.s. surfaces.

The role of conditioning films in the attachment of biofouling bacteria

A. P. Leis and R. P. Schneider
School of Microbiology & Immunology, The University of New South Wales, Sydney NSW 2052 AUSTRALIA

The attachment of fouling microorganisms in natural waters is preceded by the adsorption of a complex conditioning film of organic macromolecules and inorganic species. To study the characteristics of environmental conditioning films, marine, freshwater and brackish water samples were obtained from various sites in Sydney, Australia. The 0.1μm fractions generated from each site were used to examine the role of complex conditioning films in the initial adhesion of *Psychrobacter immobilis* SW8, a Gram-negative bacterium chosen as a model biocolloid. Conditioning films were formed for 1 hour on a series of radiofrequency plasma polymers with defined functional groups and variable surface free energies. The conditioning solutions were altered to measure the effects of ionic strength, pH and molecular weight distribution on adhesion. Contact angle measurements indicated diversity of conditioning films (1) relative to clean substrata, (2) for each type of substratum exposed to the same water sample, and (3) between similar substrata exposed to different water samples. Conditioned substrata always promoted retention relative to the unconditioned control. While the extent of bacterial adhesion was found to be influenced by the source of the conditioning film, there was no correlation between water contact angle and adhesion, indicating that surface free energy is not the dominant physicochemical regulator of adhesion. High molecular weight fractions always exhibited greater retention than the corresponding low molecular weight fractions. This effect, however, could be manipulated by changing the ionic strength, indicating a dependence on molecular size and conformation.

Fouling control in the 21st Century: an Australian Defence perspective

John A. Lewis
DSTO Aeronautical & Maritime Research Laboratory, GPO Box 4331, Melbourne 3001, Australia

The Royal Australian Navy has continued to use TBT copolymer antifouling paints to ensure optimum performance, corrosion control and fleet readiness of the major vessels of the fleet. However, a comprehensive program has been underway within DSTO, sponsored by Navy, to actively seek and evaluate potentially more environmentally benign methods of fouling control. The requirement is for 4+ years effective fouling control for both surface ships and submarines, including those clad with elastomeric materials. Tin-free biocidal coatings and fouling release coatings have been a focus of recent studies with some promising results. For steel-hulled surface ships, copper acrylate coatings have shown superior performance in static and dynamic immersion studies and patch trials, and planning is underway for the first full hull application. Silicone elastomer fouling release coatings have been under evaluation on steel, alumium and elastomeric surfaces. Results have been promising but, to ensure optimum vessel performance, a definite need exists for improved cleaning technologies, particularly for slow moving vessels or vessels spending extended periods alongside. The search for environmentally acceptable methods is, however, far from over. Looking into the 21st century, the optimist can hope for continued advances in fouling control technology to provide totally non-toxic solutions, either with improved fouling release technology or chemically deterrent rather than toxic surfaces.

ElectroMagnetic Antifouling Shield (EMAS) - a novel antifouling technique for optical sytems?

Thomas Leya[1], Annette Rother[1], Torsten Müller[1], Günter Fuhr[1], Martina Gropius[2] and Burkhard Watermann[2]
[1]Humboldt-Universität zu Berlin, Invalidenstrasse 42, 10405 Berlin, Germany
[2]LimnoMar, Bei der Neuen Münze 11, 22145 Hamburg, Germany

Optical systems such as video camera lenses and sensors immersed in the sea over prolonged periods, are subject to fouling. Conventional and pigmented antifouling paints cannot be applied for obvious reasons. We are testing high frequency alternating current (hf-ac) fields around ultramicroelectrodes on glass substrate for their effect on populations of fouling organisms such as cyprid larvae of the barnacle *Balanus amphitrite amphitrite* DARWIN, the diatom *Amphora coffeaeformis* (AGARDH) KÜTZING and zoospores of the Green alga *Ulva lactuca* LINNAEUS. Our concept is that hf-electromagnetic fields can induce breakdown at the outer and inner cell membranes so that fouling organisms are disturbed during their settling routine and rejected.
The electric regimes applied to the electrodes consist of continous hf-ac and of a combination of pulsed ac (membrane breakdown) with short term dc (direct current) components (hydrolysis and pH shifts). To detect cell damage, fluorescence microscopy and confocal laser scanning microscopy (CLSM) are in use. Investigations e.g. in cyprid larvae show paralysis effects and death. Localization of damage within cells or tissues is studied using ultra thin sections and histological stains. Field tests in the Baltic Ocean are under way. Parallel tests are being run on chips coated with a monomolecular layer of reactive polymers using the Langmuir blodget technique. It is possible to combine hf fields and such 'see-through' coatings.

Interpreting spatial relationships between marine bacteria and localized corrosion on steels

B.J. Little[1], R.I. Ray[1] and J. Jones-Meehan[2]
[1]Naval Research Laboratory, Stennis Space Center, MS 39529-5004
[2]Naval Research Laboratory, Washington, DC 20375-5320

Diagnosis of microbiologically influenced corrosion on iron-containing substrata exposed in marine environments cannot be based solely on spatial relationships between large accumulations of bacterial cells and corrosion products. Laboratory and field experiments were designed to evaluate spatial vs. causal relationships between marine bacteria and localized corrosion on stainless steel and coated carbon steel using microbiological and surface analytical techniques.
In laboratory experiments, ferric corrosion products produced by crevices in 304 stainless steel in abiotic seawater were allowed to accumulate before addition of marine bacteria. Large numbers of bacteria were associated with corrosion products after brief exposures. Carbon steel coupons coated with several topcoat/midcoat/primer combinations were scored to produce intentional defects in the coatings before exposure to natural and abiotic seawater. All coating/defect combinations were exposed with and without external zinc anodes. When either a zinc primer or a zinc anode provided cathodic protection, defects were filled with calcareous deposits and in natural seawater contained only isolated bacterial cells, similar to areas of intact coating. In the absence of cathodic protection ferric corrosion products and large accumulations of bacteria were co-located within defects in natural seawater. Bacteria were preferentially attracted to ferric corrosion products in coating defects and crevices and that attraction was more influential than topography in determining the spatial distribution of bacterial cells. The nature of the attraction is currently under investigation.

Cathodic protection studies of naval ships

Peter L. Mart, Neil Gage, Brian T. Moore and Heidi K. Millington
DSTO Aeronautical and Maritime Research Laboratory, GPO Box 4331, Melbourne Vic. 3001, Australia

Royal Australian Navy ships mostly use sacrificial anode cathodic protection (CP), although some ships are fitted with impressed current cathodic protection. With the steady improvement in marine paints, a balance must be struck between the competing requirements of achieving the maximum time between anode replacements, yet not over protecting the ship and causing paint deterioration. DSTO has three approaches to studying hull CP requirements, with the aim being to achieve an optimal potential profile for the ship, whereby critical areas are protected under all conditions. A commercial corrosion software package is used to calculate potential and corrosion current distribution over the hull. Both sacrificial anodes and impressed current anodes can be modelled. Physical scale modelling is also used to predict full-scale hull potentials, and to check the validity of computer calculations. Finally, underwater data loggers are attached to a ship's hull in regions of interest, enabling measurement and recording of the hull potential while the ship is under way. Results will be shown of ongoing studies with each of these tools in optimising the cathodic protection requirements of RAN vessels such as the new ANZAC Class frigates.

Molecular basis of larval settlement, particularly barnacles: are there unifying themes and can they be exploited in antifouling?

Kiyotaka Matsumura[1], Pauline Smith[1], John Knight[1,2], Mizue Yamazaki[1] and Anthony S. Clare[1]
[1]Marine Biological Association, Citadel Hill, Plymouth, PL1 2PB, UK
[2]Department of Biological Sciences, University of Wales, Swansea, Singleton Park, Swansea SA2 8PP, UK

The mechanisms of perception of larval settlement cues have been the subject of fundamental interest for many years and more recently, they have also been examined in the context of antifouling. The rational behind the latter studies is that if the mechanisms can be elucidated, it may be feasible to interfere with the process(es) and inhibit settlement. This presentation will focus on the nature of barnacle settlement cues and our understanding of how the cues are translated into attachment and metamorphosis. Barnacles potentially respond to multiple chemical cues at settlement. The possible outcomes of encounters between settlement stage cypris larvae and substrata are influenced profoundly by larval age. Although the hormonal control of metamorphosis bears similarity to that of holometabolous insects, the transducers and pathways involved in settlement have much in common with those of non-fouling species of marine invertebrates but not with the only other major fouling species that has been examined. Initial optimism regarding the prospect of broad-spectrum antifouling based on interference with signal transduction pathways, whether through natural or synthetic means, must now be tempered in the light of these data.

Probabilistic modelling of marine immersion corrosion of steels

Robert E. Melchers
Department of Civil, Surveying and Environmental Engineering, The University of Newcastle, NSW 2308, Australia

The study of the immersion corrosion of mild and low alloy steels occupies a fundamental position in understanding and predicting the material loss for industrial coastal structures, ships and offshore systems. Previously the mechanics of corrosion of mild and low alloy specimens in marine immersion conditons was discussed and a probabilistic model for its description given. The early part of the model has been used in the study of field data for 4x12 inch specimens, tested as part of an ASTM sponsored 1980's world-wide 5-year study.

It was found that, contrary to most opinion, a number of important influencing factors can be identified. There is a significant effect of water temperature for the field samples. This is consistent with little-known laboratory observations and other field observations. As might be expected, the other major is the degree of water aeration. This is influenced by consumption of oxygen in the corrosion process, the consumption of oxygen by biological organisms and the rate of replenishment of oxygen. In turn, the latter is affected by transport considerations. Details of these matters will be outlined.

The paper will also describe the effect of water salinity. Under normal conditions the corrosion of mild and low alloy steels is increased under lower salinity conditions, that is, provided the pH remains essentially the same. However, there are common conditions where the pH is increased and then corrosion in brackish waters may be significantly reduced. It will be shown that this could explain some historically apparently inconsistently lower than expected field corrosion observations. Finally the paper will outline the current state of the probabilistic model so far developed.

