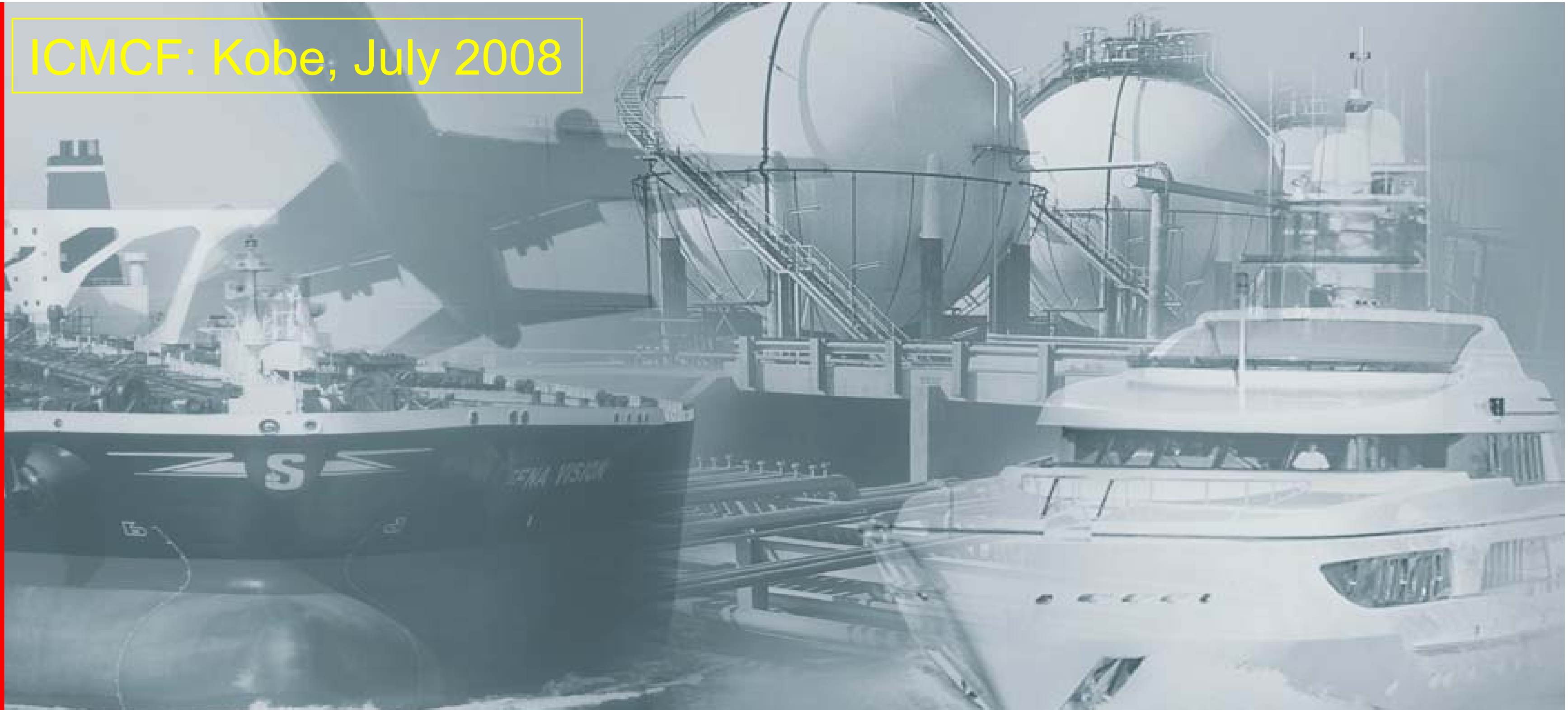
ICMCF: Kobe, July 2008



Copper and co-biocide release from antifouling paints and implications for environmental risk assessment

Alistair Finnie

International | Marine, Protective, Yacht and Aerospace Coatings | AKZO NOBEL

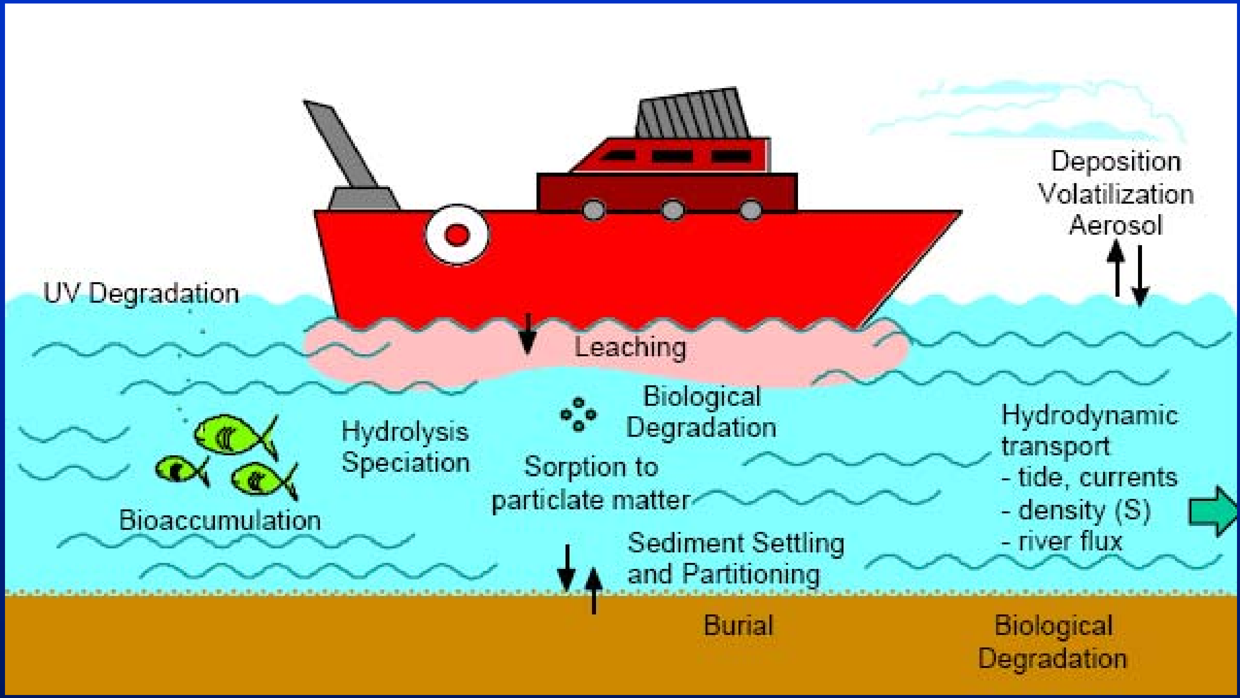
Overview

- Biocide release rate measurement
    - Why and how?

- Simultaneous measurement of copper and co-biocide release from tin-free SPC A/F paints

Introduction

Chemical fate processes of antifouling products in the marine environment



Source: (van Hattum et al, 2002)

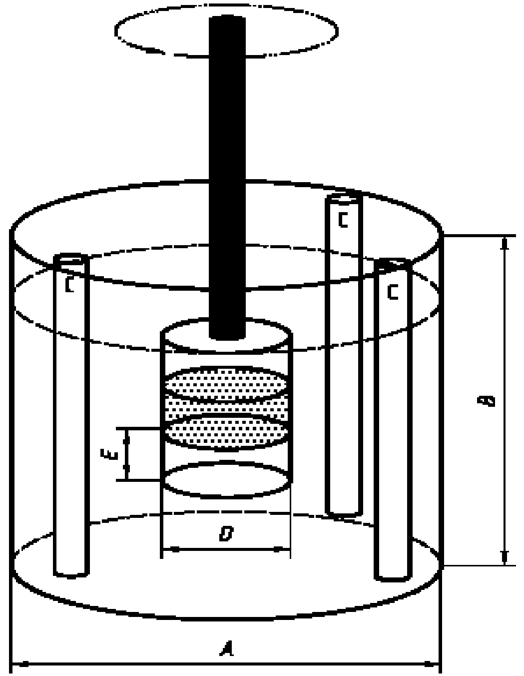
Biocide leaching rate is clearly a critical input parameter in environmental risk assessments for biocidal antifouling products

Introduction

- Environmental risk assessments are increasingly at the heart of the registration process for antifouling products
- Reliability of the risk assessment depends upon the reliability of the inputs to the model
  - vital that leaching rate estimates accurately reflect leaching rate from the antifouling coating under normal use on a ship or boat
  - Currently no widely used practical method for quantifying biocide release directly from a ship hull
- Most common indirect methods are
  - ASTM/ISO ‘rotating cylinder’ method
  - CEPE/ISO mass-balance calculation method

ASTM/ISO standard methods (rotating cylinder)

- The ISO/ASTM 'rotating cylinder' method is the only internationally recognised experimental method for quantifying biocide release rates
  - Lab method with painted cylinders immersed in artificial seawater
  - Closely controlled pH, salinity and temperature
  - 45 day test-period (minimum)
  - Common sample generation method for all paints/biocides but different analytical methods for different biocides
  - Not designed to produce 'real-life' release rate data
  - Reproducibility is questionable
- Recognised that results do not reflect release rates under environmentally relevant conditions and standards clearly state that they should not be used directly for environmental risk assessment purposes



Release rate measuring container

- capacity: 1,8 litres to 2,2 litres;
- diameter (*A*) 120 mm to 150 mm;
- height (*B*): 170 mm to 210 mm;
- baffles (C): three circular cross section rods of 4 mm to 8 mm diameter

Test cylinder

- diameter (*D*): 60 mm to 70 mm
- paint-free zone (*E*): 10 mm to 20 mm

ASTM/ISO standard methods (rotating cylinder)

Method	Description	Status
ISO 15181 – Part 1	**Generation of leachate** (generic rotating cylinder method)	Revisions published June 2007 (harmonised with ASTM D6442-06)
– Part 2	Analysis for **copper** in leachate	
– Part 3	Analysis for **zineb** in leachate	Published June 2007
– Part 4	Analysis of **pyridine triphenylborane**	Approved – publication imminent
– Part 5	Analysis of **dichlofluanid** and **tolylfluanid**	Published May 2008
– Part 6	Analysis of **tralopyril** in leachate	NWIP – **CD** – DIS – FDIS – approval (end 2010?)
ASTM D5108-90	**Organotin** leaching rate	Published Dec 1990
ASTM D6442-06	**Copper** leaching rate	Revised Aug 2006 (= ISO 15181, 1 + 2)
ASTM D6903-07	**DCOIT**) **Zinc pyrithione**) **Copper pyrithione**) leaching rates **CDMTD/Cybutryn**)	Published March 2007

ASTM/ISO standard methods (rotating cylinder)

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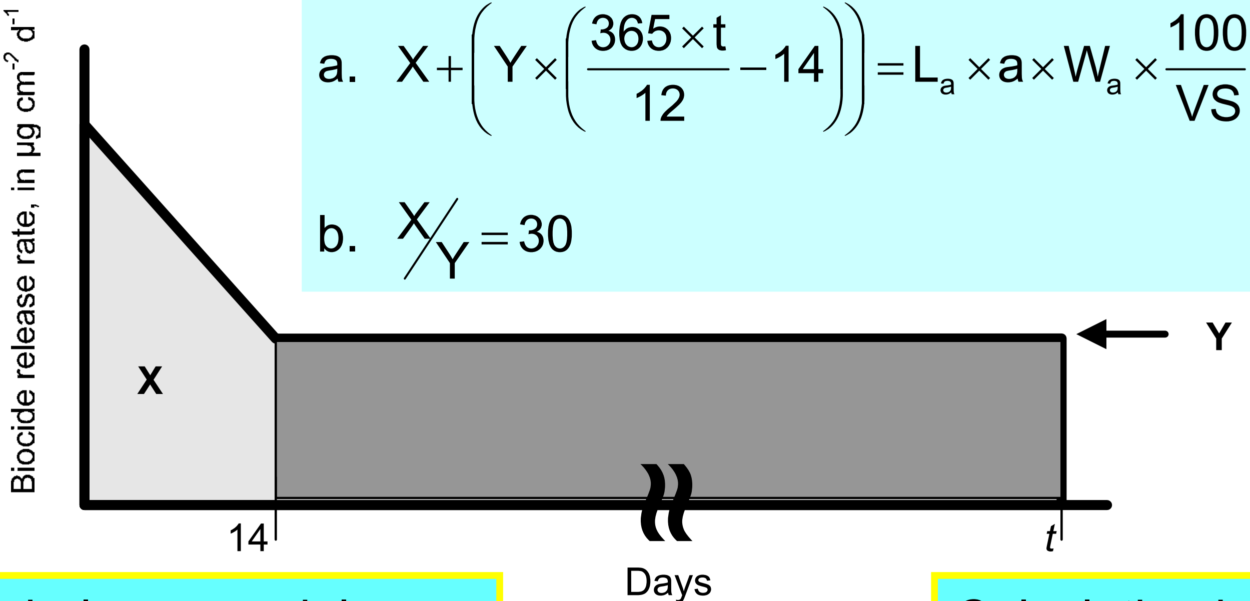
CEPE/ISO mass-balance calculation method

- Originally devised by the European Paint Makers Association (CEPE), the mass-balance calculation method is now being adapted as an ISO standard method
  - ISO/DIS 10890 (final publication late 2009?)
- Basic principle is amount of biocide released cannot exceed the amount that is added to the paint
- Model derived from extensive experience of ASTM/ISO methods for copper and organotin
- Empirical model assumes initial 14-day burst of biocide and then calculates the AVERAGE release rate over the remainder of the specified paint lifetime

CEPE/ISO mass-balance calculation method

a. $$X + \left(Y \times \left(\frac{365 \times t}{12} - 14 \right) \right) = L_a \times a \times W_a \times \frac{100}{VS} \times \rho \times DFT$$

b. $$X/Y = 30$$



Mass-balance model designed to reflect typical paint behaviour

Calculation is independent of rising /falling behaviours; also pier-side / sailing

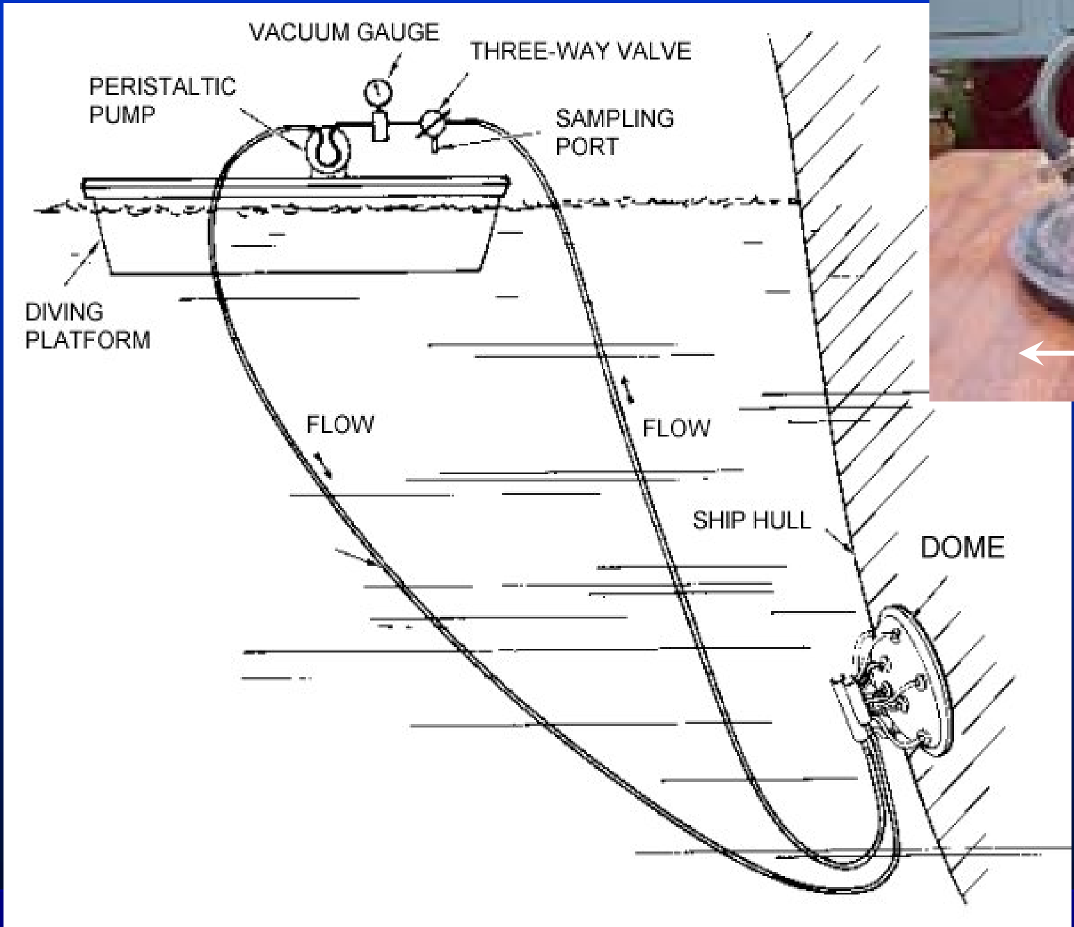
Values reflect average leaching rate over entire paint lifetime but does <u>not</u> assume LR is constant

Universal model for all biocides and all paints but so far only validated for copper and organotin