Possible inoculation in port areas resulting from spawning of hull-fouling organisms.

Dan Minchin and Stephan Gollasch
Marine Institute, Fisheries Research Centre, Abbotstown, Dublin 15, Ireland.

Fouling organisms on the hulls of ships are in transit worldwide on a regular basis. Although organotin paint coatings have considerably reduced the volume of organisms in transit, these have a limited period of effectiveness that may be less than the inter-docking time. Consequently treated vessels immersed over long periods provide opportunities for fouling communities to develop. Shipping enables many species to become generally distributed to areas outside of their natural range. Most of the fouling organisms are sessile and will remain attached until such time as they are removed in dry dock. Some individuals attached to vessels in transit will become scraped off, or will drop off hulls, but the opportunity for the development of a new population by this means is normally remote. Ships normally pass through a range of temperatures while in passage, but there are often rapid fluctuations of temperature to be found in port areas. These changes in temperature may provide cues for the spawning of some species in the fouling communities and thereby result in a release of zygotes. Should sufficient zygotes be produced that subsequently settle they will need to be in sufficient proximity to each other in order to reproduce and maintain the population. Studies of the effect of temperature fluctuations and multi-species spawnings of some temperate invertebrates in Irish sea loughs does provides a basis for this hypothesis. As vessels can carry a wide range of fauna including some commercial species there may be implications for a transfer of some diseases or pests in areas where aquaculture is practiced. As organotins become replaced by environmentally less toxic paint coatings, port areas will become less contaminated by organotins. Such conditions may promote the effectiveness of exotic species inoculations.

Investigation of strain capacity of aged polymeric coating on steel

Magdalena T. Molin and Anders Y.J. Ulfvarson
Department of Naval Architecture and Ocean Engineering, University of Chalmers, SE-412 96 Gothenburg, Sweden

Polymeric epoxy coatings are often used as corrosion protection in water ballast tanks of ships. Although the coating is not subjected to wear, except for the splashing impact of the ballast water, the coating fails. Inspections have showed coating damage in stress concentration areas. In these areas, local yielding occurs. The yielding results in locally very large accumulated strains. The ductility of the coating decreases with ageing. Thereby, the interaction system between steel and coating is weakened.
Experiments performed show the failure process in aged coating on steel substrate for tests carried out at increasing level of strain. The type of failure and crack growth process in the coating was thoroughly studied and documented by high-speed digital video recording. Examination by microscope and Scanning Electron Microscope determined the sizes and depths of the cracks in the coating. In addition, low cycle fatigue tests were performed for the aged coating on steel substrate. The numbers of cycles to failure for the coating, at certain strain levels were settled. Furthermore, a method for estimating the service life for aged coatings in ballast tanks is discussed.

Screening of the bioactive substances against the larvae of the oyster *Crassostrea madrasensis* with emphasis on toxicity and antifouling activity

P. Srivutha Murthy[1], V.P. Venugopalan[2], K.V.K. Nair[2] and T. Subramoniam[1]
[1]Department of Zoology, University of Madras, Guindy Campus, Chennai 600 025, Tamil Nadu, India
[2]Water and Steam Chemistry Laboratory, BARC Facilities, Kaplpakkam 603 102, Tamil Nadu, India

The development of non-polluting antifouling compounds that can be incorporated into antifouling coatings involves screening of compounds for their activity against a test organism and determination of their effective concentration. Extracts from *Avicennia*, a mangrove plant, *Sargassum myriocystum*, a common seaweed, and two species of sea cucumber, *Holothuria atra* and *Holothuria scabra*, were assayed for antimitotic-cytotoxic bioactivity against the fertilised eggs of the oyster *Crassostrea madrasensis*. Assays that tested toxic and antifouling activity were performed. All the three groups tested are known to be potential sources of environmentally safe compounds, have shown promising activity, and are found to be rich sources of novel compounds. The present study has been carried out using the larvae of the tropical oyster *Crassostrea madrasensis*, a common fouling organism, with regard to the toxic effects on different veliger stages and effect on the settlement of the pediveliger larvae. Significant differences in the antimitotic-cytotoxic response were observed. High mortality rates of the fertilised eggs were observed with extracts from *Holothuria atra* (82.0%), *Holothuria scabra* (69.0%), *Sargassum myriocystum* (53.0%) and *Avecenia* sp. (39.0%). Acute responses to crude methanol extracts from *Avecenia* sp., *Holothuria atra*, *Holothuria scabra* and *Sargassum myriocystum* were toxic to the larvae during their late stages of development at concentrations as low as 10 µg/ml. The respective mortality rates of pediveliger larvae were 82.6%, 65.0%, 68.3% and 74.0%. The early stage larvae (*D shaped* larvae) were more resistant to the compounds. All the assayed extracts displayed settlement inhibition activity with maximum inhibition observed with extracts of *Holothuria atra* (97.6%), *Sargassum myriocystum* (97.0%), *Holothuria scabra* (95.4%) and *Avecenia* sp. (94.3%).

Induction of settlement and metamorphosis of the larvae of pearl oyster *Pinctada fucata* (Gould) by biofilm bacteria

P. Srivutha Murthy[1], V.P. Venugopalan[2], K.V.K. Nair[2] and T. Subramoniam[1]
[1]Department of Zoology, University of Madras, Guindy Campus, Chennai 600 025, Tamil Nadu, India
[2]Water and Steam Chemistry Laboratory, BARC Facilities, Kaplpakkam 603 102, Tamil Nadu, India

The induction of settlement and metamorphosis of competent pediveliger larvae (18 d old) of the Indian pearl oyster *Pinctada fucata* by eleven different bacterial strains, isolated from biofilms formed on various surfaces, was evaluated. All the strains proved to be potent inducers of settlement. The induction resulted in more than 62% (62.8 to 88.3%) of larvae settling within 120h compared to 11.8% in the control. The strains showed marked variation (27.9 to 72.0%) in their ability to induce metamorphosis, as compared to 7.2% in the control. High incidence of metamorphosis was observed on surfaces covered by biofilms of *Alteromonas haloplanktis*, *Vibrio furnissi*, *Flavobacterium* sp. and *Pseudomonas* sp., resulting in 72.0%, 62.2%, 53.7% and 49.8% metamorphosis respectively. Settlement behaviour was initiaited within 10-15 min, and attachment within two hours upon release of larvae on to filmed surfaces. On the other hand, settlement behaviour on unfilmed surfaces was initiated only after 90 min. Generally, the morphogenetic phase of metamorphosis was initiated after 2h of larval introduction onto the filmed surfaces, as compared to unfilmed surfaces where it was initiated after 12h. The results suggested that induction of settlement and metamorphosis could differ with strains consituting the biofilm. Neither heat treatment nor treatment of the bacterial film with formalin affected larval settlement. However, lower rates of metamorphosis were observed on heat-killed biofilms of *Alteromonas haloplanktis*, suggesting the involvement of heat-labile bacterial products in the metamorphic induction. The results are discussed in the light of settlement and metamorphic behaviour of this tropical bivalve mollusc of primary importance to the aquaculture industry.

Introduced marine bryozoans of Australian waters

Radhakrishnan Nair[1], Chad L. Hewitt[2] and Marnie L. Campbell[2]
[1]Anamika Consulting, 84 Lane Street, Wentworthville, NSW 2145
[2]Centre for Research on Introduced Marine Pests, CSIRO,Hobart 7000

Many introduced marine organisms are known in Australian waters. This paper attempts to describe several bryozoans including the introduced species collected from various ports and harbours of Australia and provides information on their biogeographical distribution. The examination of material revealed the presence of a dominant representation of Gymnolaemates with high ascophorine species diversity. Cyclostomes were poorly represented. A revised list of introduced marine bryozoans is given and the possibility of various mechanisms involved in bioregional translocation of species is discussed.

Electrochemical prevention of marine biofouling using titanium nitride

Tsuruo Nakayama[1], Hitoshi Wake[1], Kin-ichi Ozawa[1], Mina Okochi[2], Noriyuki Nakamura[2] and Tadashi Matsunaga[2]
[1]Central Research Laboratory, Pentel Co. Ltd., Soka, Saitama 340-0017
[2]Department of Biotechnology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

A biocompatible material, titanium nitride (TiN), with very low resistance and good electrochemical stability was used for electrochemical prevention of marine biofouling. We have developed the technique for prevention of marine biofouling by electrochemical killing of microorganisms attached to electrode surfaces. The electrochemical killing method that is based on direct electrochemical reaction between cell and electrode, enables to kill microorganisms by application of the potential around 1.0 V. In this study, TiN layer formed onto titanium plates by reactive sputtering was used for electrochemical killing of marine bacterium, *Vibrio alginolyticus* cells. By applying a potential of 0.8 V vs. Ag/AgCl in seawater for 30 min, 98.7% of the cells attached on the electrode surface were killed. Changes in pH and generation of chlorine were not observed at this potential. Also, TiN-coated film was formed using radio-frequency arc spraying and has been applied for the electrochemical prevention of biofouling. By applying the controlled potentials in the field experiment, the attachment of the organisms on TiN-coated film was prevented.

Electrochemical prevention of marine biofouling by electroconductive paint containing metal oxidized particles

Mina Okochi[1], Makoto Tsubio[2], Noriyuki Nakamura[1] and Tadashi Matsunaga[1],
[1] Department of Biotechnology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588
[2] Research Center, Chugoku Marine Paints, Ltd., Ohtake, Hiroshima 739-0652, Japan

The expansion of microfouling is undesirable on many surfaces, such as industrial process equipment, drinking water distribution systems, and ship hulls. This results in energy loss and reduced performance due to the necessity of regular cleaning. Recently, we have developed the electrochemical method for prevention of biofouling by killing microorganisms with application of the potential around 1.0 V. This killing method is based on direct electrochemical reaction of intracellular substances and enables to kill microorganisms without generating chlorine. In this study, the use of metal oxidized particles that have relatively weak toxicity were investigated for more efficient electrochemical killing and efficient prevention of biofouling. Using the electrode containing 30% metal oxidized particles and 70% carbon, cells on the electrode surface were killed by applying the potential of 1.0 V for in 30 min. Also, the elution of metal ion measured using an atomic adsorption spectrometer by frame atomization after 1 month electrolysis in seawater was below detection level. This biofouling prevention method would be effective and might be environmentally friendly method.