‘Real-life’ methods – US Navy Dome

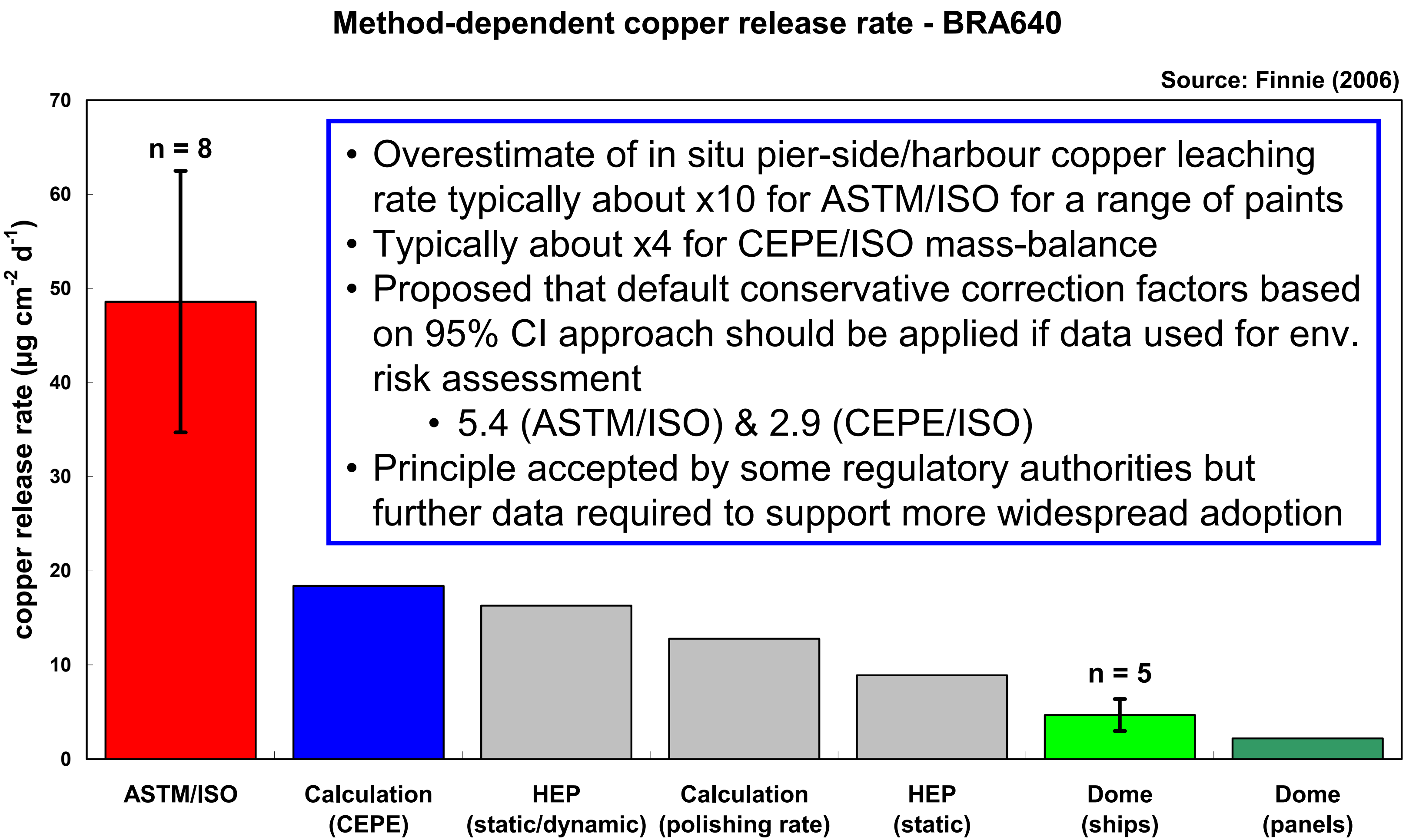
- To-date, probably the most reliable measurements of environmental copper release rates from in-service vessels have come from US Navy’s Dome method
- Direct sampling from vessel’s hull at pier-side in natural waters
- Can be used at any point in lifetime of paint system
- Labour intensive method usually requiring divers and pilot boat
  - not suitable for widespread use but further method-development is ongoing (SPAWAR)
- Published data available for copper release rates from a range of paint systems on pier-side US Navy vessels but all data from single location (San Diego Bay)

SPAWAR Dome Method



Source: Earley/SPAWAR

Comparison of determined release rates methods



- Overestimate of in situ pier-side/harbour copper leaching rate typically about x10 for ASTM/ISO for a range of paints
- Typically about x4 for CEPE/ISO mass-balance
- Proposed that default conservative correction factors based on 95% CI approach should be applied if data used for env. risk assessment
  - 5.4 (ASTM/ISO) & 2.9 (CEPE/ISO)
- Principle accepted by some regulatory authorities but further data required to support more widespread adoption

New data

- Present study uses ASTM D6442-06 and ASTM D6930-07 to simultaneously determine the release rate of copper and pyrithione biocides from a series of tin-free SPC antifouling paints
- Copper and co-biocide release rates were measured over 1 year (360 days)
- Allows observation of how:
  - Absolute Cu and co-biocide release rates vary with time
  - Relative Cu and co-biocide release rates vary with time
  - Ratio of Cu:co-biocide release rates compares with biocide content of paints
- Results are then be discussed in the context of using leaching rate data in environmental risk assessments

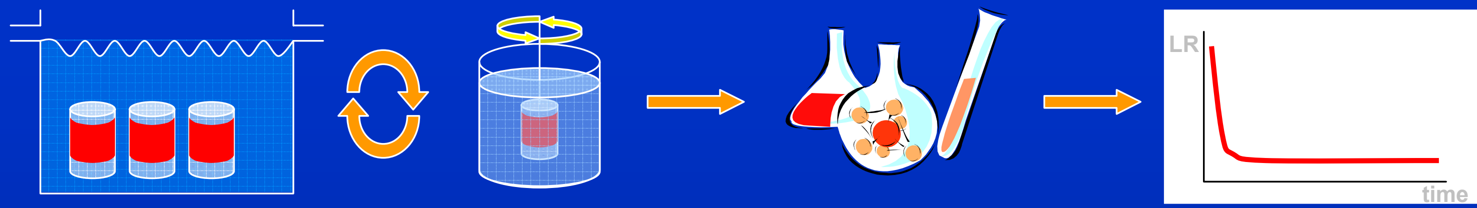
Materials

- Four different tin-free SPC antifouling paints were tested

Paint	Paint type	Copper-based biocide	Co-biocide
A	Tin-free SPC	Cuprous oxide	Copper pyrithione
B	Tin-free SPC	Cuprous oxide	Copper pyrithione
C	Tin-free SPC	Cuprous oxide	Copper pyrithione
D	Tin-free SPC	Cuprous oxide	Zinc pyrithione

- Representative formulations for this type of paint
- Biocide levels in paint are "typical" (Cu_2O, ~35-50 wt%; co-biocide, ~2-8 wt%)

Methods: ASTM/ISO rotating cylinder method



200 cm^2 painted area circulated in artificial seawater for extended period

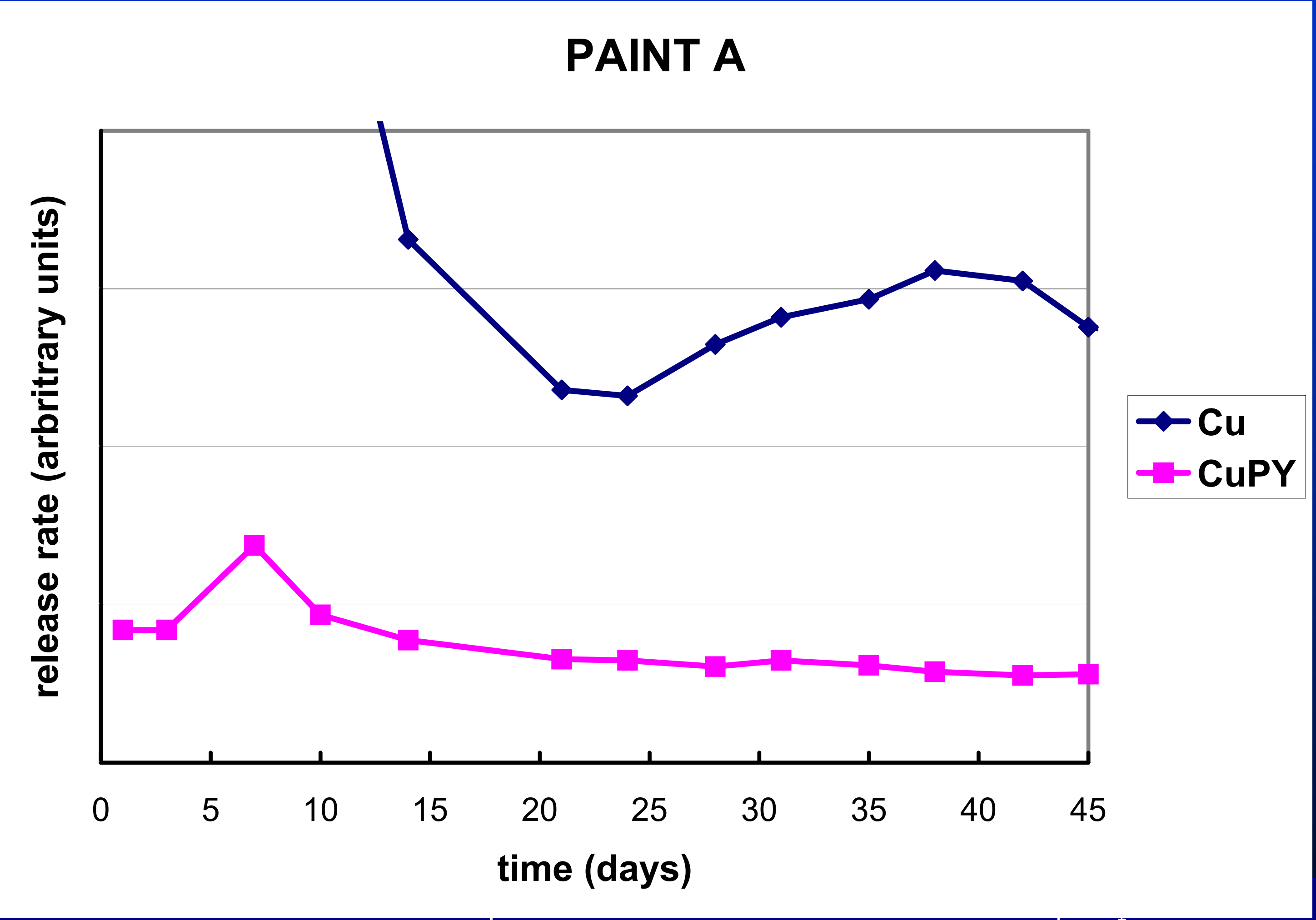
Periodic rotation in known volume of artificial seawater for 1 hour