Layered imaging studies of the marine bacteria *Pseudomonas paucimobilis*

I.Penegar, J.R.Smith, C.Toque, S.D.A.Connell and S.A.Campbell
Applied Electrochemistry Group, University of Portsmouth, St.Michaels Building, White Swan Road, Portsmouth PO1 2DT, UK

Atomic Force Microscopy Layered Imaging allows an overlay of force-distance measurements from an entire image frame. From these data, force-distance profiles may be extracted at any point on the image and, hence, surface adhesion, hardness and the elastic modulus of samples can be measured by viewing individual layers of samples. In biological systems, AFM Layered Imaging has been used to investigate cellular structure and adhesion by correlating force-indentation curves with specific locations in the cell. More recently, the elastic properties of biomaterials such as vesicles, platelets and gelatin have been evaluated.

In this paper, we report the use of this technique to determine the Young's Modulus for bacterial cells of the genus *Pseudomonas paucimobilis*. These copper-resistant microorganisms were isolated from copper-nickel panels situated on an exposure trial raft in Langstone Harbour. Such species are of particular interest as the current revival in the use of copper based materials for antifouling purposes brings with it the attendant problems of bioaccumulation of metals in the ecosystem. AFM Layered Imaging investigations into the morphology and elasticity of *Pseudomonas paucimobilis* as a function of copper concentration in the environment (Figures 1 and 2) showed changes in (a) cellular dimensions and (b) elasticity. A decrease in the Young's Modulus from 74.5 kPa in copper free media to 44.2 kPa for cells grown in copper containing media, was observed, suggesting modification or interaction of copper ions with the cell wall.

Enzyme activity of marine fungi

S.B. Pointing
Department of Ecology and Biodiversity, The University of Hong Kong, Pokfulam Road, Hong Kong, HKSAR China

The diversity of fungi isolated from decayed wood in marine environments is high. Several strains have been demonstrated to produce soft-rot or white-rot decay features, with significant biodeterioration of in-service wood as a consequence. The mechanism of wood decay by marine fungi has been investigated and activity of the enzymes responsible demonstrated. Cellulose breakdown involves a suite of hydrolytic enzymes comprising endoglucanase, cellobiohydrolase and β–glucosidase. Xylan, the major constituent of hemicellulose is hydrolysed by an endo- type xylanase to soluble reducing sugars. Lignin degradation has also been demonstrated, with associated production of the lignin modifying enzymes laccase and Mn-dependant peroxidase. Interestingly variations in salinity appear to have little effect on polyose degrading enzyme titre, whereas lignin modifying enzyme production appears more sensitive to changes in salinity. Those strains associated with relatively aggressive wood decay generally display significantly higher enzyme activities.

Novel shipboard applications of cylindrical clays

Ronald Price[1], Bruce Gaber[1] and Simon Marsters[2]
[1]Naval Research Laboratory, Washington, DC 20375
[2]New Zealand China Clays, Auckland, New Zealand

Halloysite clays are naturally occurring aluminosilicate materials that exhibit a cylindrical morphology. These clays may be used as carriers for a wide variety of active agents and employed in several of the ships systems as a mechanism for controlled release. One major applications area for which they are suited is that of biofouling control. Biofouling on ship hulls may be controlled by repellents or non-metallic biocides. However, the fouling may be internal and range from the control of mildew in the ships living quarters to microbial contamination in the fuel tanks, microbial growth in the bilge or microbial, fungal or insect infestation within the ships cargo holds.

We will discuss the mechanism and characterization of release from cylindrical clays and from clays mixed as fillers in marine coatings.

Macrofouling role of mussels in Italian Seas

Giulio Relini[1] and Manuela Montanari[2]
[1] Istituto di Zoologia, Laboratorio di Biologia Marina ed Ecologia Animale, University of Genoa, Via Balbi, 5 - 16126 Genoa, Italy.
[2] Istituto per la Corrosione Marina dei Metalli, Consiglio Nazionale delle Ricerche, Via de Marini, 6 - 16149 Genoa, Italy.

After more than 30 years of research on fouling communities and their patterns and development in different environments (ports, estuaries, lagoons, shallow and deep, inshore and offshore waters) or on structures (wharves, power stations, intakes, platforms, ship hulls...) all around Italy, a picture can be drawn of macrofouling in Italian Seas and, in particular, the role of *Mytilus galloprovincialis* Lam. mussels can be outlined.

In most environments, the community dominated by mussels is considered a final and quite stable association up to 20 m depth, something which however is not always reached because of local environmental peculiarities. Mussels are the main fouler on offshore structures where they account for 80% to 98% of the total fouling wet weight, as results from platforms (gas extraction, oil-rigs) or buoys that have been examined in the Adriatic, Ionian, Tyrrhenian and Ligurian Seas. In the Adriatic Sea (Ravenna platforms), after one year, at surface level, mussels can reach a wet weight of more than 90 Kg/m^2 with 6-7 cm of shell length. In the Ionian Sea (Crotone platform) mussels reach, at surface level, 6 Kg/m^2 and 3.5 cm length, and in the Ligurian Sea (Genoa platform), at surface level, 26 Kg/m^2 and 6.2 cm length. On concrete blocks of the artificial reef deployed near Ancona (Central Adriatic), up to 120 Kg/m^2 of mussels with 5-6 cm shell length have been harvested after a one year settlement at 7-8 m depth. In the Tyrrhenian Sea, up to 70 Kg/m^2 of mussels with average valve length of 6.2 cm were collected on concrete blocks of the artificial reef submerged off the mouth of the river Tiber, while in the artificial reefs of Sicily and Liguria mussels are absent.

The main settlement period of mussels in Italian waters occurs in spring (May); sometimes there is a second, less significant, settlement in autumn.

Macrofouling of an oceanographic buoy in the Ligurian Sea (Western Mediterranean)

Giulio Relini[1], Manuela Montanari[2], Paula Moschella[1] and Antonio Siccardi[3]

[1] Istituto di Zoologia, Laboratorio di Biologia Marina ed Ecologia Animale, University of Genoa, Via Balbi, 5 - 16126 Genoa, Italy.

[2] Istituto per la Corrosione Marina dei Metalli, Consiglio Nazionale delle Ricerche, Via de Marini, 6 - 16149 Genoa, Italy.

[3] Istituto per l'Automazione Navale, Consiglio Nazionale delle Ricerche, Via de Marini, 6 - 16149 Genoa, Italy.

The ODAS Italia 1 oceanographic spare buoy is moored in the Ligurian Sea, along Genoa-Cape Corse course (43°48.90' North - 009°06.80' East), 37 nm from the coast of Genoa, floating over a 1270 m deep sea bottom. It offers very interesting experimental conditions: the presence of a solid substratum floating in off-shore waters. The monitoring of macrofouling started on the 28th of June 1992 and it is still in progress.

Fouling was followed over time using aggregate materials panels (20 x 30 x 0.4 cm in size) which were fixed in round panel-holding frames secured to the buoy body at two particularly significant depths: 12 m and 33 m. The data presented here refer to panels removed at progressively longer intervals for a total test period of 70 months. Settlement processes of fouling community developed on panels are described; the study also included counting of settled organisms, covering index of each taxa, and biomass assessment.

During our investigations, 34 taxa were identified in total, 31 at species level, on the 12 m depth panels, and 53 taxa, 44 of which at species level, on the panels at 33 m depth. The fouling biomass, assessed as wet weight, on the panel submerged for 70 months reaches 2.8 kg/m^2 at 12 m depth and 4.8 kg/m^2 at 33 m depth.

A previous observation cycle on benthic organisms directly settling on the buoy had started on the 9th of January 1987, when the buoy was first deployed - and lasted 52 months until the 15th of April 1991, when the buoy was recovered and brought back to shore. The fouling settled along the full 40 m length of the buoy was sampled every 2 m by scraping a 50 x 50 cm square surface. Samples collected were examined and weighed. All in all, 78 taxa of which 69 species were identified. The biomass assessed as wet weight, ranges from 1.3 kg/m^2 for the fouling sample at 1 m depth to 0.3 kg/m^2 for the one at 34 m depth.

The history, current status and future prospects of natural products as antifoulants

Dan Rittschof
Department of Zoology and School of the Environment, Duke University Marine Laboratory, Beaufort, North Carolina 28516-9721, USA

Fouling, the colonization of surfaces by abiotic and biotic substances and organisms, has a variety of levels of organization and occurs by a number of mechanisms. Commercial antifouling technology includes the use of coatings that contain toxins to kill biotic colonizers. Toxic coatings are usually based upon release of toxic metal ions. Because toxic metals build up and recycle in the environment, and are environmentally damaging, alternatives including nonmetal-based toxins are reaching commercial markets. For over 40 years, experimental use of natural products as antifoulants has been reported. The basic idea is that organisms that do not themselves foul are chemically defended against fouling. This basic idea is flawed in that living organisms usually employ a suite of mechanisms to minimize fouling. At present, laboratories around the world use bioassay-directed techniques to purify and identify natural products that inhibit settlement or growth of fouling organisms. Little is know about the actual biochemical mechanisms of the antifouling compounds. Some are toxic, some paralyze and many prevent settlement by a mechanism that is neither toxic nor paralytic. Coatings based upon natural products have been tested experimentally for about 10 years. Because there are multiple mechanisms responsible for abiotic and biotic fouling, and many of the mechanisms do not include chemosensory input, the potential of natural products as nontoxic, broad-spectrum solutions to fouling is poor. However, the potential for environmentally acceptable broad-spectrum solutions to fouling that combine natural products with organic biocides are good.

Exotics across the ocean: Testing monitoring systems for risk assessment of harmful introductions by ships to European waters.