Analysis of leachate for Cu and PT (split samples)

Release rate based on biocide conc., volume, area, and rotation time ($\mu g\ cm^{-2}\ d^{-1}$)

Parameter	Limits	Accordance with ASTM?
Temperature	24 – 26 °C	Yes
pH	7.9 – 8.1	Yes
Salinity	33 – 34 ppt	Yes
Test period	360 days	Yes (min 45 d)
Sampling frequency	Twice weekly to 45 days Weekly to 134 days Every 2 weeks to 360 days	Yes Yes No
Illumination	Protect PT leachate	Yes

Results: absolute release rate over first 45 days (ASTM min.)



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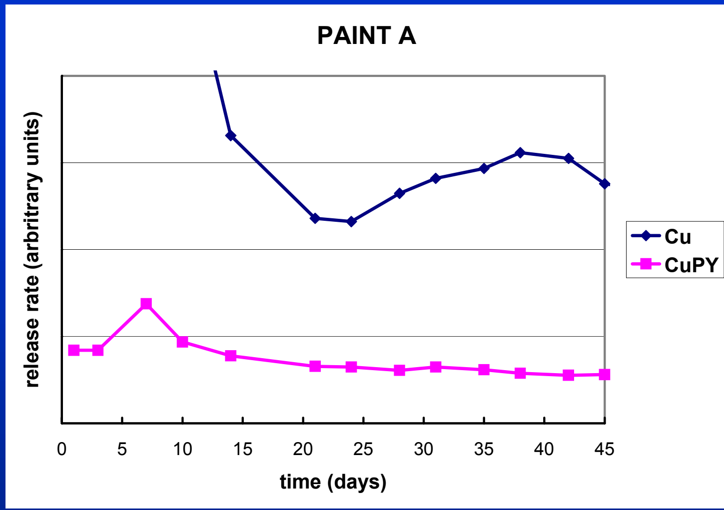
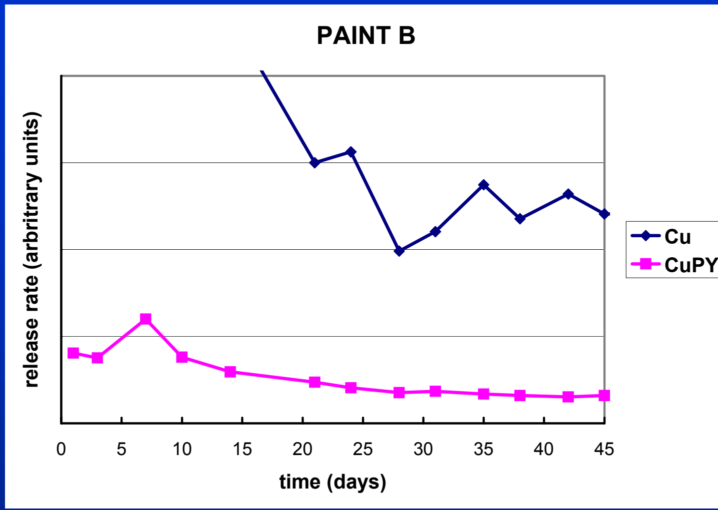
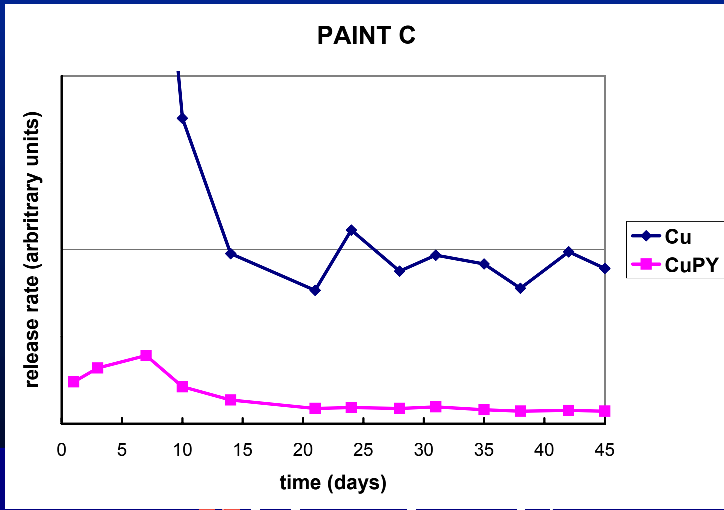
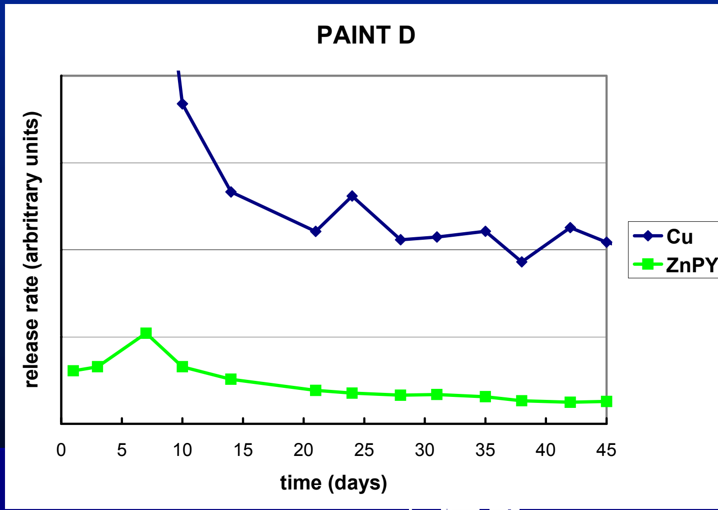
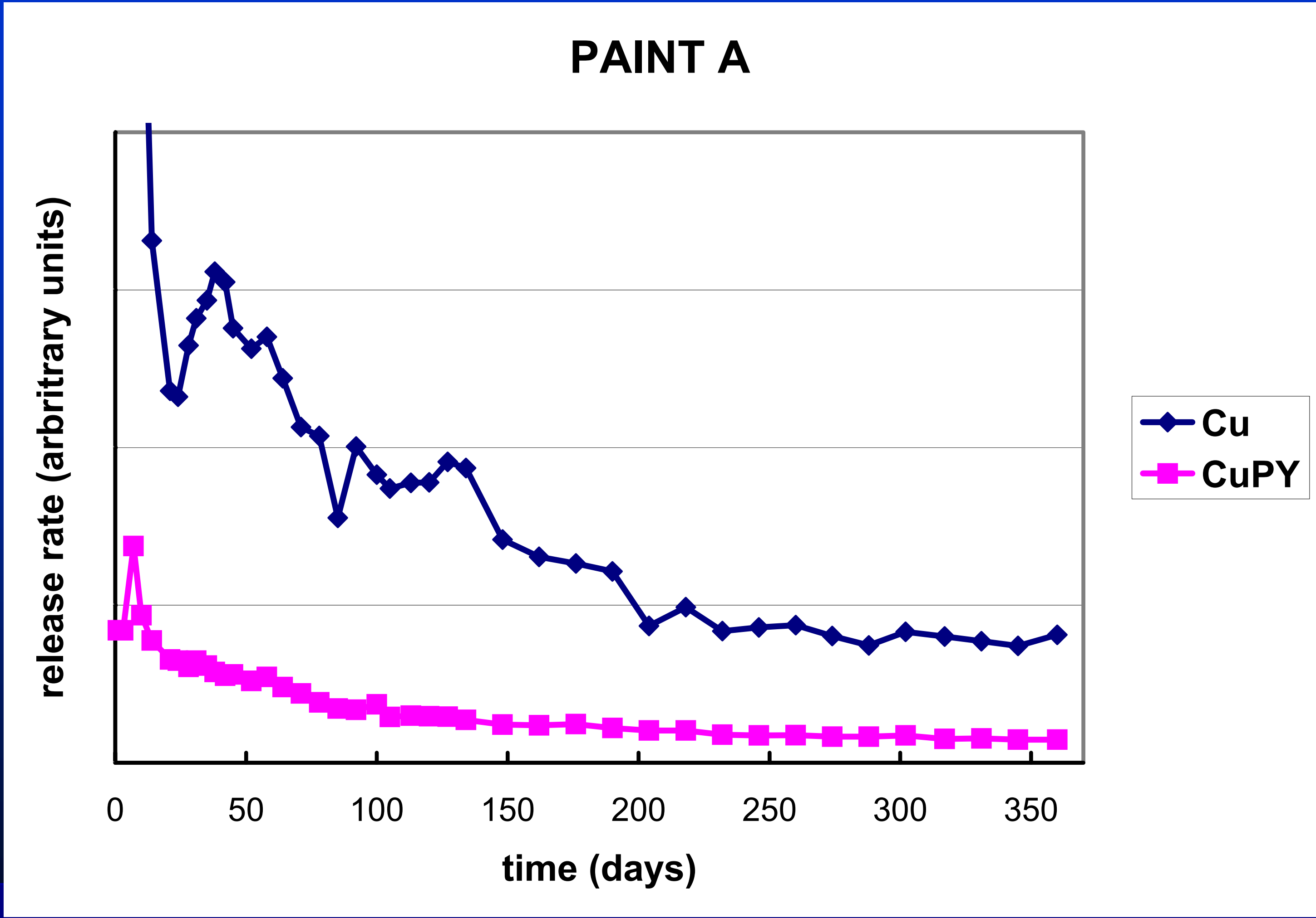