Harald Rosenthal[1], Stephan Gollasch[1], Ian Laing[2], Erkki Leppäkoski[3], Elspeth Macdonald[4], Dan Minchin[5], Manfred Nauke[6], Sergej Olenin[7], Sue Utting[2], Matthias Voigt[8] and Inger Wallentinus[9]

[1]Institut für Meereskunde, Kiel, Germany
[2]CEFAS Conwy Laboratory, Conwy, North Wales, UK
[3]ABO Akademi University, Turku, Finland
[4]Marine Laboratory Aberdeen, Scotland, UK
[5]Fisheries Research Centre, Dublin, Ireland
[6]International Maritime Organization, London, UK
[7]Centre for System Analysis, Klaipeda, Lithuania
[8]Büro Dr. Matthias Voigt, Stolpe, Germany
[9]University of Göteborg, Sweden

During the last decades ballast water discharges have increased throughout the world in most of the major ports. Discharge volumes are considerable high in some cases and the probability of introducing exotic species is expected to increase with greater volumes of ballast water and reduced ship transit times. Ships have been recognized since about 50 years as a major vector for the introduction of non-indigenous and harmful organisms. The first summarising reports appeared by (e.g.) Medcof (1975) followed by Carlton (1985, 1987), Hallegraeff & Bolch (1991) and Subba Rao et al. (1994). Rosenthal (1980) reviewed the state of knowledge and the risks associated with transplantation for fisheries and aquaculture, including ballast water. It is believed that more than 3,000 species are transported by ships each day (Carlton et al. 1995, Gollasch 1996). Six European countries: Finland, Germany, Ireland, Sweden, United Kingdom (England and Scotland), Lithuania and several experts from elsewhere (e.g. North America, some Mediterranean Countries, Australia and Asia) are involved in the Concerted Action recently funded by the EU. The IMO (International Maritime Organization) is also a partner of this study. The EU project is linked with ICES WGITMO and ICES/IOC/IMO SGBWS for the duration of the project. The study is being co-ordinated by Germany. The main objective of this Concerted Action is to compare and harmonise various sampling methods of ballast water and to study their effectiveness for sampling. Further objectives of this Concerted Action include: state of the art of ballast water studies, case histories of selected introduced species, assessing potential treatment options of ballast water, development of public awareness material, assessing European waters as potential donor area and documentation of European studies on introduced species in the past. The Concerted Action will include workshops with technical sessions, practical workshops for testing of methodologies including intercalibration exercises, methodological tests onboard ships to evaluate survival capabilities of species in-transit, and meetings to prepare documents (guidelines, manuscripts, posters, and press releases etc.). Sea-going workshops will result in a total of 6 voyages quantifying the survival of organisms in ballast tanks. It is planned to accompany vessels from North America, South America, Middle East and Asia on their way to European ports. In addition ships will be boarded on their routes from the North Sea to the Baltic and vice versa.

Recent experience with ship and laboratory evaluations of foul-release coatings

James Rudroff[1], E. Dail Thomas[2] and James A. Ellor[3],
[1]Naval Sea Systems Command, USA
[2]Naval Research Laboratory, USA
[3]Ocean City Research Corporation, USA

The following paper will describe the recent experience of the U.S. Navy, Naval Sea Systems Command (NAVSEA) with the evaluation of foul-release, underwater hull coating systems. The paper will provide a synopsis of the background leading to the Navy's interest, pertinent laboratory and ship evaluations, and future directions. Foul-release coating interest resulted from a need to consider potential future environmental restrictions on the use of toxin-containing, anti-fouling underwater hull coatings. Under NAVSEA sponsorship several laboratory and ship-trails were conceived.

Key laboratory testing included high-speed flow channel exposure of different foul-release systems at velocities up to 30 knots. This testing was designed to illustrate the minimal velocity necessary to facilitate fouling release. The testing also demonstrated the effect of longer-term coating exposure on foul-release properties. Ship testing included observations from exposure on commercial ships and Navy ships of up to five years. Based on this testing, NAVSEA is considering methods to qualify such systems for specialized use on Navy ships. The testing also provides a basis for future NAVSEA programs into anti-fouling paints.

Fouling and corrosion control in mooring systems – a practical application in highly interesting tourist and naturalistic sea areas.

G. Salvago[1], V. Mezzanotte[1], E. Poli[2], A. Benedetti[2] and E. Olzi[2]
[1]Dip. Scienze Ambientali Università degli studi di Milano
[2]CNR-TeMPE Istituto per la Tecnologia dei Materiali e Processi Energetici

Electrochemical techniques have been used for fouling control. That has been developed both to hinder and to promote the bio-mass growth of different surfaces according to the engineering necessities. An application in highly interesting tourist and naturalistic areas based on substitution of traditional anchorage sites with mooring buoys equipped with some facilities has been developed. These floating bodies should be protected against biological growth by anodic polarisation techniques. The connected bodies on sea-bottom should be obtained with local stony materials included in metallic cages protected by a coral crust whose growth is promoted by cathodical polarisation. This kind of solution let us overcome the weedy bottom dredging and damaging of the habitat. More over it should be possible to collect waste and supply services to the watercrafts. The electrochemical and biological results with the preliminary environmental impact valuations performed show the feasibility and the performances of the proposed solution.

Pollution in Tuticorin Coast, India – a threat to barnacle larvae and biofouling

R. Santhanam & A. Srinivasan
Fisheries College and Research Institute, Tamilnadu Veterinary and Animal Sciences University, Tuticorin – 628 008, India

The Tuticorin coast, once known for their pearl oysters and sacred chanks, has been rapidly industrialized during the last two decades. While the pearl production in this coast has diminished substantially, sacred chanks have become very scarce. This is mainly due to the discharge of waste waters from human settlements and sea food processing plants, heated water from shore-based thermal power plant and effluents from chemical industries and oil pollution. In order to assess the level of pollution in this coast, investigation on the biomass of nauplii of barnacles belonging to the species of *Balanus* was made during 1986, 1990, 1993 and 1997. Interestingly there was a considerable reduction in the density of barnacle nauplii as the number of industries increased year by year. The number of nauplii was found reduced from 5800 nos/m^3 (1986) to 1300 nos/m^3 (1997) during this period. The significant reduction in the density of barnacle nauplii over the years could possibly be due to pollution as evident by the concentration of BOD (261 mg/l) and phosphate (27 µg at/l) originated from domestic wastes; heavy metals such as cadmium (0.4 – 2.0 µg/l), copper (4.0 – 5.0 µg/l), lead (2.0 – 7.8 µg/l) and mercury (0.1 – 0.12 µg/l) released from two industries located in the vicinity; rise in temperature of water column (41°C) associated with the discharge of heated waters (48°C) of the nearby coal-fired thermal power plant and seafood processing plant's untreated or partially treated effluents with hydrogen sulphide (> 2 mg/l), BOD (>30 mg/l), COD (>100 mg/l) and low pH (6.5); and oil pollution with dissolved petroleum hydrocarbons (0 – 28 µg/kg) and particulate petroleum residues (0 – 69.8 mg/m^2). The density of barnacle larvae in relation to the periodic concentration of various pollutants originated from different sources and phytoplankton biomass has also been assessed. The negative impacts of marine pollution on the dispersal of barnacle nauplii and the associated biofouling are also discussed.

Studies on biofouling in a sub-seabed tunnel and its impact on the power plant cooling water quality

K.K. Satpathy[1], R. Rajamohan[1], K.V.K. Nair[1] & P.K. Mathur[2]
[1]Water & Steam Chemistry Laboratory, BARCF, Indira Gandhi Centre for Atomic Research, Kalpakkam - 603 102, India
[2]Analytical Chemistry Division, BARC, Mumbai.

More and more power stations are being located near coastal sites in order to make use of the abundant availability of seawater for cooling purpose. These plants use an open canal, a pipeline or a sub-seabed tunnel to draw seawater. Madras Atomic Power Station (MAPS), situated at Kalpakkam (12° 33'N & 80° 11'E), about 65 km south of the city of Madras, on the east coast of India uses seawater through a sub-seabed tunnel of 468 m length and 3.8 m in diameter built 53 m below the seabed for cooling purposes. In spite of various kinds of barriers to prevent the entry of large marine life, the tiny larvae of benthic organisms do get into the tunnel, settle and grow inside the tunnel, resulting in serious operational problem (pressure drop and heavy siltation in the pump house). Results of studies to assess the extent of biofouling inside the tunnel using a remotely operated vehicle (ROV) showed that colonisation by marine life was very extensive. The role of fouling organisms inside the tunnel in modifying the quality of the cooling water was studied. Results indicated a reduction in DO, Chlorophyll 'a' and increase in pH, suspended matter, ammonia, chlorine consumption from intake (entry to the tunnel) to forebay (outlet from the tunnel). The study revealed that activity such as consumption and excretion by settled marine organisms inside the tunnel considerably alter the quality of cooling water both chemically and biologically when it passes through the tunnel, though the time of contact is relatively short (5 to 40 min). When consumption of DO and Chlorophyll was computed with respect to the amount of water flow, it was found that 192 g of chlorophyll, 75 kg of oxygen per hour are removed from the incoming water. Similarly about 360 kg of suspended solid, 500 g ammonia are generated and thus added to the passing water per hour by the fouling community. The paper also discusses the role of suspended matter and ammonia on the operation of power plant cooling system.

An update of the current status of TBT copolymer antifouling paints

Uwe Schneider, Ursula Gerigk, & Ulrich Stewen
Witco GmbH, P.O.Box 1620, 59180 Bergkamen, Germany

Approximately 70 % of the world fleet are protected against fouling organisms by modern tributyltin-based selfpolishing copolymer (TBT-SPC) systems. There are ongoing discussions at the IMO about the harmful effects of the use of antifouling paints for ships. Existing world-wide regulations have significantly reduced the environmental impact of TBT-based coatings with declining TBT-levels in water, sediments and aquatic organisms.