Results: absolute release rates over 360 days



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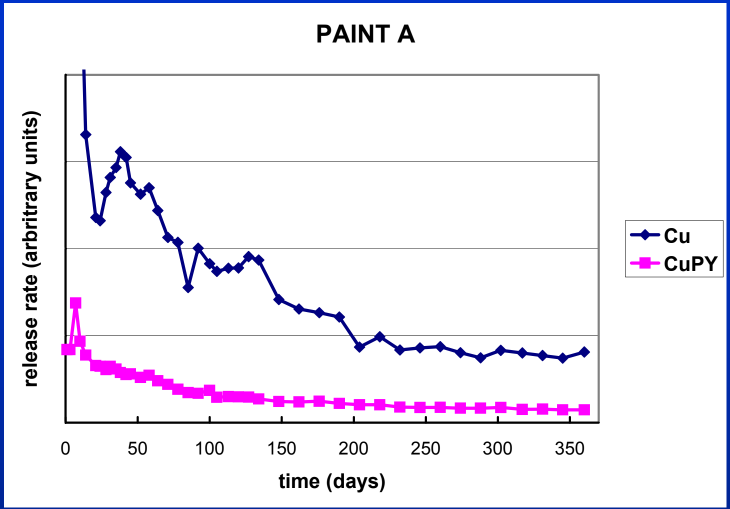
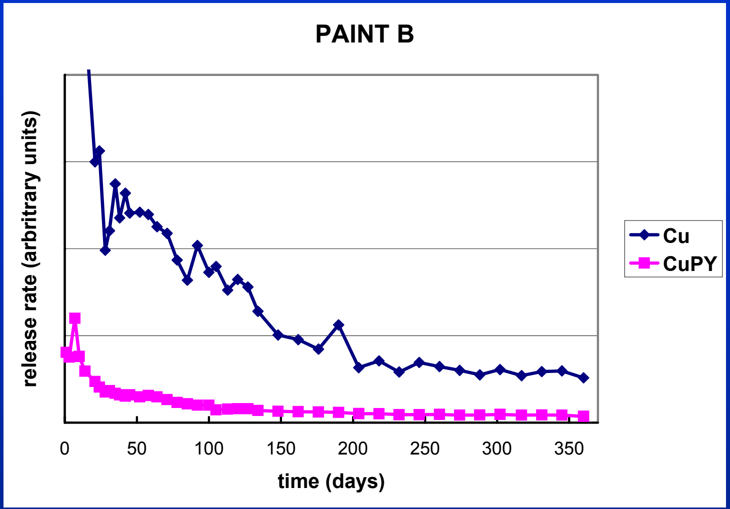
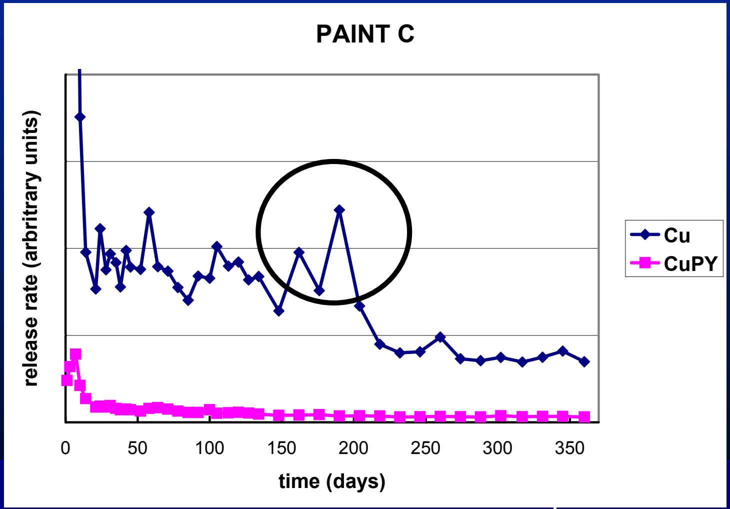
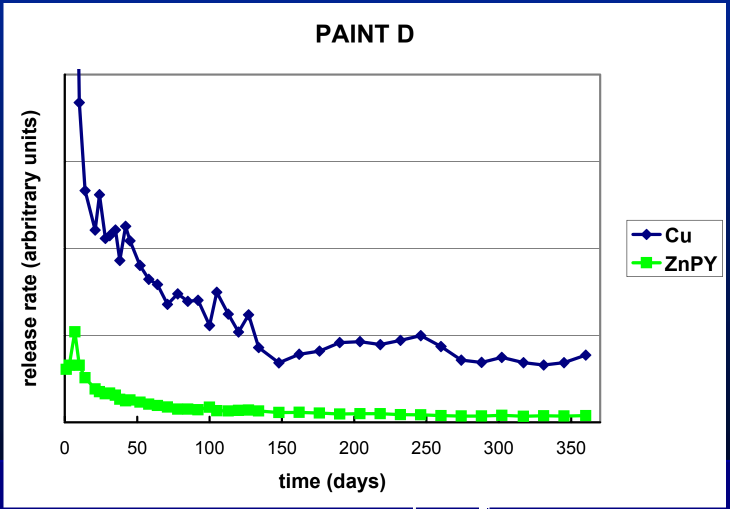








Paint C – source of outliers?