The search to develop alternative systems which completely satisfy technical and environmental demands has proved to be a complex problem. There is significant investment in research and development to introduce alternative antifouling paints that are equally effective with long-lasting performance and have a minimal environmental impact with no side-effects to non-target organisms and no accumulation potential. TBT-based selfpolishing copolymer systems exhibit a unique mechanism resulting in a controlled and slow hydrolysis at the very thin active zone of the paint surface which guarantees self-polishing properties, a controlled release of TBT and a long-lasting lifetime of the coating (5 years and longer).

The detailed understanding of this mechanism to prevent fouling is the basis for the development of alternative systems. The new suggested approaches to antifouling protection for ships to substitute TBT-SPC systems have to demonstrate their long-term performance and to prove that the increased release of new biocides and metabolites do not bear unknown environmental risks. An overview is given about recently advertised new antifouling technologies, their mechanism and potential environmental fate.

The influence of biofilms on skin friction drag

Michael P. Schultz and Geoffrey W. Swain
Ocean Engineering Program, Florida Institute of Technology, 150 West University Blvd., Melbourne, Florida 32901, USA

Materials exposed in the marine environment, including those coated with antifouling paints, may rapidly become colonized by biofilms. Their effect on the performance of ships and other structures is, therefore, of practical interest. The complex nature of biofilms including their irregular surface topography, compliance, and their ability to produce extracellular polymer substances (EPS) make flows over these surfaces difficult to predict. While rigid surface roughness has been shown to increase skin friction drag, compliant surfaces and polymer injection have both been used as mechanisms for drag reduction. In this paper, the flow regime around a ship's hull is presented. The concept of the "hydrodynamically smooth" surface is discussed. Some basics of boundary layer structure and the effects of "regular" surface roughness are given. Possible effects of biofilms on skin friction are offered and compared with the results of previous experimental studies in this area. Finally, some results of an experimental investigation carried out by the present authors in a zero pressure gradient, turbulent boundary layer flow using two-component laser Doppler velocimeter are presented.

Copper-chromium-arsenic levels in barnacles growing on timber marine piles after five years service at Townsville.

Damian K. Scown and Laurie J. Cookson
CSIRO Forestry and Forest Products, Private Bag 10, Clayton South MDC, Vic. 3169, Australia

As part of an on-going assessment of the performance of preservative treated timber piles in the sea, 36 experimental piles were installed at Townsville, Queensland. These incorporated both hardwood and softwood timbers treated to satisfy Australian Standard requirements when treated with copper-chromium-arsenic (CCA), pigment emulsified creosote (PEC) or a combination of both (double treatment). After five years, barnacles growing on these various piles were collected and copper chromium and arsenic levels in the soft tissues determined. Copper levels in barnacles on CCA treated *Pinus elliottii* piles were significantly higher than in barnacles on other piles. Chromium content was higher in barnacles collected from CCA treated piles than non-CCA treated piles, although this trend was not supported statistically. There was no statistical difference in the amount of arsenic present in the tissue of barnacles from different piles. Barnacles collected from galvanised iron mooring pipes 20-120 mm from the CCA treated *P. elliottii* pile surface did not contain elevated levels of copper, chromium or arsenic when compared to barnacles from non-CCA treated piles.

The legacy of 110 years of dockyard operations

Patricia Shaw[1] and Barbara Hickey[2]
[1]Defence Operational Technology Support Establishment, Naval Base, Private Bag 32901, Devonport, Auckland, New Zealand
[2]Headquarters New Zealand Defence Force, Private Bag, Wellington, New Zealand

The Naval dockyard and Calliope Drydock in Devonport, Auckland have been in operation since the 1880's. Historically, process water from the drydock and stormwater from the dockyard were discharged untreated into the coastal marine area. In the late 1980's the regulatory authority introduced a requirement to document sediment quality as part of the authorisation process for dredging. In 1993 routine testing revealed unexpectedly high levels of contamination in sediment adjacent to the dry dock. Further investigations confirmed that there is a plume of serious contamination which extends in an arc of 150 metres out from the dry dock discharge point. There is a range of contaminants present including mercury, TBT, DDT, PCBs, copper, lead and zinc. Ongoing investigations are being undertaken to define the spatial extent and level of contamination; to identify the source(s) of the contamination; and to determine appropriate future action. The issues are further complicated by changes in ownership and management of the dockyard and drydock over the years. This has made it difficult to get accurate information on historic practices in the dockyard and the former owner of the drydock, the Auckland Harbour Board, is no longer in existence. Environmental legislation in New Zealand has undergone significant changes in recent years, particularly with the enactment of the Resource Management Act in October 1991. The Act is not retrospective and therefore no liability accrues for events that occurred prior to October 1991. However, if contamination is shown to be causing an ongoing adverse environmental effect, then the land owner can be required to avoid, remedy or mitigate the adverse effect, regardless of when the contamination occurred.

Antifouling activity of phenolic acids on attachment for spores of *Ulva fasciata* Delile

Hyun-Woung Shin[1], Celia M. Smith[2] and Elizabeth G. Haslbeck[3]
[1]Department of Aquatic Resources, Soonchunhyang University, Asan City, Korea
[2]Department of Botany, University of Hawaii, Honolulu, HI 96822 USA,
[3]Department of Navy, Division of Caderock, Surface Warefare Center, Annapolis, MD USA

The antifouling(AF) activities of five phenolic acids: trans-cinnamic acid (TCA), ferulic acid (FA), ρ-hydroxybenzoic acid (BA), ρ-coumaric acid (CA) and zosteric acid (ZA) were examined with a attachment assay that uses spores of the cosmopolitan fouling green alga, *Ulva fasciata*. These phenolic acids were examined at given flux rates of 1, 10, and 100 μg/cm^2/hr through a membrane perfusion device system. Antifouling dose required for 50% $(AF)_{50}$ reduction in fouling effectiveness of the cinnamic acids TCA_{50} and ZA_{50} were determined at 79.34 and 59.65 μg/cm^2/hr respectively. The non-sulphate phenolic acids FA_{50} and CA_{50} were shown to have a dose-effectiveness at 89.52 and 104.13 μg/cm^2/hr respectively. BA did not show effective AF action. These determinations for phenolic acids will establish the first such measure for any weedy algae, and are hoped to contribute to the baseline for further non-toxic AF agent evaluation.

Stress corrosion cracking of duplex stainless steels and their weldments in marine environments : a review

R.K. Singh Raman, B.C. Muddle and B.W. Cherry
Department of Materials Engineering, Monash University, Clayton (Melbourne) - Australia

This paper presents a review of stress corrosion cracking (SCC) problems in duplex stainless steels and their weldments in chloride-containing marine environments. As a precursor to the topic the paper also reviews SCC of traditional austenitic stainless steels and their weldments and necessity of using recent versions of stainless steels, *viz.*, duplex stainless steels (DSS), in order to alleviate corrosion problems in marine environments. Given that the performance of weldments of such steels is often unsatisfactory, this review also assesses the research needs in this area.

Austenitic stainless steels have been a very popular class of materials for marine application because of their unique combination of mechanical properties and corrosion resistance; however, in several environments, including chloride ion solutions, they suffer SCC. Ferritic stainless steels have inferior fracture toughness to the austenitic variety, but they possess better strength and resistance to SCC. Duplex ferritic-austenitic stainless steels (with a ferrite/austenite volume ratio typically of 1:1) show considerable resistance to SCC. Hence, duplex stainless steels are candidate materials for those industrial applications exposed to chloride-containing environments. However, with the high temperatures experienced during welding, the ferrite/austenite volume ratio and the morphology of the ferrite phase undergo undesirable changes in the weld metal and neighbouring heat affected zone (HAZ) in the weldments of DSS. Such variations are reported to impair SCC resistance of weld metal and HAZ of DSS.

The effects of regulating the use of TBT-based antifouling paints on TBT contamination

Rebecca Smith and Stewart M. Evans
Dove Marine Laboratory, Cullercoats, Tyne and Wear, NE30 4 PZ, UK.

There was severe TBT contamination in coastal waters in the mid-1980s, particularly in areas of high shipping and mariculture activity. Organotin concentrations were high in water samples, sediments and the tissues of marine molluscs. Responses, such as imposex in whelks and shell growth abnormalities in oysters, which can be caused by TBT, were also well-developed. They were associated with reproductive failure, and even local extinction of species, in the most severe cases. However, several governments have regulated the use of TBT-based anti-fouling paints, prohibiting their application to vessels <25m in length. These regulations have been highly successful in reducing TBT pollution. Environmental concentrations of TBT have decreased, and there has been substantial recovery of populations of whelks and oysters. Serious TBT contamination is now restricted largely to ports and harbours, especially those with dry-docking facilities.

Temporal variation in fouling of silicone coatings in Pearl Harbor, Hawaii.

Celia M. Smith[1], E. R. Holm[2] and M. G. Hadfield[2]
[1]Department of Botany, [2]Kewalo Marine Laboratory, University of Hawai'i, Honolulu HI 96822 USA

No antifouling or foul-release coating can be globally effective if it does not perform well in a range of environmental conditions and against a diversity of fouling organisms. From 1996 to 1998, the field test sites participating in ONR's 6.2 Biofouling Program examined global variation in performance of 3 silicone coatings; GE RTV11, Dow Corning 3140, and International Intersleek, and a control anticorrosive coating. At the University of Hawaii's test site in Pearl Harbor, there were significant differences among the coatings in the rate of accumulation of fouling. Control coatings failed rapidly; after 200-250 d of immersion, a community dominated by oysters and sponges developed that persisted for the remainder of the experiment. Fouling of the GE and Dow Corning silicones was slower, but eventually reached a similar community structure and coverage as the control coatings. The Intersleek coatings remained lightly fouled throughout the experiment. Rate of accumulation of fouling reflected differences among the coatings in adhesion of the tubeworm *Hydroides elegans*. Surface properties of these coatings may affect rate of fouling and community structure through their influence on larval settlement and subsequent interactions with other residents, predators, and the physical environment.

Biochemical characterisation of the glycoproteins involved in *Enteromorpha* spore adhesion.

Michele S Stanley, James A Callow and Maureen E Callow
School of Biological Sciences, The University of Birmingham, Birmingham B15 2TT, UK.

The major fouling macroalga, *Enteromorpha*, initiates attachment through motile spores which secrete a glycoprotein adhesive from vesicles contained in the anterior region of the spore Monoclonal antibodies have been raised to settled spores of *Enteromorpha* displaying the adhesive on their surfaces. Candidate antibodies towards the adhesive have then been selected by a combination of cellular, biochemical and functional criteria (see paper abstract by Callow, Stanley and Callow). This poster describes progress on the use of these antibodies to partially characterise a polydisperse glycoprotein antigen and its purification by immunoaffinity prior to amino acid sequence determination.

Design and development of nontoxic, self-cleaning silicone foul release coatings

Judith Stein, John Carpenter, Judith Serth-Guzzo, James Cella, Kathryn Truby, Owen Harblin, Timothy Burnell, Christina Darkangelo Wood, Deborah Wiebe, Anne Meyer, Celia Smith, Eric Holm, Geoff Swain, Chris Kavanagh, Brett Kovach, Jean Montemarano, Karen Poole, and David Lapota
General Electric Corporate Research and Development, One Research Circle, Niskayuna, New York 12309, USA

Biofouling on the hulls of Navy vessels adversely affects both fuel consumption and maximum attainable speeds. Traditional antifouling paints containing toxic triorganotin species or cupric oxide are highly effective in controlling biofouling; however, because of environmental concerns, the Navy has discontinued the use of organotin paints and it is expected that the use of cupric oxide paints may be limited in the near future.

Nontoxic low surface free energy silicone coatings that reduce the adhesion of biofouling to substrates have been developed as an alternative to antifouling paints. Tests have shown that while silicone coatings do not completely eliminate biofouling attachment, the fouling can usually be removed by water pressure wash or gentle scrubbing with a brush.

During the past several years, GE under funding from ONR and ESTCP, has developed VOC-free silicone topcoats with improved durability and improved application profiles. Technical issues that remained to be addressed largely centered around optimizing the fouling release performance of the topcoats without compromising durability and the non-toxic nature of the coating.

The results of our DARPA sponsored research to address the issues delineated above are described herein. Enhancement of foul release performance by oil incorporation, the effective state of the oil (free or surface bound), and whether oil leaches from the coatings in the aqueous environment will be discussed. In addition, using a worldwide robust statistical design, correlations of release performance between sites, animal species and coating composition were determined. The hydrodynamic properties of the coatings and quantification of their ability to self-clean at operational speeds as well as the results of speed trials on a boat painted with a top performing composition will be discussed.

Colonisation of seaweeds by epibiota; the ecology of natural chemical cues.

Peter Steinberg
School of Biological Science and Centre for Marine Biofouling and Bio-Innovation, University of New South Wales

A number of natural products from macroalgae (seaweeds) strongly deter the settlement of marine organisms in laboratory assays. However, the broader importance of such "natural antifoulants" in the ecology of seaweeds is largely unknown. This is for several reasons, including the difficulties in quantifying metabolites on or near surfaces *in situ*, in developing relevant field assays, and in integrating the role of natural antifoulants into the overall ecology of seaweeds. We have addressed these issues for the Australian red alga *Delisea pulchra*, which produces non-polar secondary metabolites known as halogenated furanones. Furanones occur at the surface of the alga in concentrations which strongly inhibit settlement of epibiota in lab and field assays, and are in most circumstances effective natural antifoulants. However, the compounds are not always effective in deterring fouling in the field. Shallow *D. pulchra* can be heavily fouled in summer, corresponding to a sharp decrease in levels of furanones on the surface of these plants. This in turn is driven by the high levels of UV light incident on these habitats in summer. In contrast to *D. pulchra*, many chemically rich seaweeds do not appear to use natural products as antifoulants, either because the compounds are not present at the surface of the plant (*e.g.*,terpenoids in *Laurencia* spp.), or they do not persist at the surface in high enough concentrations to deter epibiota (phlorotannins in *Ecklonia radiata*). We suggest that natural antifoulants in seaweeds will be most common for plants which produce non-polar metabolites and have morphologies which allow appropriate release of the metabolites. In contrast to this, recent research with *D. pulchra* and other red algae indicates that the polar sugar floridoside is the basis for a positive metamorphosis cue for some invertebrate larvae. Polar metabolites appear to be generally common as inducers of settlement and metamorphosis of invertebrate larvae, suggesting different constraints on the production of negative *vs.* positive cues by seaweeds.

Criteria for a successful non-toxic fouling-release coating

Geoffrey Swain, Angela Cook, Chris Kavanagh, Brett Kovach, Kathy Naum, Nagahiko Shinjo, Mike Schultz & Kirk Schumacher
Florida Institute of Technology, 150 West University Blvd., Melbourne, Florida 32901, USA

During the last ten years we have evaluated a large number of non-toxic fouling release coatings. These have included coatings applied to static immersion panels, boats, ships, structures and nets. To quantify their performance we developed test equipment and methods to measure biofouling adhesion strengths. We have also investigated the hydrodynamic and mechanical forces required for fouling removal, and the viscous drag associated with biofilms. This paper will review the data to date and provide criteria, which can be used to predict the performance of existing and new coating systems.

Development of a new antifouling paint based on a novel zinc acrylate copolymer

Yoichi Taki, Yoichi Yonehara, Fumihiko Nakakita and Mahamedi H. Jadliwala
Kansai Paint Co., Ltd. Technology and Products Development Division,
17-1 Higashi-Yawata 4-chome, Hitatsuka-Shi, 254 Japan.

Antifouling paints based on tributyl tin acrylate copolymers have proved to provide excellent performance when applied to ocean going vessels. However, pollution of the marine environment from the release of tributyl tin has been a matter for concern for some time now, such that their use has been restricted in many countries and it seems likely that these products will be phased out by 2006 at the very latest.

We have managed to develop a zinc acrylate copolymer for use in antifoulings, which is the most suitable replacement for the tributyl tin copolymer. Zinc ions from the new copolymer exchange with sodium ions from the sea, the resulting structure will then dissolve in a controlled manner into the seawater. It is possible to control the erosion rate of this novel copolymer by altering the one or more of either the molecular weight of the polymer, the concentration of the functional group or the hydrophilicity of the zinc acrylate polymer.

The performance and long term physical properties, the erosion rates and the surface profiles of the new antifouling paints formulated with the various zinc acrylate copolymers have already been evaluated after dynamic immersion. After testing, the results that we have assessed with paints formulated using this new zinc acrylate copolymer have proved to provide excellent results in all aspects.

Butyltin contamination in marine mammals

Shinsuke Tanabe
Department of Environment Conservation, Ehime University, Tarumi 3-5-7, Matsuyama 790-8566, Japan

For the understanding organotin accumulation in marine mammals, the present study determined the concentrations of butyltins (BTs) in various tissues and organs and described their distribution pattern relative to sex, age and geographical factors. Both cetaceans and pinnipeds showed higher BTs concentrations in the liver among various tissues and organs. In addition, noticeable high concentrations were found in the hair of pinnipeds, indicating possible excretion of BTs through shedding. BTs composition in mammals and their prey organisms suggested that pinnipeds have a stronger capacity to degrade BTs rather than cetacean. No age trend of BTs concentrations was observed in pinnipeds, while cetaceans showed increasing levels in immature growth stage. Comparing butyltin concentrations in various marine mammals, cetaceans retained higher butyltin concentrations than pinnipeds. The above specific accumulation patterns found in marine mammals are probably attributable to the lower breakdown capacity of BTs in cetaceans and the significant excretion of BTs through shedding in pinnipeds. Unlike organochlorines, comparable residue levels of butyltins were found in male and female of marine mammals. Such a trend suggested that butyltins are less transferable through gestation and lactation from mother to fetus/pup. On a global perspective of butyltin contamination in marine mammals, residue levels were found to be prominent in the coastal water of developed nations. The present contamination by BTs may pose a toxic threat to some coastal species of cetaceans.

Green fluorescent protein - shedding new light on biofilms

Somkiet Techkarnjanaruk[1], Serina Stretton[1], Marina W. Delpin[1], Alan M. McLennan[1], Peter Kolesik[2], Ace M. Baty[3], Gill G. Geesey[3] and Amanda E. Goodman[1]
[1]School of Biological Sciences, The Flinders University of South Australia, Australia
[2]Plant Research Centre, The University of Adelaide, Australia
[3]Center for Biofilm Engineering, Montana State University, USA

We are investigating environmentally regulated genes in marine biofilm-forming bacteria using a *gfp* gene which encodes green fluorescent protein. Using strains engineered to contain *gfp*, in conjunction with epifluorescence microscopy and laser scanning confocal microscopy, it is possible to visualise directly gene expression in single living cells in biofilms. In addition, this technology allows us to determine the in situ structure of living biofilms. *Pseudoalteromonas* S91CGFP contains a promoterless *gfp* gene inserted into the chromosome under the control of a chitinase (*chi*) gene, such that expression of the *chi* promoter causes green fluorescence in the cell. S91CGFP is being used to investigate biofilm formation on, and degradation of, squid pen, a natural marine biodegradable substratum. The same *chi* gene promoter, driving *gfp* expression from a plasmid construct in S91, has been found to be switched on in "hot spots" of cells forming biofilms on spin-cast chitin substrata. Using *Vibrio* sp. S14 wild type and flagellum negative derivative strains, marked with the *gfp* gene, we are examining the contribution that the cell's flagellum makes to the living biofilm architecture.