- Small paint flakes observed in test chamber after testing Paint C at 162 and 190 days

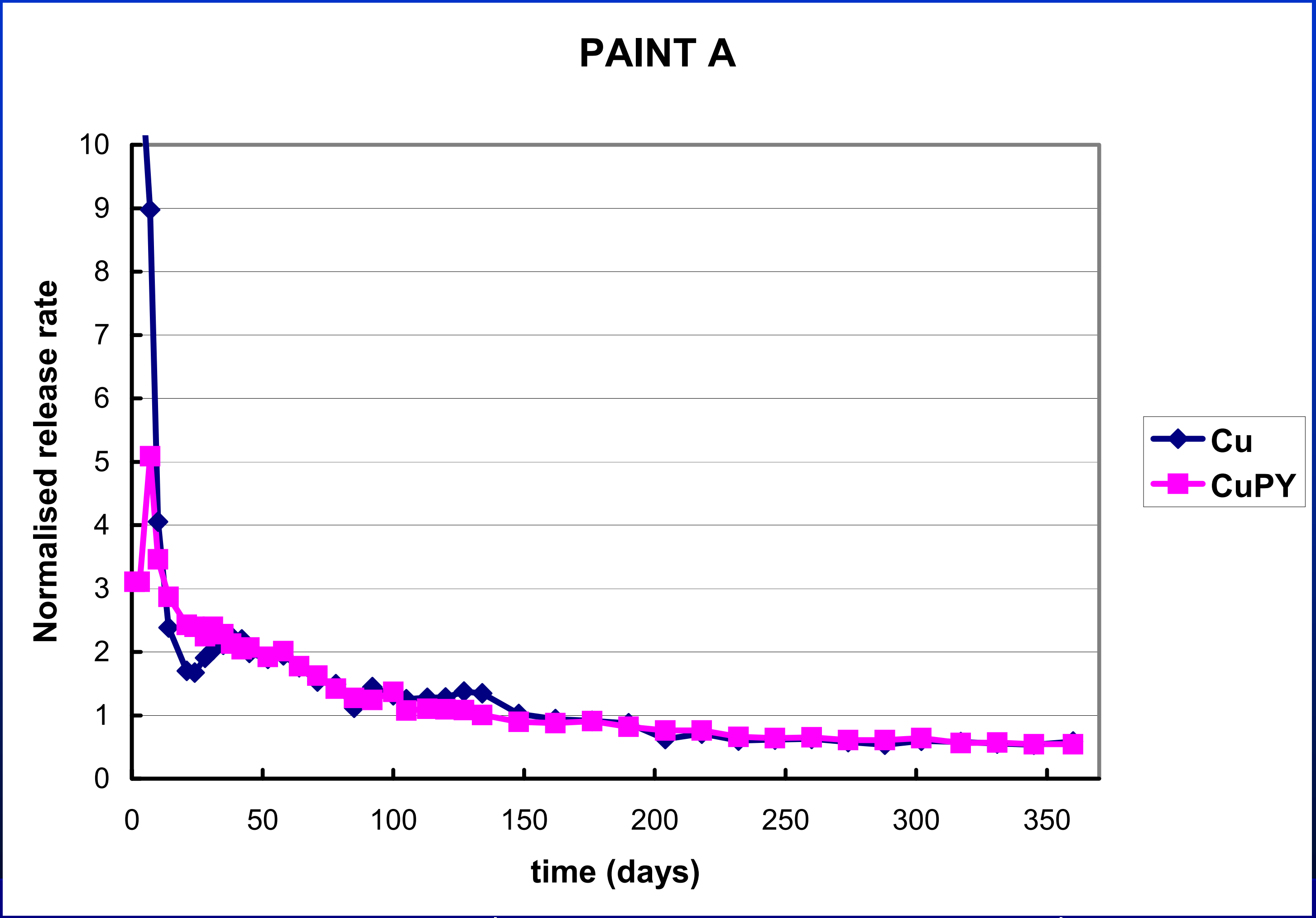
Data-treatment 1: normalisation

- Release rates are expressed relative to the long term mean release rate for each paint and each biocide
  - For each paint, mean release rate for each biocide calculated from 21-360 days according to ASTM procedure
  - Each individual release rate data point is then divided by the long term (21-360 day) mean release for that biocide and paint

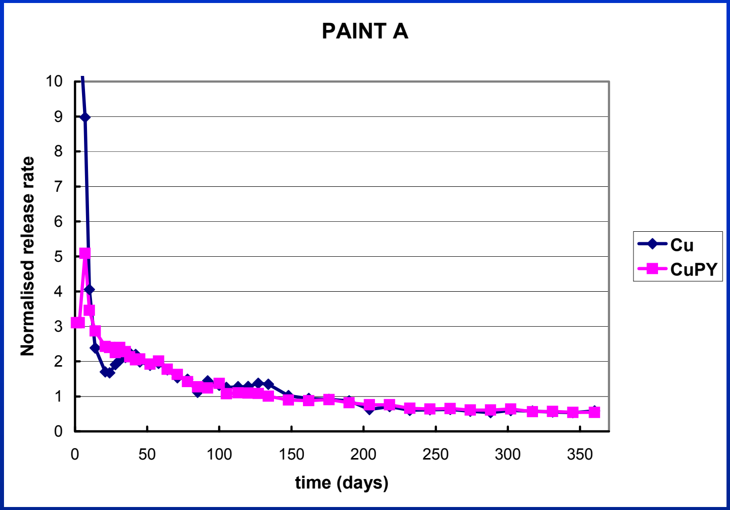
$$(\text{Release Rate})_{\text{norm}} = \frac{(\text{Release Rate})_{\text{obs}}}{(\text{Mean Release Rate})_{21-360\ \text{days}}}$$

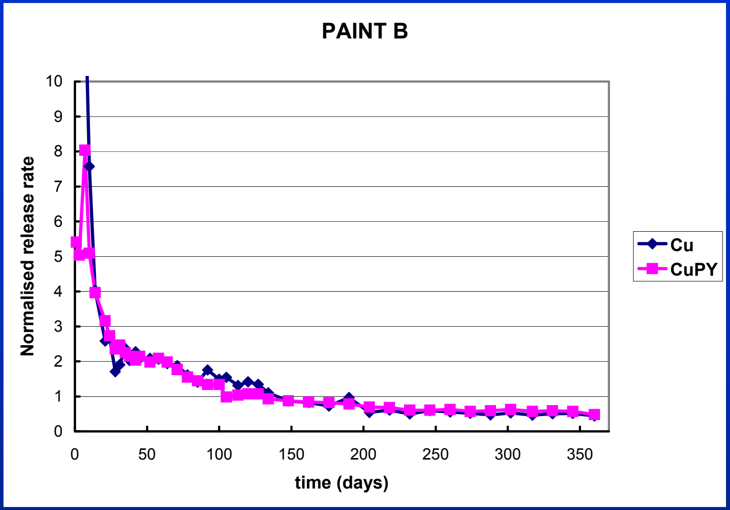
- Normalised relative release rates are then plotted (long term (21-360 day) average release rate = 1)

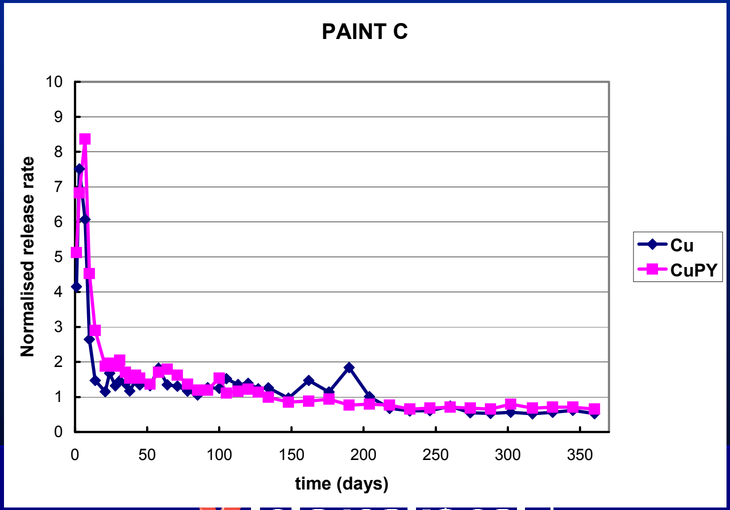
Results: Release rate normalised against 21-360 day mean

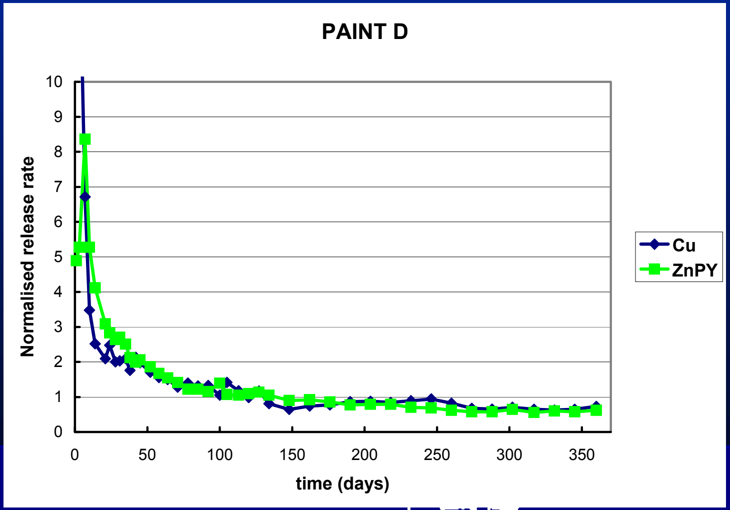


Results: Release rate normalised against 21-360 day mean









Data-treatment 2: ratio of Cu and co-biocide release rates

- For each paint, the observed ratio of Cu:PT release rate is calculated at each measurement point

$$= (\mathrm{Cu:PT})_{\mathrm{obs}}$$

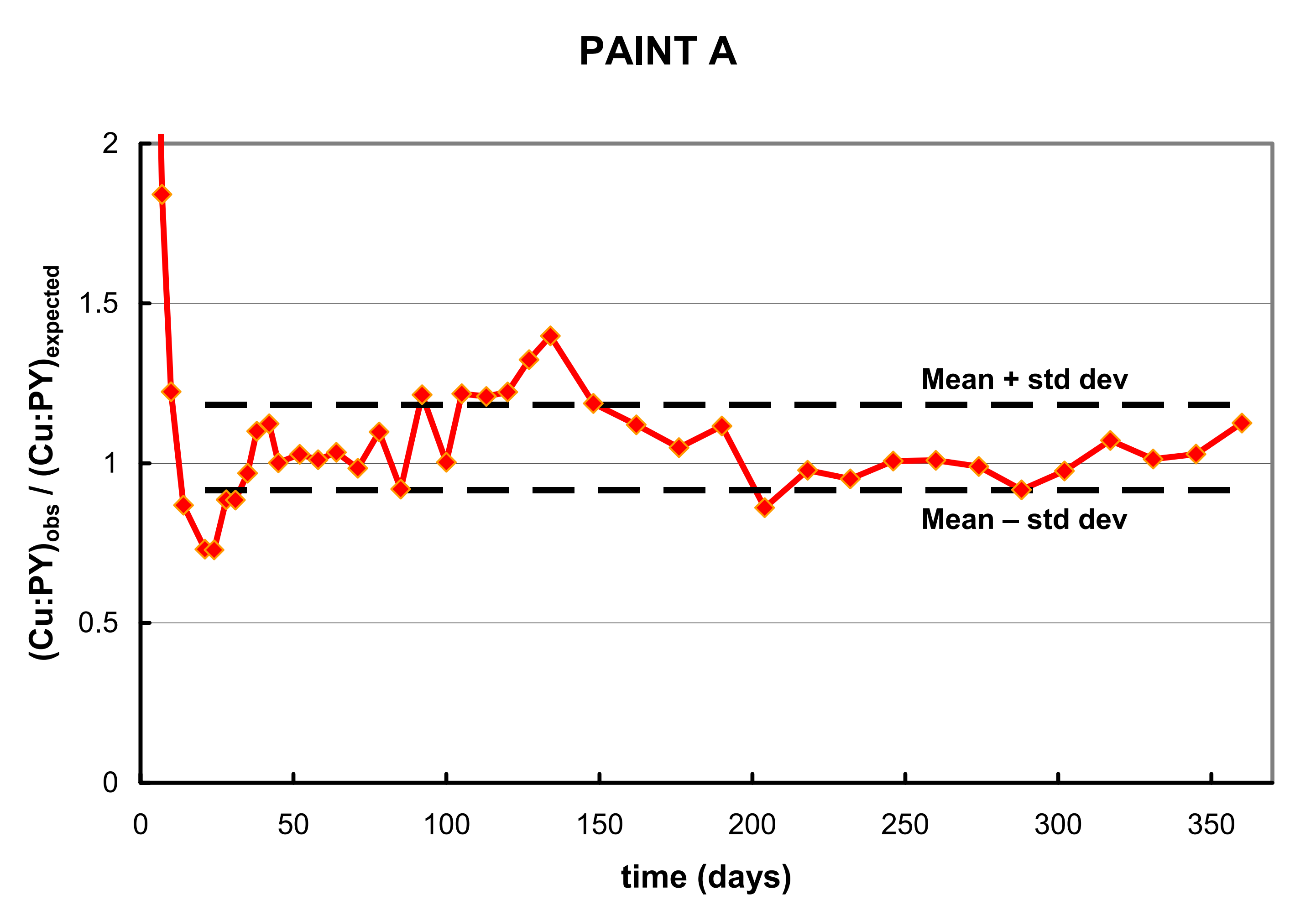
- For each paint, the expected ratio of Cu:PT release rates is accurately calculated from the paint formulations

$$= (\mathrm{Cu:PT})_{\mathrm{expected}}$$

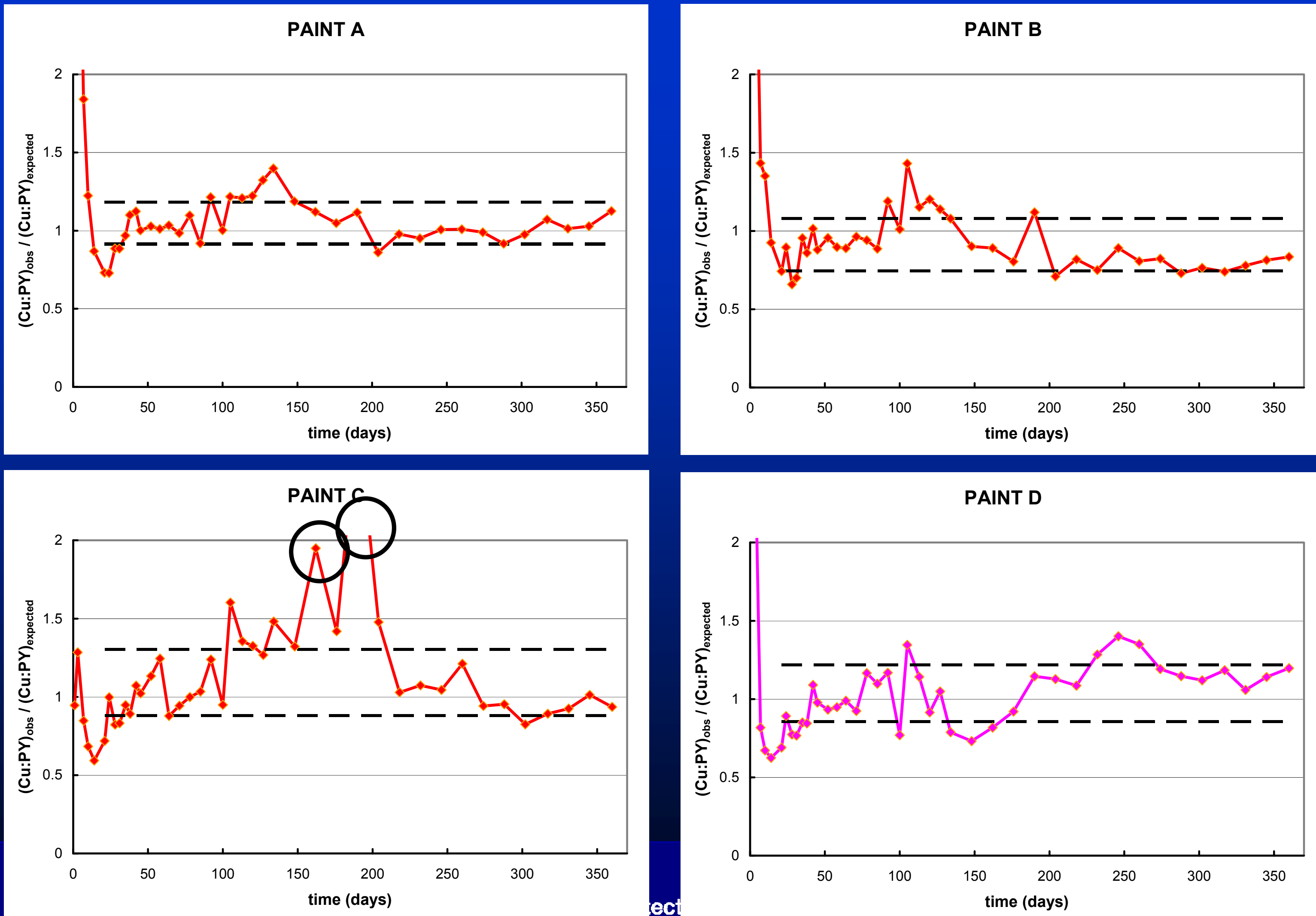
- Observed ratio of Cu:PT release rates for each paint is then normalised against expected release

$$(\mathrm{Cu:PT})_{\mathrm{norm}} = \frac{(\mathrm{Cu:PT})_{\mathrm{obs}}}{(\mathrm{Cu:PT})_{\mathrm{expected}}}$$

Results: Observed/expected Cu and co-biocide release rate ratios



Results: Obs/exp Cu and co-biocide release rate ratios



Results: Variation of Cu:co-biocide release rates with time

Summary results for 21-360 day period

Paint	Co-biocide	Mean $(Cu:PT)_{norm}$	Std. deviation	Relative std. dev. (%)
A	CuPT	1.05	0.13	12.7
B	CuPT	0.91	0.17	18.3
C#	CuPT	1.09	0.21	19.4
D	ZnPT	1.04	0.18	17.4
Mean for paints** **A-D		1.02	0.17	16.9

 # Note: Outlying data-points for Paint C have been disregarded in this data analysis

Discussion

- Copper and co-biocide leaching is highly synchronous over a 1 year period despite major differences in physico-chemical properties

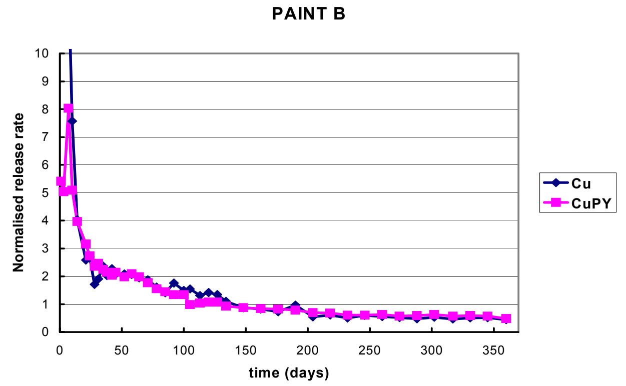
Biocide	Water Sol. (20 °C) #	Dissolution
Cu_2O	< 7 µg $litre^{-1}$	Complex
CuPT	60 µg $litre^{-1}$	Simple
ZnPT	8000 µg $litre^{-1}$	Simple

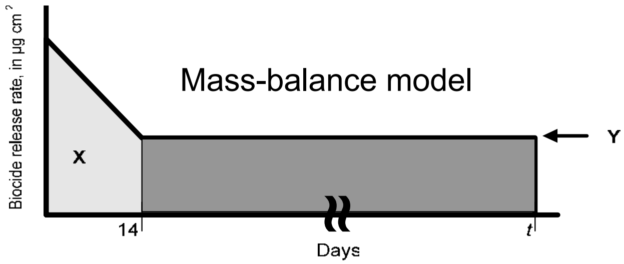
UK-HSE (1999, 2003, 2005)

- Coupled release kinetics for widely different biocides
- Biocide release is controlled by the properties of the paint, not the properties of the biocide
  - Behaviour highly likely to be independent of test method/conditions
  - i.e. same synchronous release behaviour expected under in-service conditions for these paints
- Anticipate similar behaviour for other biocides in paints of this type

Discussion

- Typical early "burst effect" seen for Cu and co-biocides
  - Mean $(X/Y)_{PT}$ = 69% $(X/Y)_{Cu}$
  - Range = 48-105%
- Long term leaching ratios reflect biocide content of paints
  - Mean $(Cu/PT)_{norm}$ = 1.02



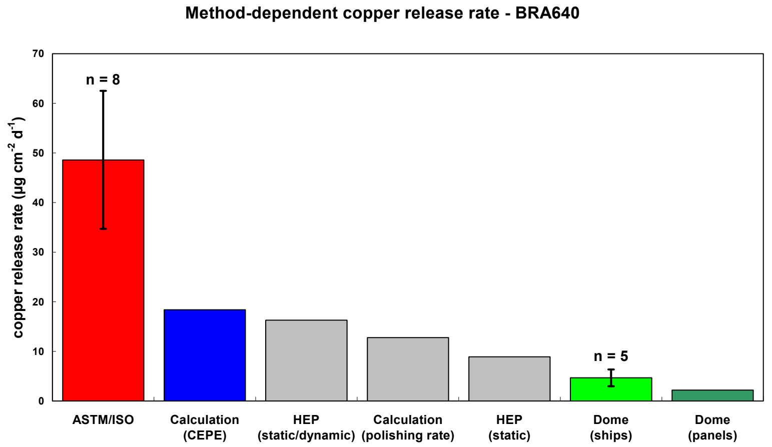


- Observed behaviour fits well with CEPE/ISO mass-balance model
- Average initial co-biocide pulse slightly lower than for copper
- Env. risk assessments based on 14-day cumulative release will tend to be slightly more conservative for co-biocide than for copper
- Short and long term behaviour validates CEPE/ISO model for co-biocide release from paints of this type

Discussion

- ASTM/ISO method shown to overestimate in-service Cu release by factor of <u>at least</u> 5.4 in harbours/marinas
- Minimum factor for CEPE/ISO mass balance is <u>at least</u> 2.9

Source: Finnie (2006)

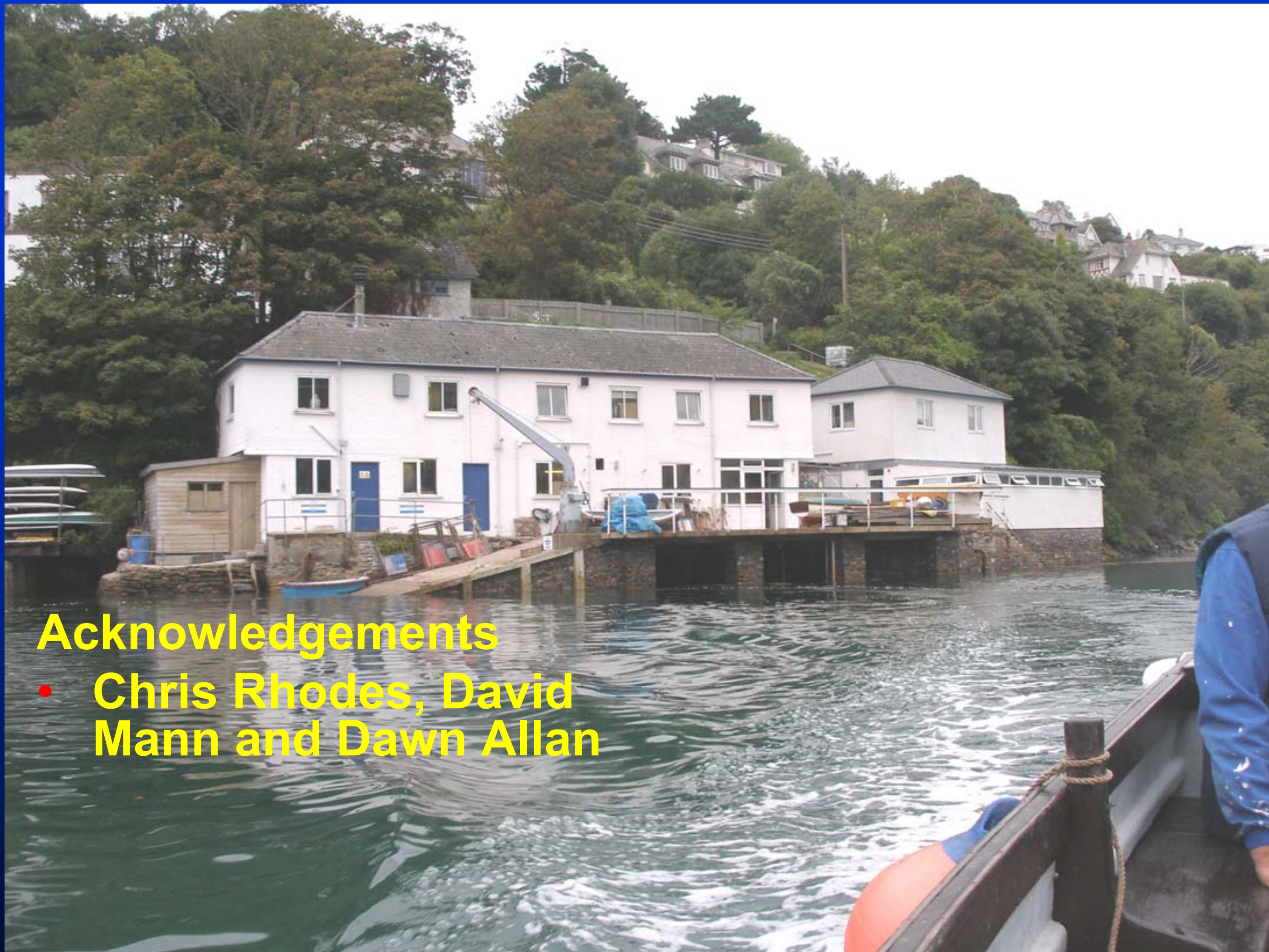


- Observed synchronous biocide likely to be independent of test conditions
  - Same behaviour likely under in-service condition
- ASTM/ISO method will overestimate in-service co-biocide release by same extent as for copper
  - Likewise for CEPE/ISO mass-balance model
- Appropriate to use same correction factor approach for copper and co-biocide leaching data when used for environmental risk assessments

Conclusions

Copper and co-biocide release rates measured over 1 year by ASTM rotating cylinder method for a range of tin-free SPC paints containing Cu_2O and CuPT or ZnPT:

- Copper and co-biocide release rates are highly synchronous
- Long term mean ratios of copper: co-biocide release rate are 91-109% of formulated ratios (variation about mean <20% RSD for each paint)
- Short and long term behaviour fits well with CEPE/ISO mass-balance model so model now consider validated for this type of paint
- ASTM/ISO rotating cylinder method and CEPE/ISO mass balance calculations known to overestimate in-service release rates for copper in harbours and marina scenarios
- These methods will overestimate co-biocide release from these paints by the same extent, so same correction factor approach should be used for copper and for co-biocides
- *Strongly recommend widespread adoption of correction factor approach to improve accuracy of Environmental Risk Assessments*



Acknowledgements

- Chris Rhodes, David Mann and Dawn Allan