The effects of environmental variables on biocide release from antifouling formulations

Kevin V. Thomas[1], John Chadwick[2], Andrew Fisher[3], Steve Hill[3], Katherine Raymond[2], and Mike J. Waldock[1]

[1]Centre for Environment, Fisheries and Aquaculture Science (CEFAS), Burnham Laboratory, Remembrance Avenue, Burnham-on-Crouch, Essex,CM0 8HA, UK

[2]Health and Safety Executive (HSE), Magdalen House, Trinity Road, Bootle, Merseyside, L20 3QZ, UK

[3]Department of Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, Devon, PL4 8AA, UK

Understanding the effects of environmental variables on the rate of biocide release from antifouling formulations is necessary so that the measurements obtained by laboratory-based tests are correctly interpreted in environmental risk assessment. To allow the effects of anti-fouling actives on aquatic systems to be predicted effectively, our study has progressed in two parts; (i) the evaluation of laboratory-based leach rate methods combined with participation in international competency testing of similar methods to ensure that comparable data is generated in support of product registration and (ii) the evaluation of changes in leach rate as environmental variables change during normal use of the formulations.

The effect of slight changes in all test parameters, within the specification of the protocol, on the release of copper and tin, was tested on the ASTM leach rate method (ASTM D5108-80). It was clearly shown that leach rate data obtained using this method were extremely dependent on pH and salinity. An ISO steering group charged with designing a robust methodology for product testing and to validate the testing procedures has modified the ASTM protocol so that there is less variability in the data generated (ISO/DIS 15181-1,2). International competence testing of this modified protocol has confirmed this. The method has since been used to obtain laboratory-determined leach rate data for a number of biocides; TBT, CuO, Irgarol 1051, diuron, dichlofluanid, zinc pyrithione, Kathon 5287, TCMS pyridine and TCMTB.

The effects of environmental variables, such as temperature, pH, salinity, suspended matter and vessel speed, on leach rates has also been investigated. Since the laboratory-based methods for product testing are inappropriate to evaluate the effects of vessel speed and suspended matter on biocide release, a purpose-designed flume was used. All the actives listed above were tested and compared with laboratory-based release rates. The effects of short-term changes in conditions on biocide release was also closely examined with certain environmental parameters having a significant effect on the release of certain biocides from tin- and copper-based antifouling coatings. Comparisons between the data obtained from both laboratory and environmentally relevant test systems along with possible implications on the environmental risk assessment of antifouling paint biocides is discussed.

Comparisons of risks to aquatic life from using tin-free biocides versus tributyltin in antifouling paints.

John Toll, Mary Sue Brancato and David DeForest
Parametrix, Inc. 5808 Lake Washington Blvd. NE, Suite 200, Kirkland, Washington, USA 98033.

Tin-free biocidal additives are currently being promoted as alternatives to tributyltin (TBT) for use in antifouling paints. As part of a cost-benefit analysis of antifouling paint additives, we found a significant cost penalty to the shipping industry if TBT paints were banned and currently available tin-free biocides were used. Given this, it is important to compare the environmental risks of tin-free biocides and TBT self-polishing copolymer paints. TBT risks to aquatic life have dropped as water concentrations have declined in all regions of the United States since the Organotin Antifouling Paint Control Act was passed in late 1988. Unfortunately, the toxicity data for alternative biocides are for acute exposure durations, and therefore unsuitable for assessing antifouling paint risks (because antifouling paints are continuously leached from hulls). Despite the data shortcomings, we have been able to draw some conclusions about the potential environmental risks associated with some of the tin-free alternative antifouling paints. The results of this comparison will be presented along with conceptual issues affecting the comparative risk assessment.

Pyrithiones as antifoulants: Environmental chemistry and risk assessment

P.A. Turley, R.J. Fenn, P.M. Figura and J.C. Ritter
Olin Biocides Technology, 350 Knotter Drive, Cheshire, CT 06410

Pyrithiones are effective microbiocides which are widely used in shampoos, metal working fluids, adhesives, sealants, and coatings. Zinc OMADINE® is the most familiar pyrithione, having been sold for over 30 years as the active ingredient in antidandruff shampoos. The solubility and availability of pyrithione can be influenced by complexation with different metals. The low water solubilities of zinc and copper pyrithiones together with their broad antimicrobial activity and favorable environmental chemistry make them ideal candidates for replacing TBT in antifouling paints. We have carried out several studies of these metal pyrithiones in fresh and salt water systems to determine aquatic toxicities, release rates, degradation rates and the pattern of formation and decline of degradates. Pyrithione degrades rapidly in the water column by both abiotic and biotic pathways to products that are orders of magnitude less toxic than the parent compound. Cleavage of a critical functional group precludes accumulation in anaerobic sediment. Predicted environmental concentrations (PEC), persistence, and distribution were calculated for pyrithione and TBT using EXAMS2.95. Comparison of PECs and toxicities strongly suggest that the pyrithiones are environmentally more favorable than TBT. These findings are consistent with zinc pyrithione's long history of safe usage, including eight years in marine antifouling paints.

Structure and carbohydrate chemistry of biofilm surfaces in relation to settlement patterns of *Hydroides elegans* and *Enteromorpha flexuosa*.

Catherine R.C. Unabia, Teena Michael, and Celia M. Smith
Kewalo Marine Laboratory, University of Hawaii, 41 Ahui St., Honolulu, HI 96813, USA.

Differential patterns in settlement of the polychaete tubeworm *Hydroides elegans* and the green alga *Enteromorpha flexuosa* were observed on natural Pearl Harbor biofilms and cultured monospecific bacterial films developed for 3, 24 and 72 hr on glass slides. Both organisms are early and conspicuous colonists typical of fouling communities in Pearl Harbor and other tropical and subtropical waters, and as representatives of two biological kingdoms are dramatically different in scale, mode of response and physiology. In an attempt to compare and explain observed settlement patterns, three dimensional structure of the biofilms was surveyed with confocal microscopy using 24 fluorescently-tagged lectins to visualize a variety of carbohydrate moieties on biofilm surfaces. Density of microorganisms and their spatial association with the settled macroorganisms were also quantified. Bacterial density was not sufficient to explain settlement patterns, but *E. flexuosa* cells were associated with bacteria, diatoms and organic matter rather than free space. We found distinctive heterogeneity in the sugar components of bacterial cells and extracellular polymeric secretions (EPS) in biofilms that may contribute to specific interactions between settling cell surfaces and substrata. Lectin binding indicated that glucose and/or mannose, N-acetyl-glucosamine and N-acetyl-galactosamine were common on cell surfaces and EPS, while fucose moieties were rare. Three dimensional structure and representational chemistry of biofilms were mapped to gain a sense of the physical and chemical topography appropriate to the scales of the settling invertebrate and algal propagules.

Durability of marine reinforced concrete structures in India - a review

C. Venugopal
Marine Corrosion & Materials Research Division, National Institute of Oceanography, Dona Paula - Goa 403004, India

The present paper gives a review on various environmental and design parameters affecting the durability of marine concrete structures in India. It is often found that the service failure of marine concrete structures are due to inadequate design methodologies and materials to suit the local marine environment. Chloride and sulfate ions are found to be main factors contributing to the rebar corrosion. Macrofouling growth plays vital role in the optimum design and ingress of chloride ions. Thickness of 100-120mm biofouling growth as a factor of safety is considered in the design of the marine concrete structures and is often contradictory. Cement (5-6% C3A) content of 360 kg m-3 and W/C ratio of 0.4-0.45 are for practice of construction. It is found that the hydrodynamic loading in the design should be based on the wave characteristics of the location. The mechanisms involved in the deterioration of marine concrete structures are highlighted. Effect of hydrodynamic loading, material selection, chemical and biological attack on the performance of the marine concrete structures in Indian marine waters are briefly set out in the present paper and the need for further work in certain areas highlighted.

Sulphate-reducing bacteria influenced corrosion of steel in marine media: An updated overview

Héctor A. Videla.
Department of Chemistry. Faculty of Pure Sciences, University of La Plata, Av. 51-337, La Plata 1900, Argentina.

Sulphate-reducing bacteria (SRB) growth in marine environments induces several relevant modifications at the steel/seawater interface, such as local changes in pH, redox potentials, variations in anions and cations concentrations and alterations in the composition and structure of corrosion products layers. Complex chemical and biological reactions and equilibria are also markedly altered during bacterial growth. These effects that are absent in abiotic media, lead to drastic changes in the corrosion behaviour of the steel.

Recent results from our laboratory and from the literature involving the use of electrochemical techniques for corrosion assessment, surface analyses by EDAX, XPS, X-ray diffraction and electron microprobe complemented with electron microscopy as well as innovative techniques such as specific micro sensors and atomic force microscopy are briefly described.

The complexity of the local environment at the steel/seawater interface is enhanced in the presence of the microorganisms and their extra cellular polymeric material. Thus, areas with different ions concentrations and corrosion products layers of dissimilar protective characteristics are formed as a consequence of the heterogeneity of the biofilm.

Biochemical design of the mussel holdfast

Herbert Waite
Marine Science Institute, University of California, Santa Barbara, CA 93107 USA

Marine mussels (*Mytilus*) secrete byssal threads to mediate their opportunistic attachment to hard surfaces. The threads are complex structures with shock-absorbing proximal portions and stiff distal portions ending in flattened adhesive plaques. Recent studies have shown that excluding the plaques, threads consist largely of 3 natural fusion proteins: 2 of these (preCol-P and preCol-D) have graded distributions in the threads; the third (preCol-NG) is uniformly distributed. All are rod-shaped homotrimers with three distinct domains: i) a central collagenous domain ii) flanked on both sides by structural motifs, i.e. elastin in P and dragline silk in D, and iii) capped by histidine-rich domains at both termini. Terminal domains also contain 2-4 residues of 3,4-dihydroxyphenylalanine (DOPA). We believe these rod-like proteins to form linear polymers in which D decreases proximally as P increases e.g. D-NG-D-NG-D-NG-D-NG-P-NG-D-NG-P-NG-P-NG-D-NG-P-NG-P-NG-P-NG-P. Thus, NG mediates the transition from stiff to stretchy in each polymer.

Five proteins have been isolated and characterized from the plaques. These are known as *Mytilus edulis* foot proteins (mefps). We have used matrix laser desorption analysis of the adhesive face of plaques to determine which proteins are at or near the interface. Two are consistently present: mefp-3 and mefp-5. These are distinguished by having the highest DOPA levels of any byssal precursor proteins, 20 and 30 mol%, respectively. Curiously, mussels appear to "tailor" mefp-3s according to substrate type. Thus only a few of the more than 20 variants expressible by each mussel are deposited on any given surface. The extent of post-translational modification (hydroxylation, phosphorylation, etc) of each variant may also be affected.

(Supported by the US Office of Naval Research and Public Health Service)

Shipboard protective coatings: the RAN experience.

Lindsay Wake and Stefan Danek
DSTO Aeronautical & Maritime Research Laboratory, GPO Box 4331, Melbourne 3001, Australia

A wide range of shipboard coatings are employed on RAN vessels, many with specific requirements including: corrosion protection (ship side, superstructure, and ballast tanks); antifouling; camouflage (visible); radar absorbing materials (RAM); near-infrared reflecting (NIRR), non-skid and non-slip coatings; fire resistant and intumescent coatings. In recent years DSTO has been involved in the development and/or evaluation of many coatings, and has been working with RAN, ship builders and paint manufacturers in introducing new coatings into RAN service.

This presentation will discuss the successful trial of a NIRR polyurethane topcoat on a RAN patrol boat which significantly reduced the internal temperatures of habitable compartments; at the same time the camouflage topcoat was changed from Storm Grey to Haze Grey with favourable results. Results from a shipboard fire test of an intumescent coating on a decommissioned RAN DDG will also be discussed, along with recent problems with the discolouration of the presently employed non-skid epoxy topcoat and corrosion in ballast tanks.

The effects of copper based antifoulants and marinas on the development of marine fouling assemblages

J. Angus Webb and Michael J. Keough
Department of Zoology, University of Melbourne, Parkville Vic. 3052, Australia

Concern over the ecological effects of copper based antifouling paints has been widespread despite a lack of studies on the effects of these paints in the field. Copper from antifouling paints might exert immediate or long term ecological effects. Immediate effects could be experienced by organisms living near a recently painted surface, whereas longer term effects could occur when there is a sufficient build up of copper to affect local inhabitants over both a wider spatial scale, and an evolutionary time frame. Using fouling assemblages as a model, we have studied both immediate and long term ecological effects of copper antifouling paints in and around two marinas near Melbourne, Australia. Fouling assemblages were allowed to develop both inside and outside the marinas while exposed to either a copper antifoulant or control compound. Transplants examined the effects of novel locations and doses on both established assemblages and on individual animals and colonies. We found that the marinas generally had a greater effect on the assemblage composition, and also on the performance of any particular species, than did the dosing regime. This suggests that while copper antifoulants can have an immediate restructuring effect on an adjacent assemblage, these effects are usually minor compared to those caused by the environment found inside marinas as compared to that found outside. This so-called 'marina effect' can only be partly caused by the build up of copper from antifouling paints and other aspects of the marina environment must affect fouling assemblages.

In-vitro studies of signal – receptor interactions in bacterial cell density dependent AHL-signaling.

Maria Werthén, Malte Hermansson and Hans Elwing
Department of Cell and Molecular Biology, Microbiology, Göteborg University, Göteborg, Sweden.

The dependence of quorum sensing in biofilms system may provide an opportunity for the control of bacterial surface attachment and biofilm formation. Analogues to AHLs capable of interfering with cell-communication, e.g furanones, have been shown to disturb surface colonization (swarming) as well as other bacterial AHL-dependent processes.
Although a strong link between quorum sensing and biofilm formation has been demonstrated, still little is known about the interaction between the AHL-signal molecule and its receptor protein which is central to the understanding how the signal is sensed by the bacterial cell and how the cell responds.
We study the interaction between the AHL-molecule and its receptor using a surface sensitive optical method (Surface plasmon resonance). The AHLs are immobilized at the solid surface by adsorption, chemical coupling or insertion in a phospholipid monolayer. The AHL-surface is allowed to react with solute cell fractions of our model bacteria, *Vibrio fischeri* or *Serratia liquefaciens*. Any additional macromolecules binding to the surface will be detected, without labelling, which opens up a possibility to isolate and identify the binding molecules. Encouraging results show a concentration dependent binding of macromolecules from the cytoplasma membrane fraction to the AHL-surface. With the use of this methodology, we hope to elucidate whether the the AHL-receptor is the transcription factor (LuxR homologue) that is activated in the quorum sensing circuit or if another protein is involved in the signal transduction.

Tributyl tins - environmental friend or foe? The shipper's perspective

Lynda Wilson, BHP Transport, 600 Bourke Street, Melbourne 3000, Australia

The shipping industry acknowledges that the use of tributyl tin by its toxic nature presents environmental issues that must be addressed. Shippers also recognise that operating with fouled hulls does not make good business sense, and is not good for the environment. A responsible approach requires a holistic assessment of the risks associated with biofouling and the risks associated with various management control options. A blanket ban on the use of effective control measures i.e. tributyl tins before equally effective alternatives are available may not be the best outcome for the environment when some of the following issues are considered:

- less effective alternatives could result in:
    - heavier biofouling leading to associated increased risks of introducing unwanted aquatic organisms;
    - increased NOx, SOx and CO2 emissions caused by greater drag associated with heavier fouling;
    - greater consumption of fossil fuels because of reduced fuel efficiency.
    - more frequent drydockings resulting in:
        - greater consumption of resources eg paints, grit-blast, fresh water, etc;
        - increased waste production including fouling organisms, stripped/blasted paints, and contaminated water;
        - increased risk of introducing unwanted aquatic organisms in dock areas, particularly if the establishment of exotic species is influenced by spawning seasons, etc.

Marine antifoulants: Current requirements and experience in the United States / Challenges in negotiating the global treaty

Bryan C. Wood-Thomas
U.S. Environmental Protection Agency, Washington D.C., USA
Chairman, IMO Working Group on Antifouling Systems

The presentation is divided into two components. The first is an overview of current requirements and experience in the United States including 1) a summary of U.S. legal restrictions applicable to tributyltin, 2) national monitoring results; and 3) requirements for approval of antifouling systems in the United States. The second area of discussion shifts attention to the international arena - focusing on the specific challenges faced by Member States of the International Maritime Organization in negotiating a global treaty addressing anti-fouling systems.

New biocidal coating materials for control of marine fouling

S.D. Worley[1], M. Eknonian[1], J.F. Williams[2], J. Bickert[2] and J. Santiago[2]
[1]Department of Chemistry, Auburn University, Auburn, Alabama 36849 USA
[2]Halosource Corporation, Seattle, Washington 98104 USA

A new source of N-halamine compounds has been synthesized and tested for efficacy at inactivating microorganisms when employed as coatings on various substrates. The compounds which are derivatives of 3-halo-4-(alkylacryloxymethyl)-4-ethyl-2-oxazolidinone can be homopolymerized, copolymerized with other monomers, and grafted to commercial polymers. The polymers can be emulsified in water to produce coatings which, once chlorinated, act as disinfectants. The action of the biocidal polymers produced against such microorganisms as *Staphylococcus aureus* and *Pseudomonas aeruginosa* under a variety of test conditions will be discussed. The substrates for the coatings included glass, cloth, metal, and polyurethane. Test procedures included quantitative recovery over time of test organisms from challenged surfaces, zone of inhibition observations, and electron microscopy evaluation of treated surfaces. The coatings should find usage in a variety of applications including as coatings to prevent marine fouling.

Nontoxic fouling release: Correlation of polymer surface properties with ease of fouling removal

Kenneth J. Wynne
Office of Naval Research 331, 800 North Quincy Street, Arlington VA 22217-5660

Nontoxic coatings with minimally adhesive surfaces with respect to biofouling are of interest to Navy, from both environmental and economic standpoints. This paper is aimed at the correlation of physical surface characterization data on silicone "fouling release" polymer coatings with measurements of the tenacity of adhesion of hard fouling in the marine environment. The design criteria for the optimal fouling release coatings are: (1) a low surface energy to minimize chemical interactions; (2) a low glass transition temperature, Tg, to minimize mechanical locking of a prospective fouling organism; and (3) temporal and chemical stability in water; that is, conditions (1) and (2) must not change with immersion time in water. This paper addresses the success in meeting these criteria for two well known PDMS classes, namely *alkoxysilane* cured networks and *Pt cured* networks. In addition, preliminary data for new fluoropolymer elastomers is presented. The importance of temporal stability of surface properties is emphasized in the optimization of fouling release. Progress toward the development of a fouling release coating with barnacle adhesion (estimated by the method of Swain) between 5 and 6 psi will be described.

Application of Confocal Laser Scanning Microscopy (CLSM) in wood biodeterioration study

Ying Xiao, Robin N. Wakeling and Adya P. Singh
Manufacturing Technologies, New Zealand Forest Research Institute Ltd., Private Bag 3020, Rotorua, New Zealand

Confocal laser scanning microscopy (CLSM) is a powerful new tool being used to increase our understanding of the mechanism of action of wood degrading fungi and bacteria. Assisted with digital image processing techniques, CLSM has several unique features: 1. it enables non-invasive optical sectioning, allowing structures to be examined at any depth within a relatively thick specimen (1/20mm) without incision; 2. rapid sequential examination of serial images on a visual display unit (VDU), gives a three dimensional (3D) perception of structures; 3. computer software can be used to reconstruct 3D models from sequential 2D images, and models can then be cut and rotated so that any surface and geometrical relationships between objects can be analysed.

Use of specially tailored multi-fluorescent staining techniques with CLSM has produced new information concerning the spatial relationships between fungi and bacteria and the wood substrate particularly in regard to their 3D characteristics. Glutaraldehyde fixation and a chitin fluorescent probe were used to locate fungal hyphae in wood. Bacteria colonising wood were examined using a fluorescent phospholipid probe. By counterstaining wood with this probe and a fluorescent dye specific for gram-positive bacteria it was possible to clearly distinguish between gram types through simultaneous, multi channel fluorescent CLSM imaging. A combination of glutaraldehyde fixation and phospholipid probing was found to be a very reliable method detecting wood degrading bacteria in wood cell walls.

Author Index

Notes: