JOHN A. LEWIS

13th International Congress on Marine Corrosion and Biofouling

Brazil - Rio de Janeiro

23 – 28 July 2006

ORGANIZING COMITTEE

Chair Dr. *Ricardo Coutinho*
Instituto de Estudos do Mar Almirante Paulo Moreira
E-mail: rcoutinhosa@yahoo.com

Dr. *Bernardo A.P. da Gama*
Universidade Federal Fluminense
E-mail: bapgama@vm.uff.br

Dr. *Renato C. Pereira*
Universidade Federal Fluminense
E-mail: egbrecp@vm.uff.br

Dr[a]. *Ilana R. Zalmon*
Universidade Estadual do Norte Fluminense
E-mail: ilana@uenf.br

Dr[a]. *Helena P. Lavrado*
Universidade Federal do Rio de Janeiro
E-mail: hpasseri@biologia.ufrj.br

Dr. *Luis Felipe Skinner*
Universidade do Estado do Rio de Janeiro
E-mail: lskinner@uerj.br

Welcome to the 13th International Congress on Marine Corrosion and Fouling

The first International Congress on Marine Corrosion and Fouling was held in France in 1964. Since then, it has occurred at approximately four year intervals until recently, when the growing interest of the scientific, technical and political communities led it to occur every two years. The last Congress was held in Southampton, U.K., and this Congress, the 13th, will be held in Rio de Janeiro, Brazil, in July 2006.

The Congress has become the foremost international scientific conference on all aspects of deterioration of materials in the sea. This interdisciplinary conference brings together scientists from academia, industry, and government organizations (defense, regulatory) to present and discuss recent scientific developments in understanding and combating the degradation of materials, structures, and the performance of man-made structures in the marine environment.

The topics approached in this meeting range from purely basic research in the fields of biofouling and corrosion to applied aspects, such as antifouling paints or the pollution derived from them, the role of ship hull fouling and ballast water as vectors for the introduction of non-indigenous species, the discovery of natural or synthetic new materials for fouling and corrosion prevention, etc.

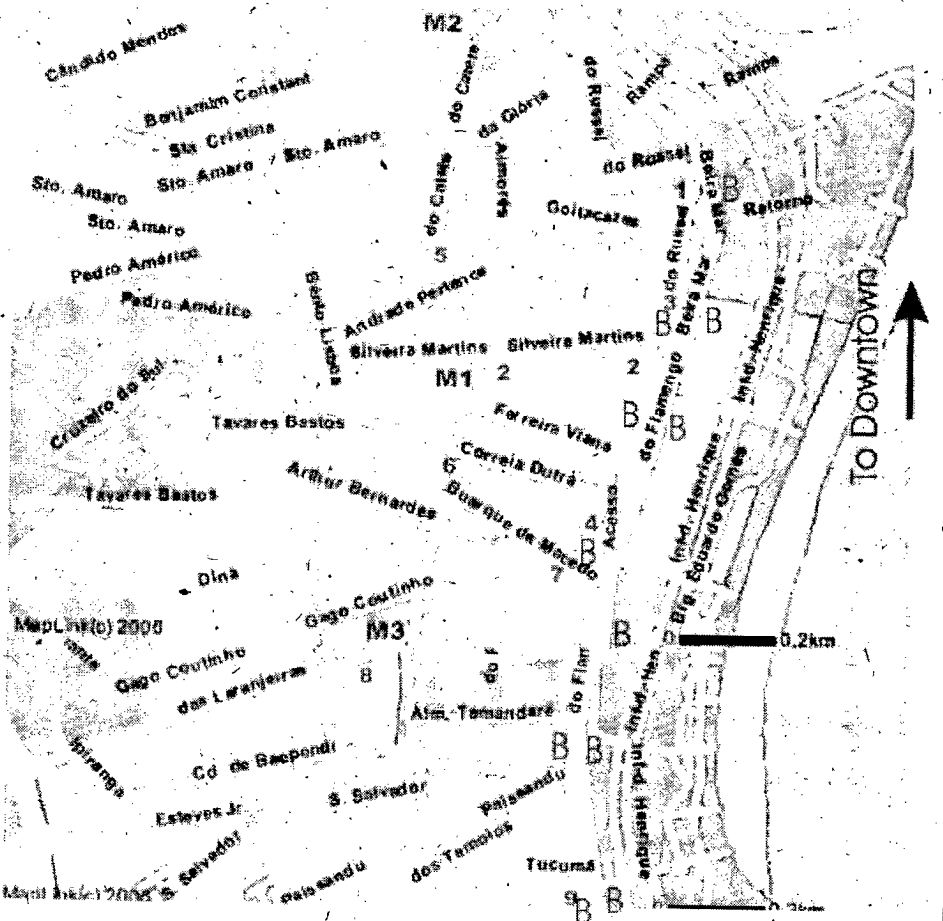
This is the first time the Congress will be held in a South American country, and it is hoped that, in addition to maintaining the high quality standard of the Congress, the 13th Congress will be noted for bringing together scientists, engineers and other professionals concerned with marine corrosion and biofouling in the atmosphere of warmth collaboration that is so characteristic of Rio de Janeiro.

We hope you enjoy it.

Ricardo Coutinho
Chair
13th ICMCF

13TH BIOFOULING RIO 2006 - 24 - 28 July 2006

Reference map



1 Hotel Glória - Congress Location

M - Metro - Subway (1Catete, 2 Glória, 3 Largo do Machado)

B - Bus stop (regular lines)

2 - Museu da República (Republic Museum)-A very nice park with Restaurant on gardens and cafe

Main streets: Praia do Flamengo (Hotel Glória location), Rua do Catete (Metró and Buiness street with banks, markets and some shopping)

OFFICIAL PROGRAMME

	Sunday 23th July 2006	
4pm – 7pm	**Registration**	
7pm – 8pm	**Brazilian Coffee**	
	Monday 24th July 2006	
8am – 8.30am	**Registration**	
8.30am – 8.45am	**Opening Remarks**	
8.45am – 9.30am	**Plenary presentation**: Past, present and future of marine antifouling research: coherent ramblings of an ancient mariner **Andy Jacobson**	
9.30am	**Coffee break**	
10am –12.30pm	**Mini-symposium:** New methods in biofouling research **Organizer: Maureen Callow** New bacterial biofilm assays for assessing the biofilm formation and release properties of novel antifouling coatings and materials P. Willemsen, R. Biersteker, F. D'Souza and J. Klijnstra High throughput laboratory screening methods for evaluation of antifouling and foul-release performance of marine coatings S.J. Stafslien, J. A. Bahr, J.W. Daniels, J.A. Finlay, F. Cassé, M. E. Callow and J.A. Callow Exploring attachment of marine invertebrates A. S Clare, J-P. Marechal and N. Aldred Application of underwater digital in-line holography in antifouling research A. Rosenhahn, M. Heydt and M. Grunze Rapid measurement of barnacle adhesion strength D. Rittschof, S. Stafslein, E. Holm, G. Swain, B. Orihuela and E. Ralston High-throughput workflow for developing new antifouling and fouling-release coating systems D. C. Webster, P. Majumdar, A. Ekin, R. J. Pieper, B. J. Chisholm, J. A. Bahr, D. A. Christianson and C. Gallagher-Lein	
12.30am – 2pm	**Lunch**	
2pm	**Session A**: Biofouling control mechanisms **Chair: John Lewis** Beyond biocides: where lies the future for biofouling control John Lewis	**Session B**: Natural anti-fouling mechanisms **Chair: Peter Steinberg** Interaction between micro-organisms, surface topography and antifouling properties of a simple polymer A. Afsar, T. Charlton, P. Steinberg
2.15pm Stefan	Enzymes in antifouling coatings, a review S. M. Olsen, L. T. Pedersen, S. Kill, M. Laursen and K. Dam-Johansen	A highly potent antifouling compound from a deep-sea bacterium Ying Xu, Xiancui Li, Ning Zhou, Xiang Xiao and Pei-Yuan Qian

2:30pm Diego	Accelerated optimization of chemically-active AF paint products D. M. Yebra, S. Kill, C. E. Weinell and K. Dam-Johansen	Fouling remediation through the use of grazers in shellfish aquaculture D. I. Watson, S. Durr, D. Beaz, E. Bergtun, R. Breur, J. Cebria, J. Davenport, D. Fowler, C. Hough, J. Icely, A. Lane, J. Maguire, A. Manjua, M. Martuenda, K. Maroni, J. McElwee, H. Mortensen, D. Murphy, J. Murphy, J. Newman, A. Pereira, J. Power, S. Prieto, J. Thomason, J. Watters and P. Willemsen
2.45pm Denny	Antifouling control utilizing stenoprophiluric technology D. A. Guritza, L. A. Kiefer, J. C. Baummer	Novel antifoulants: inhibition of larval settlement by proteases S. Dobretsov, H. Xiong and Pei-Yuan Qian
3pm Dida	A methodology for evaluating biocide release rate, surface roughness and leach layer formation in a TBT-free, self-polishing antifouling coatings D.J. Howell and B. Behrends	
3pm 3.15	**Session A**: Microbiological corrosion and microfouling **Chair**: **Brenda Little**	**Session B**: Natural antifouling mechanisms **Chair**: **Renato Crespo Pereira**
	Evaluation of deoxygenation as a corrosion control measure for seawater ballast tanks J. S. Lee, R. I. Ray and B. J. Little	Chemical defense in the red seaweed *Laurencia obtusa*: Do natural surface elatol concentrations inhibit herbivore and fouling organisms? D. B. Sudatti, S.V. Rodrigues, R. Coutinho, B.A.B. da Gama, R.C. Pereira
3.15pm 3.30	Role of EPS of fouling bacteria on the corrosion of mild steel F. D'Souza and N. B. Bhosle	Study of anti-settlement activities of meroditerpenoids purified from *Halidrys siliquosa* G. Culioli, R. Valls, J-P. Marechal, A. Ortalo-Magne, L. Piovetti, A. S. Clare and C Hellio
3.30pm 3.45	In-situ monitoring of corrosion in Singapore offshore seawater Hu Xiaoping, D. J. Blackwood and S. L. M. Teo	Antifouling activities of avarol/avarone and their derivatives against marine bacteria, microalgae and barnacles J-P Marechal, C. Hellio, B. Veron, A. S. Clare, I. Novakovic, S. Tufegdzic, D. Sladic, J. M. Gasic, M. Tsoukatou, C. Vagias and V Roussis
3:45pm 4.00	Specific epibacterial communities on macroalgae: phylogeny matters more than habitat T. Lachnit, M. Blumel, J. F. Imhoff and M. Wahl	Anti-microfouling activities of two invasive macroalga extracts from Brittany (France): *Sargassum muticum* (Fucales) and *Grateloupia turuturu* (Halymeniales)

		E. Plouquern, C. Hellio, O. Bertrand, E. Deslandes, B. Veron and V.Stiger
4pm 4.15	**Coffee break**	
4.30pm		**Session B**: Non-biocidal coatings based on silicone for biofouling control **Chair: Geoffrey Swain**
		Field demonstration and economic evaluation of nontoxic hull coatings on pleasure craft in San Diego Bay, California. L. T. Johnson and J. A Gonzalez
4.45pm		Statistical adhesion study of silicone coatings: the interaction of thickness, modulus, and shear rate on adhesion force J. Kim, B. Chisholm and J. Bahr
5pm		
5.15pm		Superhydrophobic coatings and fouling resistance A. J. Scardino, H. Zhang, R. Lamb and R. De Nys
6.30pm – 8.30pm	**Conference cocktail for all attendees**	
	Tuesday 25th July 2006	
8.00am – 8:45am	**Plenary presentation:** Novel antifouling concepts **Dan Rittschof**	
	Session A: New materials **Chair: Dean Webster**	**Session B**: Ship coatings and design **Chair: M P Schultz**
8.45am	Novel, environmentally-friendly, antifouling/fouling release coatings developed using combinatorial methods B. J. Chisholm, D. A. Christianson, S. J. Stafslien, C. Gallagher-Lein, J. Daniels and D. Webster	Frictional drag of ship coating systems M. P. Schultz
9am	Novel acrylic nanodispersions in controlled-release self-polishing antifouling paints D. M. Yebra, H. Tanabe, S. Arias, H. Sasaki, M. Porsbjerg, Y. Iwase, A. Sánchez, T. Tanabe, S. Kiil	Analysis of the relative performance of marine coatings from 1974-2004: the effects of the TBT-Ban J. C. Thomason
9.15am	Microencapsulation to control dcoit release from antifouling coatings S.E. Reybuck, E.G. Haslbeck, and P. Andreassen	Towards environmental sustainable clean ship design O. Yaakub, Ab. Saman Ab. Kadir and O. Sulaiman
9.30am	Stenoprohiluric coatings – The Dawn of Sustainable non toxic marine.	Measuring the performance of today's antifouling coatings.

	antifoulants D. A. Guritza, J. C. Baummer and A. Lynda.	G. Swain, B. Kovach, A. Touzot, F. Casse and C. Kavenagh
9.45am	**Coffee break**	
10.15am – 12.30pm	**Mini-symposium:** Novel non-biocidal coatings and technologies (non-silicone) **Organizer: James Callow** Surface energetics of fluorinated/siloxane copolymer films for marine biofouling release G. Galli, M. Andreucci, E. Martinelli and E. Chiellini Engineered non-toxic, anti-fouling designs for marine environments A. Brennan, M. Callow, J. Callow, M. Carman, T. Estes, J. Finlay, M. Hardfield, B. Neved, R. Perry, J Schumacher, D. E. Wendt and L. H. Wilson Development of nonfouling materials and coatings for marine applications Shaoyi Jiang Novel no-biocidal hydrophobic antifouling coatings Y. Erbil, C E Ozen, I Orkan, E. Doganci, M. Dandan and C. Hamamci Maleic acid copolymer thin films-eletrosurface studies on a potentially fouling-resistant material C. Wemer and T. Osaki Development of siloxane-urethane fouling-release coatings: initial screening studies D. C. Webster, P. Majumdar, A. Ekin, R. J. Pieper, D. A. Christianson, C. Gallager-Lein and S. Stafslien	
12.30pm – 2pm	**Lunch**	
2pm	**Session A**: Regulation of A/F products and environmental Issues **Chair: Helena P. Lavrado** Do we need an uncertainty factor for PEC? K. Shibata, R. Kojima, Y. Yamaguchi, S. Sugasawa, T. Shibata, O. Miyata and T. Senda	**Session B**: Invertebrate and algae macrofouling **Chair: M. Wahl** The ecology of epibiosis M. Wahl
2.15pm	Improved estimates of environmental copper release rates from antifouling products A. Finnie	Fouling and antifouling in aquaculture - a review S. Durr, D. I Watson, D. Beaz, E. Bergtun, R. Breur, J. Cebria, J. Davenport, D. Fowler, C. Hough, J. Icely, A. Lane, J. Maguire, A. Manjua, M. Marhuenda, K. Maroni, J. McElwee, H. Mortensen, D. Murphy, J. Murphy, J. Newman, A. Pereira, J. Power, S. Prieto, J. Watters, P. Willemsen, J. C. Thomason
2.30pm	Water quality, Invasive species and tourism policies affecting biofouling control for	Patterns of recruitment and development of biofouling at

	California and Baja California boats in Saltwater L. T. Johnson and J. A. Gonzalez	European aquaculture facilities S. Durr, D. I. Watson, D. Beaz, E. Bergtun, R. Breur, J. Cebrá, J Davenport, D. Fowler, C. Hough, J. Icely, A. Lane, J. Maguire, A. Manjua, M. Marhuenda, K. Maroni, J. McElwee, H. Mortensen, D. Murphy, J. Murphy, J. Newman, A. Pereira, J. Power, S. Prieto, J. Watters, P. Willemsen and J.C. Thomason
2.45pm	From laboratory to field: dissipation of the marine antifoulant active DCOIT A. Jacobson, I. Guo, R. C.A. Steen, F. Ariese, B. Van Hattum and J. Jacobsen	Pattern of antifouling defence in mussels: aspects of biogeografphy, phylogeny and component synergy A.V. Bers and M. Wahl
3pm	Photochemical behavior of zinc pyritione: degradation kinetics and byproduct identification V. A. Sakkas, K. Shibata, Y. Yamaguchi, S. Sugasawa and T. Albanis	Investigation on marine fouling on floating structures west of dongsha islands, the northern south China sea T. Yan, W.X. Yan, Y. Dong, H. J. Wang, Y. Yan and G. H. Liang
3:15pm	Are current risk assessments for copper antifoulings appropriate? M. J. Waldock, S, Brooks, B. Jones and T. Bolam	Antifouling chemical defense in neritid gastropods *Nerita albicilla* and *N. Oryzarum* from tuticorin, Gulf of Mannar, Southeast coast of India. M. S. Ramasamy and A. Murugan
3.30pm	The role of dermal penetration in operator exposure assessment for antifouling paints: How do we most accurately measure systemic exposure? G. Prowse, C. Roper and N. Skoulis	Antifouling activity of extracts of 30 species of temperate marine algae against barnacle (*Balanus amphitrite* and *Semibalanus balanoides*) cypris larvae J-P. Marechal, A. S. Clare and C. Hellio
3.45pm	Marine paint: from multidisciplinary research to environmentally sound antifouling paints B Dahlbäck	Quantitative surface characterization and fouling resistance of marine mollusks from the great barrier reef A. J. Scardino, D. Hdleston, Z, Peng and R. De Nys
4pm	**Coffee break**	
4.30pm – 5.30pm	**Special plenary presentation:** Marine endophytes: a source of new chemical natural products, a review **Gareth Jones**	
5.30pm – 7pm	**COIPM Meeting**	
Wednesday 26th July 2006		
Day out – excursion		

Thursday 27th July 2006	
8am– 8.45am	**Plenary presentation**: "Are larvae of marine invertebrates smart enough to distinguish biofilm developed under contrasting environments?" **Pey- Yuan Qian**
8.45am	**Coffee break**
9.15am – 12pm	**Mini-symposium:** Invasive species **Organizer: Coutts, A. D. M** Ships' sea chests: an overlooked mechanism for species transfers Coutts, A. D. M., and Dodgshun, T. J. And *En route* survivorship of biofouling organisms on various vessel types. Coutts, A. D. M.,Taylor. M. D, Gardner. J. P.A. and Hewitt, C. L. Is the invasive potential of a fouling community a function of its diversity? First results from a global experiment M. Lenz and M. Wahl Vessels' hulls as intra-regional vectors of species F. B. Mostacato and R. Coutinho Every nook and cranny: niche biofouling as a potential vector for invasive marine pests J. Lewis and A. Gillham
12pm – 2pm	**Lunch**
	Poster Session A –Student Award Pedicellariae of the crown-of-thorns sea star as a natural defence against fouling: at a pinch! J. Guenther and R. de Nys Epibiont communities on sea stars: only specialists need apply J. Guenther and R. de Nys Proximity to antifouling treatments affects the ecology of invertebrate assemblages K. A. Dafforn, T. M. Glasby and E. L. Johnston Short term testing of antifouling surfaces: the importance of color E. Ralston, M. Tribou and G. Swain Initial Bacterial adhesion in Marine Environment C. Wang, Q. Zhao, Y. L. Liu and S. Wang The Interactions of season, surface texture, flow regime and glass transition temperature on the development of marine biofilms C. M. Zuern and J. C. Thomason Does pollution effects the seaweeds fouling activity to artificial substrate placed in Guanabara Bay, RJ, Brazil? J. Torres, L. M.S. Gestinari and Y.Yoneshigue-Valentin

Poster Session A –Student Award

The secret history of a paint flake: using SEM and EDX analysis to investigate the coating cycle of a commercial vessel and assess potential point sources
D. J. Howell and B. Behrends

Study of exploration behavior of algae using in-line holography
M. Heydt, A. Rosenhahn and M. Grunze

Enzyme activities and imposex level in *Hexaplex trunculus* as biomarkers of TBT in Mediterranean sea
F. Garaventa, A. Jemec, M. Faimali, A. Ramsak, K. Stopar, K. Sepeié, G. Greco, C. Corrà, L. Lipej and A. Malej

Biomonitoring of the environmental contamination by TBT (tributyltin) in the Mediterranean sea: new implications in the use of imposex as a suitable tool.
F. Garaventa, M. Faimali, A. Terlizzi, S. Fiorini, E. Centanni and B. Pavoni

In vitro antibacterial and antimicrofouling activity of some synthetic derivatives and natural polymeric 3-alkylpyridinium salts purified from the sponge *Reniera sarai*
E. Chelossi, I. Mancini, K. Sepeié, T. Turk, F. Garaventa, M. Faimali

Measurements of the adhesion strength of permanently attached cyprids and newly metamorphosed barnacles (*Balanus amphitrite)* using a fully turbulent flow channel
A. Cavaco, A. S. Clare, M. J. Downie, A. Beigbeder, Ph. Dubois and Ph Degée.

Underwater hull crooming as a means of improving ship hull coatings performance
M. Tribou and G. Swain

Marine Biocorrosion: the influence of macrofouling in the carbon steel API 5L X65 Corrosion Behavior
L.V. R. de Brito-Messano, R. Coutinho and E. H. S. Cavalcanti

Interaction between environments factors and larvae density under eutrophic and oligotrophic conditions on the Rio de Janeiro coast, Brazil.
J. E. A. Gonçalves, R. Coutinho, I. R. Zalmon

Sucession of Biofouling under eutrophic and oligotrophic conditions on the Rio de Janeiro coast, Brazil.
J. E. A. Gonçalves, R. Coutinho, I. R. Zalmon

Antifouling activity evaluation of the glycerophospholipids isolated from marine organisms from Arraial do Cabo region – Rio de Janeiro – Brazil.
W. R. Batista, C. C. Lopes, R. S. C.Lopes, M.H.C.B. Neves and J.N.Cardoso

Semiochemichals: influence of co-specific factors on the settlement of cirripeds on rocky shores
M. Ballesté, L. M. Lage and R. Coutinho

Metals of antifouling paints are transferred to marine organisms of Guanabara Bay?
W. C. Paradas and G. M. Amado Filho

	Poster Session A –Student Award Barnacle settlement behavior on the micro-textured metal surface R. Horiuchi, Y. Kameyama, J. Komotori, S. Kobayashi and I. Katsuyama
4pm	**Coffee break**
4.30pm – 6.30pm	**Poster Session B** A new automated method to measure the adhesion strength of adult barnacles to surfaces and its comparison to ASTM D5618 S. Henry, A. S. Clare, R. J. Mutton, M. J. Downie, D. Williams and O. Willemsen Biofouling zonation in fotonegative environment at Maceió coast, Alagoas, Brasil. M. D. Correia, H. H. Sovierzoski, A. G. A. Borba Jr. and V. R. Cedro The effects of marine natural product extracts in a paint system L. D. Chambers, F. C. Walsh, R. J. K. Wood and K. R. Stokes Organotin antifouling effects along the Brazilian coast as indicated by imposex in marine neogastropods I. B. de Castro and M. A. Fernandez The effect of hybrid sol-gel films and (nano) structuring on antifouling and fouling release J. Van Zanten, C. H. A. Rentrop and P. R. Willemsen A three-year biomonitoring study on organotin pollution in Maceió, Alagoas State: imposex development in *Thais rustica* M. A. Fernandez, I. B. Castro, J. P. Quadros and E. Camillo Jr. A new, nondestructive imposex intensity evaluation protocol for biomonitoring organotin pollution in the Brazilian coast M. A. Fernandez, F. M. Pinheiro, J. P. Quadros, E. Camillo Jr, A. R. de Rezende, F. Ostritz, S. C. da Silva, D. O. Folha and T. Veloso Model sensitiviy analyses of benthic invertebrates dynamics as experiments to regulate population abundance M. A. de Guimaraens, D. C. P. da Costa and M. I. S. da Costa Development of Anti-fouling solutions for use in marine coatings J. L. Kristensen, K. V. Gothelf, F. Besenbacher, T. Rand and C. H. Poulsen Antifouling painting effect on 1-12 months benthic community sucession on an artificial reef W. Krohling, D. S. Brotto and I. R. Zalmon Scaling up to avoid the noise: the tool of globally replicated experimentation M. Lenz, M. Molis and M. Wahl Evolution of oxygen reduction current and biofilm on cathodically polarised stainless steels in seawater A. Mollica, M. Faimali, E. Chelossi, F. Garaventa, C. Corrà and G. Greco

4.30pm – 6.30pm	**Poster Session B**

Field experiments of trial antifouling paints using isocyano compounds
Y. Nogata, Y. Kitano, E. Yoshimura and I. Sakaguchi

Antifouling compounds from Japanese alga
T. Okino, T. Kamada, T. Ishii, E. Yoshimura and Y. Nogata

Life in the slip-lane: The effect of molecular level friction on algal cell adhesion
M. E. Pettitt, J. Bowen, M. E. Callow, J. A. Callow, J. A. Preece and G. J. Leggett

Advanced nanoscale characteration of marine biofouling interfaces
I. Y. Phang, N. Aldred, A. S. Clare, G. J. Vancso

Prior settler density overrides texture and orientation cues in settling *Semibalanus balanoides* cypridis in the Clyde Sea
G. S. Prendergast, C. M. Zurn, L. J. Hannson, R. M. Head, A. V. Bers, J. C. Thomason

A monolayer for antifouling with enzymes as the bioactive component
Ib Schneider, F. S. Kamounah, K. Allermann, K. Schaumburg

CoatZyme- an enzyme based, water born, self polishing coating for antifouling
Ib Schneider, K. Allermann.

Use of marine invertebrate larvae as indicator of environmental impact on fouling prevention: the Brazilian nuclear power plant case
L. F. Skinner, S. H. G. Silva, H. P. Lavrado, M. S. Viana and A. O. R. Junqueira

Field settlement induction of the mussel *Perna perna* in response to natural products from the Brown seaweed *Stypopodium zonale*
A. R. Soares, B. A. P da Gama, C. L. Teixeira, R. C. Pereira and V. L. Teixeira

Degradation of borocide® P triphenylboron-Pyridine in the marine environment
R. L. Amey and C. Waldron

Evaluation of antifouling activity of the crude organic extract of seaweed *Laurencia flagelliffera,* collected from Penha (SC-Brazil)
J. Benvenutti, K.N. Kuroshima, K.R. S. Sauer-Machado, L. L. Valle de Lacerda, M. A. B. Barreiros and L. Laçava

Substratum preference during recruitment of two invasive alien corals onto shallow subtidal reefs
J. C. Creed and A. F. De Paula

Stereological analysis of biofouling
S. Durr and J. C. Thomason

Performance of Benzoate-based epoxy coatings under simulated marine corrosion conditions
G. Blustein, R. Romagnoli, A. Di Sarli, B. Del Amo

Approaches to the control of golden mussel settlement
M. C.Pérez, M. Garcia, R. Romagnoli, M. Stupak

4.30pm – 6.30pm	Inhibition of marine biofouling by natural tannins M. C. Pérez, M. T. Garcia, G. Blustein and M. E. Stupak Environmental assessment of the effects of a nuclear power plant effluent on the fouling assemblages of Angra dos Reis (RJ) Brazil S. H. G. Silva, M. Mayer-Pinto, B. L. Ignácio, M. S. Viana, E. P. Vilanova, H. P. Lavrado, A. O. R. Junqueira, M. T. M. Széchy and M. P. Curbelo Fernandez. Iron Benzoate as environmentally-friendly pigment for paints technology : corrosion and fouling control G. Blustein, M. Garcia, M. Pérez, R. Romagnoli, B. Del Amo and M Stupak Effects of the thermocline generated by a nuclear power plant effluent on the recruitment of the fouling assemblage at Angra dos Reis (RJ) Brazil M. S. Viana, H. P. Lavrado and S. H. G. Silva Tannin capsules: a promising antifoulant L. Deladino, A. Navarro, M. Martino, R. Romagnoli, M. Garcia, M. Stupak and M. Pérez Evaluation of antifouling paints in Guanabara Bay and Arraial do Cabo, Rio de Janeiro, Brazil. J. E. A. Gonçalves, C. E. L. Ferreira, D. L. de F. Menezes, R. Coutinho Heavy metal concentrations in an artificial reef with antifouling painting C. R. Rezende, C. E. Gobo, M. Almeida, R. R. Gobo, T. P. Range, W. Krohling, I.R. Zalmon Effect of the epibiosis on the susceptibility of macroalgae to grazing M. G. N. de O. Jackson, R. Coutinho, L. M. Lage and R. C. Pereira Aquatic ecological risk assessment for Pyrithione antifoulants based on laboratory and field studies J. C. Ritter, N. P. Skoulis and R. J. Fenn MAM-PEC: A computer model to predict environmental concentrations of antifouling compounds in estuarine and coastal environments M. B. Pereira, B. van Hattum and A. Baart. Epibiosis on red seaweed *Cryptonemia seminervis* (HALYMENIACEAE): Effects on herbivory and fouling R. P. de A. Santos, B A P da Gama, J H S Miyamoto and R C Pereira Effects of temporal variability of disturbance, sequence and age on fouling communities from a tropical bay T F Porto, S Hampl, B A P da Gama, R C Pereira, M Lenz and M Wahl Antifouling mechanisms in the green sea turtle *Chelonia mydas* G. Freitas, B. A. P. da Gama, R. C. Pereira & L. T. Salgado Antifouling activity of synthetic analogues of kuanoniamine L. C. S. Pinheiro, B. A. P. da Gama, A. M. R. Bernardino & R. C. Pereira

4.30pm – 6.30pm	Test strategy and hazard assessment for medetomidine - a new antifouling candidate. H Blanck, Å Granmo, L Förlin, G Birgersson, A Hilvarsson, A Lennqvist, C Petersson, J Bellas, R Ekelund, M Haraldsson, L Norrgren, T Backhaus
8pm – 10pm	**Banquet**
	Friday 28th July 2006
8.30am – 9.15am	**Plenary presentation**: Biomimetic inspired designs for prevention of Biofouling **Rocky de Nys**
9.15am –9.45am	**Coffee-break**
9.45am –12pm	**Mini-symposium:** Marine adhesives: composition, surface interactions and curing mechanisms **Organizer: Antony S. Clare** Mechanical and molecular properties of the *Ulva* spore adhesive system J. A. Callow A great marine adhesive: diatom mucilage contains adhesive nanofibers made of supramolecular assemblies of a modular protein T. M. Dugdale, R. Dagastine and R. Wetherbee. Barnacle cement from the molecular aspect K. Kamino The byssus of the blue mussel: form and functions N. Aldred, J. A. Callow and A. S. Clare Genetic variation in adhesive tenacity and adhesive plaque characteristics in the Barnacle *Balanus amphitrite* E. R. Holm, B. Orihuela, C. J. Kavanagh and D. Rittschof.
12pm – 12:30pm	**Closing remarks**

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

PAST, PRESENT, AND FUTURE OF MARINE ANTIFOULING RESEARCH: COHERENT RAMBLINGS OF AN ANCIENT MARINER

Andrew Jacobson, Rohm and Haas Company
727 Norristown Road P.O. Box 904 Spring House, PA 19477 USA
ajacobson@rohmhaas.com

The problem of fouling on boats is almost as old as the oceans as fouling has degraded the performance of ships for millenniums. Initially seafarers employed many remedies, a few even scientifically based. As scientists began investigating fouling, chemistry started to play a more prominent role in developing marine antifoulants. Copper was one of the early antifoulants and in more advanced molecular forms is still a leading active today. The development of Self-Polishing Paints in the 1970's was a significant advancement in delivery systems of antifouling actives because it improved the efficacy, economics and longevity of the coating system. The subsequent discovery that tributyltin antifoulants caused detrimental environmental effects started an exponential increase in our understanding of marine antifouling as environmentally benign alternatives were sought. In addition to the development and marketing of environmentally friendly actives and coatings, research on the biology and chemistry of how fouling organisms (e.g., barnacles) attach to hulls, the understanding of how natural products derived by aquatic organisms prevent fouling, and the use of surface topography to prevent fouling have increased our understanding of how to reduce and perhaps prevent fouling on submerged surfaces. Hopefully this research will yield the Holy Grail; an inexpensive, low maintenance, and environmentally safe marine antifouling system.

13th International Congress on Marine Corrosion and Fouling

23th July to 28th July 2006 - Rio de Janeiro - Brazil

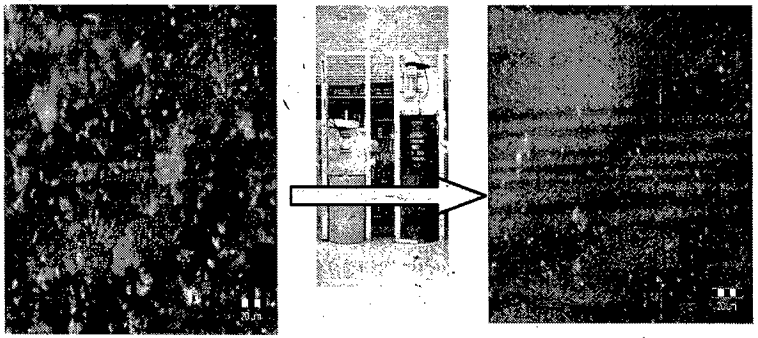
NEW BACTERIAL BIOFILM ASSAYS FOR ASSESSING THE BIOFILM FORMATION AND RELEASE PROPERTIES OF NOVEL ANTIFOULING COATINGS AND MATERIALS

P Willemsen*, R Biersteker, F D'Souza, J Klijnstra

*Presenting author: TNO Science and Industry, PO Box 505, 1780 AM Den Helder, The Netherlands, peter.willemsen@tno.nl, fax +31 2236 38888, ph.: +31 2236 38850

TNO has developed new bacterial biofilm assays for the rapid evaluation of experimental fouling-release surfaces. The paper describes the development of the protocols and gives some recent results of work conducted in the scope of the AMBIO program.

The assays evaluate the anti-biofilm formation and fouling-release properties of test materials applied to standard glass slides with respect to single-species or mixed marine bacterial biofilms composed of *Cobetia marina, Marinobacter hydrocarbonoclasticus* and *Vibrio alginolyticus*. Bacterial enumeration is carried out by staining the biofilms with the molecular probe SYTO-3 green-fluorescent nucleic acid stain and measuring fluorescence in a SPECTROFluor multi-well plate reader from TECAN. The plate reader has been adapted to enable fluorescence quantification of complete slides. The fouling-release properties of the materials are assessed hydrodynamically through exposure to shear force (turbulent flow) on a rotary device and quantifying the biofilm before and after rotation. The speed of the device can be controlled from 5-25 knots.



Left: Mixed biofilm on a nanostructured AMBIO coating after one hour settlement and 4 hours growth. Right: Image of the remaining biofilm after the rotor release step (10 minutes at 17 knots). The biofilms have been stained with the fluorochrome SYTO-13. Rotation on the rotor resulted in the release of 98% of the biofilm.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

HIGH-THROUGHPUT LABORATORY SCREENING METHODS FOR EVALUATION OF ANTIFOULING AND FOUL-RELEASE PERFORMANCE OF MARINE COATINGS

SJ Stafslien, JA Bahr, JW Daniels, Center for Nanoscale Science and Engineering, North Dakota State University, USA
JA Finlay, F Cassé, ME Callow, JA Callow, School of Biosciences, University of Birmingham, UK

Major efforts are currently underway to rapidly discover new and environmentally friendly marine coatings utilizing a combinatorial or high-throughput approach. The combinatorial workflow consists of a suite of automated tools to carry out polymer synthesis, coating formulation, coating deposition and analysis of key physical and mechanical properties. The established workflow has recently been augmented with the addition of high-throughput biological assays to adequately accommodate the large numbers of samples produced and quickly assess antifouling (AF) and or foul-release (FR) performance for identification of promising materials.

Formulated coatings are cast into modified 24-well tissue culture plates and pre-conditioned by immersing plates in a circulating, deionized water tank to remove any toxic components (such as un-reacted monomers, catalyst or residual solvent). Coatings are then assessed for leachate toxicity to ensure assay results are attributed to a surface associated phenomenon. Once preconditioned, plates are challenged with a combination of marine organisms including bacteria (*Cytophaga lytica*, *Halomonas pacifica*), diatoms (*Navicula perminuta, Amphora coffeaeformis*) and macro algae (*Ulva linza*) to assess AF/FR performance.

Measurements of AF performance are determined by quantifying either growth (bacteria and diatoms) or the 96hr growth of *Ulva* spores on each coating surface. Bacterial biomass is assessed via crystal violet staining, extraction and absorbance measurements at 600 nm. Algal biomass is determined by fluorescence of chlorophyll. All spectrophotometric measurements are made with a multi-well plate reader.

Measurements of FR performance are determined by quantifying the total amount of attached biomass remaining in the wells after exposure to hydrodynamic shear forces generated by an automated or semi-automated water jet apparatus. Plate wells are inverted over a nozzle that delivers a uniform stream (at a constant duration and pressure) of artificial sea water perpendicular to the coating surface. The nozzle is offset (~5 mm) and rotates upon jetting to achieve uniform removal across each well.

Performance standards are included in each plate to facilitate comparisons and rankings between experimental coating formulations. Details of each assay and their implications in the rapid discovery of new AF/FR marine coatings will be discussed.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

EXPLORING ATTACHMENT OF MARINE INVERTEBRATES

A S Clare, J-P Marechal and **N Aldred**
University of Newcastle upon Tyne, UK

The colonisation of surfaces is generally regarded as a critical stage in the pelagobenthic life cycle of marine invertebrates. This complex process is achieved by planktonic larvae that explore and discriminate surfaces based on innate criteria. 'Choices' made at settlement are usually final and, thus, for sessile forms largely dictate future fitness and survivorship. Many species have evolved stringent, specific requirements and are able to delay settlement until a suitable site is located. An understanding of the factors that govern surface selection would aid the development of fouling-resistant surfaces. Several different measures are available to the experimenter to evaluate surfaces, including larval settlement rate, exploratory behaviour, adhesion strength and adhesive spreading. Measures of 'behaviour' are rare, perhaps reflecting difficulties with larval culture and/or the need for relatively sophisticated instrumentation to record and analyse the data. Here we describe the use of EthoVision video tracking software to measure barnacle, *Balanus amphitrite*, cyprid settlement behaviour. Using video recordings of individual cyprids we correlated EthoVision parameters, such as 'distance moved', 'meander' and 'velocity' to the 'classical' descriptions of cyprid searching behaviour (Crisp 1976). For 3-day-old cyprids we determined that the proportion of time spent 'swimming' (derived from the EthoVision movement parameter), 'searching' and in 'inspection' was 58.0%, 27.3% and 14.7% respectively. An analysis of transitions between behaviours showed that the main switch (> 50% of transitions) was between 'swimming' and 'inspection' followed by 'close search' to 'swimming', 'inspection' to 'close search' and 'swimming' to 'close search'; all other transitions being relatively minor. Contrary to the expectation that surface exploration would increase with cyprid age as settlement rates increase, no simple trend was found. For example, 'young' day 0 cyprids displayed a high level of searching behaviour, whereas day 3 cyprids spent the majority of their time swimming; a behaviour which decreased subsequently with age. The protocol described here enables detailed analyses of the surface modulation of settlement behaviour. Changes in swimming behaviour in response to waterborne compounds can also be measured. These analyses provide a wealth of information compared to conventional settlement assays and may inform future developments in marine antifouling coatings.

12th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

APPLICATION OF UNDERWATER DIGITAL IN-LINE HOLOGRAPHY IN ANTIFOULING RESEARCH

A. Rosenhahn, M. Heydt, M. Grunze
Heidelberg University, Germany

Digital in-line holography is a novel microscopy technique that allows the investigation of three dimensional processes like tracking of particles in real time [1,2]. Following the original idea of D. Gabor's "new microscopic principle" [3], coherent scattering of radiation can be used to record patterns which contain three dimensional information about the investigated object due to the presence of a reference wave. Applying reconstruction algorithms, real space information can be restored from these holograms by the help of computers [1]. By using divergent laser radiation, holographic microscopy e.g. in liquid volumes can be used to track objects with submicron resolution. Especially under water, where focusing with a conventional microscope is not feasible, holographic instruments have great advantages as the focusing can be done subsequently to the measurement either optically [4] or digitally [1,2]. We are using underwater digital in-line holographic microscopy [5] to visualize and analyze the motion and exploration behavior of marine organisms towards different antifouling surfaces. The three dimensional tracking experiments are used complementary to general biological screening experiments performed within Ambio [6], to gain a more detailed understanding about the early attachment stages of marine organisms towards surfaces.

[1] W. Xu, M.H. Jericho, I.A. Meinertzhagen, and H.J. Kreuzer, PNAS 2001; 98 (20), 11301
[2] W.Xu, M.H. Jericho, H.J. Kreuzer, Opt. Lett. 2003, 28(3), 164
[3] D. Gabor, Nature 1948, 161, 777-778
[4] J. Watson, S. Alexander, G. Craig, D.C. Hendry, P.R. Hobson, R.S. Lampitt, J.M. Marteau, H. Nareid, M.A. Player, K. Saw, K. Tipping, Meas. Sci. Technol. 2001, 12, L9
[5] S.K. Jericho, J. Garcia-Secerquia, W. Xu, M.H. Jericho, H.J. Kreuzer, submitted
[6] Ambio : Advanced Nanostructured Surfaces for the control of biofouling, FP6 EU integrated project, http://www.AMBIO.bham.ac.uk/

18th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

RAPID MEASUREMENT OF BARNACLE ADHESION STRENGTH

D Rittschof[1], S Stafslein[2], E Holm[3], G Swain[4], B Orihuela[1], E Ralston[4]

1 Duke University Marine Laboratory, Nicholas School, 2 North Dakota State University, 3 Naval Surface Warfare Center Carderock Division, 4 Florida Institute of Technology, USA

Accompanying the experimentation with foul-release surfaces is the need for assays that measure adhesion strength of macrofoulers such as barnacles. The ASTM standard approach for measuring adhesion strength is used with barnacles settled and grown in the field or rearing of larval barnacles to settlement stage, settling the larvae on experimental surfaces and growing them to the size where the measurement can be conducted. The field approach requires a field site and relatively large amounts of coating material. The laboratory approach requires a labor intensive sophisticated larval rearing facility. Both approaches are logistically difficult and require several months work to obtain adhesion data. Here, we report a technique for reattaching barnacles detached from a control silicone surface onto experimental surfaces. After one week of reattachment, adhesive strengths are comparable to those of field barnacles and laboratory reared barnacles. There are many advantages to the new technique. It requires less experimental material and less biological sophistication. It can be done on surfaces with latent toxicity and bifunctional coatings that combine antifouling and foul- release. An attractive feature of the technique is adult barnacles can be placed and oriented precisely enabling studies using small amounts of material, attachment to optical surfaces, and the potential for automation.

18th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

HIGH THROUGHPUT WORKFLOW FOR DEVELOPING NEW ANTIFOULING AND FOULING-RELEASE COATING SYSTEMS

D C Webster, P Majumdar, A Ekin, R J Pieper, B J Chisholm, J A Bahr, D A Christianson, C Gallagher-Lein

North Dakota State University, Fargo, North Dakota, USA

While a significant worldwide effort continues to be directed toward the development of non-toxic alternatives to antifouling coatings, a generally applicable solution has yet to be identified. A particular challenge in developing any new coating system is the large compositional space involved. Time and materials availability generally restricts the number of compositions that can be explored. This usually represents a small subset of the entire compositional space and thus it is likely that a good performing coating composition may be overlooked. To address this, high throughput methods can be used. High throughput methods involve the preparation and testing of a large number of materials in a single experiment and this approach can significantly accelerate the process of research. For the development of novel marine coatings, we have implemented a comprehensive workflow that includes polymer synthesis and characterization, coating preparation and screening for key properties. Polymer synthesis is carried out in either a parallel batch reactor system or a sophisticated semicontinuous system. Polymers are characterized using Rapid GPC, high throughput FTIR, HPLC, and MALDI-TOF. Coatings formulations are prepared using a parallel formulation system where polymers, crosslinkers, catalysts, solvents and other ingredients are automatically dispensed and mixed. Arrays of coatings are then deposited onto test substrates. Coatings are then screened for key properties such as modulus and T_g using a parallel dynamic mechanical thermal analysis system, surface energy, pseudobarnacle pull-off adhesion. To determine stability in an aqueous environment, coatings are immersed in water and then key measurements repeated. A sophisticated software and database system is used to track all of the composition and characterization data. By using the high throughput approach systematic sets of coatings can be prepared and screened and then analysis of the data can be used to identify key trends and relationships. From this analysis, unimportant variables can be quickly eliminated and promising areas of the design space can be selected for more detailed study.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

BEYOND BIOCIDES: WHERE LIES THE FUTURE FOR BIOFOULING CONTROL

John A Lewis

Defence Science & Technology Organisation, Australia
DSTO Maritime Platforms Division, 506 Lorimer St, Fishermans Bend, Vic 3207, Australia.
Ph: +61 3 9626 8418 Fax: +61 3 9626 8341 E-mail: john.lewis@dsto.defence.gov.au

Biofouling prevention on ships, whether on hull surfaces or in seawater piping systems, still relies mostly on biocides. For hull surfaces, reliance is mostly on copper-based antifouling paints, and for internal pipework, electrochemical generation of either copper or chlorine. However, the release of biocides into the marine environment continues to be of concern and the search for non-toxic methods of biofouling prevention continues to be a priority. Silicone-based fouling release coatings do show promise, and have already made inroads as biofouling control coatings for some classes of vessel, but they do have limitations, particularly for slow or low activity vessels. DSTO have a broad research program underway on innovative means of non-biocidal biofouling control which includes both internal research and collaboration and support for university research projects. The scope of the research encompasses investigations on bioadhesion to fouling release coatings, suprahydrophobic and microtextured surfaces, deterrence of fouling settlement by sound, surface vibration and bubble curtains, and novel methods for biofouling control within pipework. An overview of this research will be given, along with some of the findings to date and directions for future research.

18th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ENZYMES IN ANTIFOULING COATINGS, A REVIEW

S M Olsen[ab1], L T Pedersen[b2], S Kiil[a], M Laursen[b], K Dam-Johansen[a]

[a]Department of Chemical Engineering, Technical University of Denmark (DTU), Building 229, DK-2800 Kgs. Lyngby, Denmark
[b]Hempel A/S, Lundtoftevej 150, DK-2800 Kgs. Lyngby, Denmark

Antifouling paint based on enzymes as the active antifoulant is generally considered to be biocide-free. Even though the legislation on the subject is not clear, several paint producers are taking active parts in the race towards enzyme based antifouling paint.
The concept of enzymatic antifouling is relatively old. A patent describing a paint composed of enzymes as antifouling agents was applied for in 1985 in France by Maurice[3]. Today, more than 20 years later, enzyme-based antifouling is just about to reach the marked as an exotic product.
The paint system described by Maurice is based on proteases. Proteases catalytic activity is to cleave proteins by hydrolyzing the peptide bonds. The glue of fouling organisms consist primarily of protein, therefore proteases can inhibit fouling by hydrolyzing the extra cellular proteins[4]. This direct use of enzymes is still being investigated[4]. A more indirect use of the enzymes catalytic activity is to produce short lived biocides that would otherwise not be utilizable, due to concerns regarding operational time of the paint. A patent concerning a wide variety of possible enzymes, substrates and products is described by Hamade & Yamamori[5].
Independent of the choice of approach, the application of enzymes as antifouling agents will combine problems from coating engineering and biotechnology. After application of the paint, the enzyme must be stable during drying, and until in contact with seawater neither denaturation, nor activity should occur. On the other hand, paint performance should be unaffected by the addition of the large proteins.
The purpose of this paper is to discuss the ongoing development of enzyme based antifouling paints. In this context the paper seeks to elucidate why one or both of the concepts (i.e. direct and indirect application of the enzyme) has not been made available for ship operators sooner. Reviewing articles and patent literature on the subject, the discussion aims at presenting the main obstacles still to be overcome by coating engineers, before an antifouling paint based on enzymatic activity is commercialized.

---

[1] Presenting author
[2] Corresponding author, Telephone:(+45)4527 3812, Fax:(+45)4527 3700, Email: ltp@dk.hempel.com
[3] N. R. Maurice; *Antifouling coatings containing proteolytic enzymes;* FR 2562554A1 - 1985
[4] I. Schneider, K. Allermann; *Antifouling composition comprising an enzyme in the absence of its substrate;* US2005147579 – 2005
[5] R. Hamade, N. Yamamori; *Method for controlled release of compounds having antimicrobial activity, and coating composition*; EP0866103B1 – 2003

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ACCELERATED OPTIMISATION OF CHEMICALLY-ACTIVE AF PAINT PRODUCTS

D M Yebra[a34], S Kiil[a5], C E Weinell[b], K Dam-Johansen[a]

[a]Department of Chemical Engineering, Technical University of Denmark (DTU), Building 229, DK-2800 Kgs. Lyngby, Denmark
[b]Hempel A/S, Lundtoftevej 150, DK-2800 Kgs. Lyngby, Denmark

Chemically active antifouling (AF) paints base their performance on the slow release of active substances over extended periods of sea water exposure (typically no less than 5 years). The latter makes "real time" testing of those products a costly and time-consuming practice. Furthermore, the sea water environment (i.e. chemical properties and fouling pressure) is strongly dependent upon a number of variables (e.g. sea water compositions, season, depth). The relative performance of a given AF system in each of these different scenarios is difficult to asses even after expensive and slow tests on ocean-going ships. Our goal is to understand the working mechanisms of AF paints as a tool to devise accelerated tests which, combined with mathematical models, can provide reliable estimations of the chemical performance of the paint at different exposure conditions. In this way, only selected formulations are subject to long-term testing of their AF performance.

In this paper, lab rotor tests are combined with SEM-EDAX analysis of the samples exposed to characterise the polishing mechanisms of simplistic rosin-based model paints. The erosion of the soluble binder-depleted surface is hypothesised to be responsible for the paint polishing, thus strongly dependent upon the load of insoluble paint components. Additionally, the mathematical modelling of the copper leaching process points at very fast rates nourished by high binder hydrophilicity and low leached layer tortuosity. If such paints were to be optimised, the rosin content should be partially substituted by co-binder resins providing film hydrophobicity without spoiling the polishing pattern.

As an example of how to accelerate this optimisation process, it is shown how the model is capable of reproducing copper leaching rates from standardized "rotor methods" (e.g. ASTM D6442 and ISO 15181-1&2) after very short testing times. If such experiments were found to be representative of real life leaching scenarios, the use of the model would help predicting e.g. the biocide concentration at the paint surface, the potential influence of biofilm formation on the biocide leaching process, and the risk of basic copper carbonate (BCC) precipitation in a fast and effective manner.

---

[3] Presenting author
[4] Current address: Pinturas Hempel, Carretera de Sentmenat 108, E-08213, Polinyà, Barcelona, Spain
[5] Corresponding author. Telephone (+45) 45 25 28 27 Fax: (+45) 45 88 22 58 Email: sk@kt.dtu.dk

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ANTIFOULING CONTROL UTILIZING STENOPROPHILURIC TECHNOLOGY

D. A. Guritza; Natural Science Technologies, Inc. **L. A. Kiefer**; MeadWestvaco Corporation, and **J. C. Baummer,** E.A. Engineering.

The search for non-toxic and effective antifouling and corrosion coating systems which provide cost effective performance while meeting various regulatory and ecological pressures has been varied and increasingly demanding for decades as more information concerning health and habitat effects of various approaches has come to light. Many aspects of natural systems used by plants and animals whereby antifouling activity is achieved with no net negative ecological effect have been evaluated for physical, chemical, and allelochemical functionality and as well as other secondary metabolic cues in attempts to identify a mechanism or combination of properties that might permit the introduction of similar surface management solutions by design. Over the last twenty years, research has been conducted on a novel technology identified as Stenoprophilicity. Stenoprophiluric coating systems provide for the formation and continual support of naturally occurring micro-communities (biofilms), utilizing innate functionalities of micro-communities, which functionally control the surfaces for fouling management through natural means.

Specific formulations utilizing common coating materials of epoxy and copper metal have been developed and tested globally which provide for the efficacy to be both commercially and ecologically successful. Standardized formulations have been tested for parameters addressing toxicology, copper release rates, durability, husbandry requirements and effects, as well as VOC's and other secondary application issues. In order to provide comprehensive review of all parameters in a context of field efficacy, methods have been developed which provide for concurrent measurement of toxicity (with multiple species), copper release profiles, and performance that have been found reproducible over time in multiple locations. This presentation will provide a brief outline of the methodology developed and present data on efficacy of a standardized coating system. Included will be toxicology data, copper release profiles, a comparison between copper release profiles generated by our field method and the laboratory ASTM test method, delineation of application and husbandry methods, definition of the stenoprophiluric technology, and future expectations for the ongoing research. Data will demonstrate that the Stenoprophiluric coating meets or exceeds current industry and regulatory goals for a non-toxic durable, scrubable and efficacious coating system.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

A METHODOLOGY FOR EVALUATING BIOCIDE RELEASE RATE, SURFACE ROUGHNESS AND LEACH LAYER FORMATION IN A TBT-FREE, SELF-POLISHING ANTIFOULING COATING

Dickon

D J Howell and B Behrends

University of Newcastle Upon Tyne, UK

Due to the forthcoming IMO ban on tributyltin (TBT) (AFS 2001), a new generation of TBT-free antifouling (AF) coatings have been developed that typically contain copper (I) oxide and an organic co-biocide. Accurate and repeatable test methods are needed to evaluate the performance and environmental impact of these new coatings.

This study investigated a methodology for evaluating TBT-free, AF coatings containing copper (I) oxide. A commercially available AF coating underwent rotary immersion testing at 0, 0.51 and 2.05 m s^{-1}. Scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) analysis were used to assess leach layer formation, pigment volume concentration (PVC) and particle size distribution (PSD). Biocide release rates and surface roughness were also measured.

An increase in rotary speed caused a spike in biocide release rate after which the release rate stabilised to previous levels and a concomitant increase in leach layer thickness. A model is suggested of the processes involved before, during and after this observation and is compared to the results of a model proposed by Kiil et al (2001).

18th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

INTERACTION BETWEEN ENVIRONMENT FACTORS AND LARVAE DENSITY UNDER EUTROPHIC AND OLIGOTROPHIC CONDITIONS IN THE RIO DE JANEIRO COAST, BRAZIL

J E A Gonçalves[1,2]*, R Coutinho[1] and I R Zalmon[2]

[1]Instituto de Estudos do Mar Alte. Paulo Moreira, Brazil - *arrudagoncalves@yahoo.com.br
[2]Universidade Estadual do Norte Fluminense, Brazil.

The paper "Supply-Side Ecology (Lewis, 1986) showed that the amount of larvae and propagules in the water column is a key factor of the benthic succession process. Afterwards, several papers pointed out that environment factors can influence this process as well. Based on these informations, a 75 months larvae, α chlorophyll, nutrients (PO_4 - NO_2 - NO_3 - NH_4), pH, temperature, salinity and O_2 monitoring was performed in a eutrophic (Guanabara bay, RJ) and in a oligotrophic environment (Arraial do Cabo, RJ). These two environments of the Brazilian Southeast coast are 164 km distant each other, and have several equal benthic species or similar groups. In both areas 14 larvae types were identified, and Cirripedia was the group with major larvae concentration. The groups Decapoda, Bivalvia, Ascidiacea e Mytilidae had lesser but significant concentrations. In Guanabara Bay, the greatest Cirripedia larvae concentrations occurred in autumn and winter, with means varying from 2.000 to 6.000 larvae/m³. Other groups with significant larvae concentrations were the Polychaeta, D larva, and Mytillidae, reaching concentration peaks of 180, 163 and 140 larvae/m³, respectively. The abiotic data were analyzed in the same time scale used for larvae, and showed that the phosphate values were higher during winter and spring. Corelated to the increase of phosphate and the increase of some larvae availability, the nitrito, nitrate and amonia monitoring also made, evident the abundance peaks in these same seasons, indicating an effect in the increase of plankton community. Even though this pattern had not been constant along the whole years monitored, such periods might be indicated as critical to fouling on hard substrata. Temperature, salinity and oxygen showed little seasonal variation, on the contrary to nutrients (phosphate, nitrito, nitrate and amonia) and α chorophyll that oscillated significantly along time. In Arraial do Cabo, the Cirripedia larvae had the highest concentrations with a peak of 1000 larvae/m³ during spring and winter. Polychaeta and Mytillidae larvae also showed significant concentrations reaching means above 100 larvae/m³. The temperature, salinity, dissolved oxygen and pH data had values with low seasonal variation. Conversely, the nutrients and α chorophyll varied enough along time.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

INTERACTIONS BETWEEN MICROORGANISMS AND SURFACE TOPOGRAPHY ENHANCES ANTIFOULING PROPERTIES IN A SIMPLE POLYMER

Anisul Afsar, Tim Charlton and **Peter Steinberg**

Centre for Marine Biofouling and Bio-Innovation and
School of Biological, Earth and Environmental Sciences, University of New South Wales,
Sydney 2052, Australia

Abstract

Structured micro- and nanotopographies are emerging as a new general theme in studies of antifouling. We have been exploring the utility of waxes as non-leaching antifouling technologies for aquaculture, and found that different waxes varied greatly in their antifouling efficacy in the field and that the surfaces of the most effective waxes changed noticeably in appearance following 4-8 weeks of immersion in the field. Hypothesizing that this change in surface appearance was due to biological (microbial) activity, we exposed waxes in running seawater aquaria to antibiotics, and found that they lost their inhibitory activity against propagules of fouling organisms in laboratory assays, relative to waxes exposed to a mixed bacterial community. Surface characterisation by AFM, confocal microscopy and XRD revealed substantial changes in the surface topography, surface roughness, and proportion of amorphous vs. crystalline phases in waxes exposed to "aging" by bacteria. We suggest that differential biodegradation of the surface amorphous phase (relative to the crystalline phase) in these waxes by marine bacteria results in surfaces that are "spiky" at different scales, thereby inhibiting settlement of fouling organisms.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

A HIGHLY POTENT ANTIFOULING COMPOUND FROM A DEEP-SEA BACTERIUM

Ying XU[1], Xiancui LI[1], Ning ZHOU[2], Xiang XIAO[3] and Pei-Yuan QIAN[1]

[1]Department of Biology, HKUST, Clear Water Bay, Hong Kong, China
[2]Chinese Ocean Mineral Resource Research and Development Association, Beijing
[3]Third Institute of Oceanography, SOA, Xiamen, China

60 deep-sea bacterial strains isolated from the sediments collected at 5000 m deep from the Pacific Ocean were screened for their anti-larval settlement activity using cypris larvae of *Balanus amphitrite* as the test organism. The ethyl acetate extracts of six bacterial cultures showed strong inhibitive effect on larval settlement, with B290 strain showing the highest bioactivity. An active compound was then isolated and purified from 60 liters of the spent culture medium of B290 using bioassay-guided fractionation procedure; its chemical structure was determined through NMR and GC-MS. Barnacle larvae lost their swimming ability and could not settle or metamorphose as soon as they were exposed to this compound even at a very low concentration but could recover their swimming ability and complete the settlement and metamorphosis when they were returned to clean seawater, even after 24 h of exposure to this compound. This compound inhibited larval settlement completely but did not kill any larvae at a concentration of 2μg ml^{-1}. No toxic effect was observed at a concentration of 60μg ml^{-1}. Besides, this compound at a similar concentration was also very effective in inhibiting the larval settlement of the polychaete *Hydroides elegans*, another major fouling organism in tropical and subtropical waters. Optimal conditions for bacterial growth and compound production of this strain were different. Our results suggest that the largely unexplored microbes in deep-sea can indeed be an alternative promising source for antifouling bioactive compounds.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

FOULING REMEDIATION THROUGH THE USE OF GRAZERS IN SHELLFISH AQUACULTURE

Douglas I. Watson, Simone Dürr, Daniel Beaz, Eivind Bergtun, Rik Breur, Juan Cebria, John Davenport, Donald Fowler, Courtney Hough, John Icely, Alistair Lane, Julie Maguire, Ana Manjua, Manuel Marhuenda, Kjell Maroni, Joe McElwee, Halvor Mortensen, David Murphy, John Murphy, James Newman, Ana Pereira, John Power, Sergio Prieto, Jeremy Thomason, John Watters, Peter Willemsen

Aquaculture & Fisheries Development Centre,
Dept. Zoology, Ecology & Plant Science,
University College Cork, Ireland.
d.watson@ucc.ie

Multi-trophic aquaculture techniques are becoming more prevalent within the sector and can have many benefits to the farmer. The aim of this pilot study was to identify potential grazers, which are successfully able to reduce biofouling on scallop trays. The build up of fouling on such aquaculture structures impacts water flow within the trays and, therefore, the health and growth rate of shellfish.

Two different species (*Monodonta lineata* – a gastropod grazer and *Paracentrotus lividus* – the purple sea urchin) at three separate densities (2, 5, and 10 animals) were utilised. The study was carried out at James Newman's scallop farm in SW Ireland from April 2005 until October 2005. Densities of both species and controls (no grazers) were randomly distributed among eight stacks of eight trays, which were set up along a single long line system. Tray stacks were initially placed on site for two weeks to allow for the initial build up of fouling in order to reduce mortality of the grazers when they were introduced. Sampling was then carried out on an approximately monthly basis. This consisted of weighing the trays, measuring the grazers (size and weight) to allow the identification of grazer size increases to potentially marketable sizes. Photographing of trays was also undertaken to follow the build up of fouling in order to identify differences in the fouling present and the success of the grazers to keep open the tray mesh by eliminating fouling

This initial study will lead on to interaction studies looking at the behaviour of grazers and stock species as part of the CRAB (Collective Research on Aquaculture Biofouling) European study – data from which will also be presented.

NOVEL ANTIFOULANTS: INHIBITION OF LARVAL SETTLEMENT BY PROTEASES

Sergey Dobretsov1, **Hairong Xiong**2, **Pei-Yuan Qian**2

1IFM-GEOMAR, Kiel University, Kiel, Germany
2Coastal Marine Laboratory, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, SAR China

The undesirable attachment of organisms to man-made substrates is a serious problem for marine industries. Current antifouling technology is based on the application of highly toxic compounds and new non-toxic antifoulants are urgently needed. We investigated the effect of commercially available enzymes (α-amylase, α-galactosidase, papain, trypsin, and lipase) as well as proteases from deep-sea bacteria on the attachment of *Bugula neritina*. The fifty percent effective concentrations (EC50) of the commercial proteases were 10 times lower than that of amylase or galactosidase. Partially purified proteases from 6 deep-sea *Pseudoalteromonas* species significantly ($p<0.05$; ANOVA, Dunnet test) decreased larval attachment at concentrations of 0.03 - 1 mIU ml-1. The EC50 of the pure protease from the bacterium *Pseudoalteromonas issachenkonii* UST041101- 043 was 0.1 mIU ml-1. The effect of proteases was reversible; larvae after washing with seawater were able to settle and etamorphose. The protease from *P. issachenkonii* and trypsin individually incorporated in a water-soluble paint ignificantly inhibited biofouling in a field experiment. There are certain correlations between productions of proteases by bacterial films and induction of larval attachment. None of bacteria whose biofilm induced attachment of *B. neritina* produced proteolytic enzymes, whereas most of bacteria which formed inhibitive biofilms produced proteases. Our investigation demonstrated the potential use of proteolytic enzymes for antifouling defense.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

EVALUATION OF DEOXYGENATION AS A CORROSION CONTROL MEASURE FOR SEAWATER BALLAST TANKS

Jason S. Lee, Richard I. Ray, and **Brenda J. Little***

Naval Research Laboratory, Stennis Space, Center, MS 39529
Ph: 228-688-4494; Fax: 228-688-5494

Edward J. Lemieux
Naval Research Laboratory, Key West, FL 33041

Deoxygenation of seawater has been demonstrated as an environmentally friendly ballast water treatment to control introduction of non-native aquatic species. Some investigators have proposed that the same treatment provides a low-cost, effective corrosion control measure for uncoated carbon steel ballast tanks based on the concept that reducing oxygen concentration from ballast tank water and headspace will limit oxidation. Field experiments were designed to evaluate deoxygenation as a corrosion control measure for uncoated carbon steel ballast tanks exposed to natural seawater when tanks were maintained with cycles of potential operating conditions: (1) oxygenated seawater followed by an oxygenated atmosphere (oxygenated/oxygenated), (2) hypoxic (<0.2 ppm O_2) seawater followed with an oxygenated atmosphere (hypoxic/oxygenated) and (3) hypoxic seawater followed with a inert atmosphere (hypoxic/hypoxic). Coupons in the hypoxic/oxygenated tank had the highest corrosion rates as measured by polarization resistance and weight loss over the experiment, while coupons in the hypoxic/hypoxic tank had the lowest. Introduction of oxygen into an hypoxic enviroment resulted in an immediate increase in corrosion rate and severity. The increase in instantaneous corrosion rate did not correspond directly with the amount of oxygen introduced at any one time. Instead the increase was related to the prevailing oxygen concentration at the time oxygen was introduced. The specific appearance of the coupons varied with oxygen concentration in the water or atmosphere at the time of collection. In general all exposure conditions produced a two-tired corrosion layer. In the presence of oxygen, the outer extremely fragile layer was reddish orange and contained halite, lepidocrocite and goethite. The inner layer was black, tenacious maghemite. All outer layers contained concentrations of twisted bacterial filaments that, in some cases, were encrusted in iron. Trace amounts of mackinawite were identified in the corrosion products formed under hypoxic/hypoxic conditions. Experiments described in this paper demonstrate the potential application of deoxygenation as a corrosion control measure for unprotected carbon steel ballast tanks. However, they also demonstrate the impracticability of such an approach to corrosion control. Attempts to maintain hypoxic seawater are complicated by the consumption of oxygen by aerobic respiration and corrosion reactions, as well as the inadvertent introduction of oxygen from the atmosphere.

* presenting author blittle@nrlssc.navy.mil

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ROLE OF EPS OF FOULING BACTERIA ON THE CORROSION OF MILD STEEL

Fraddry D'Souza* & **Narayan B. Bhosle**

National Institute of Oceanography
Dona Paula – 403 004
Goa, India

Bacterial cultures were screened for EPS production and their potential to inhibit the corrosion of mild steel. Bacteria produced EPS at various levels and also influence the corrosion at different level. The concentration of EPS appears to have a direct role in corrosion inhibition. This was evident from a significant inverse relationship observed between the concentrations of EPS and the rate of corrosion. Four of the cultures showed good corrosion inhibition of mild steel and also produced high EPS, however, the extent of corrosion inhibition varied between these cultures. They were tentatively identified as *Pseudomonas* sp. (CE-2); *Pseudomonas* sp. (CE-7), *Bacillus* sp. (CE-10) and *Bacillus* sp. (SS-15). Electrochemical potentiodynamic polarization studies also confirm that presence of these bacteria inhibited the corrosion of mild steel. The I_{corr} and V_{corr} were low as compared to the control indicating the inhibition of corrosion of mild steel. The resistance of polarization increased over the period of immersion, which means that there is formation of protective film on the surface of the mild steel panel. EPS isolated from *Pseudomonas* sp. (CE-2), *Pseudomonas* sp (CE-7), and *Bacillus* sp. (SS-15), inhibited the corrosion of mild steel and the inhibition increased with increasing concentration of EPS. While, in the presence of EPS isolated from *Bacillus* sp. (CE-10) the corrosion inhibition rate decreased with increasing concentration of EPS. Chemical characterization of these bacterial polymers indicates that the chemistry of the EPS influences the kinetic of corrosion reaction. In addition, molecular weight fraction of the EPS isolated from the *Pseudomonas* sp. (CE-2) influenced the corrosion of mild steel. The high molecular weight EPS showed good corrosion inhibition as compared to low molecular weight. Based on this study it could be well argued that EPS influences the kinetic of corrosion reaction. Moreover, the presence of certain functional group and their concentration in the EPS either enhances or reduced the corrosion of mild steel.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

IN-SITU MONITORING OF CORROSION IN SINGAPORE OFFSHORE SEAWATER

Hu Xiaoping [1,2], D. J. Blackwood [2], Serena L. M. Teo [1]

Tropical Marine Science Institute, National University of Singapore, Singapore [1]
Materials Science & Engineering, National University of Singapore, Singapore[2]

The weight loss method has been commonly used in the study of marine corrosion on metals. However, the results of weight loss do not provide details of the initiation, propagation and failure processes. To help investigate these processes six alloys, namely mild steel, stainless steel 316L, Monel alloy400, 70Cu-30Ni, SMO254 and Titanium, were exposed to Singapore offshore seawater for three months with their open-circuit potentials being continuously recorded via a data logger and their *in situ* corrosion rates determined weekly by linear polarization measurements (LPR). An additional set of test coupons were also placed in a filtered seawater aquarium to allow the influences of micro-fouling and macro-fouling on corrosion to be assessed. The open circuit potential results showed that all the metals were ennobled shortly after immersion, a process which is believed to be caused by the formation of biofilms. However, the onset time for ennoblement was found to be dependent on the corrosion resistance of the alloys and the extent of the shift in the open circuit potentials was found to be greater in nature seawater than in filtered seawater. Good agreement was found between the extent of ennoblement and the corrosion rates determined by LPR, the more ennobled the lower the corrosion rate. The one exception to this was the Monel which preformed worst than expected in the LPR experiments; visual inspection of the Monel coupons at the end of the tests revealed that the LPR sample had suffered much more extensive pitting and crevice corrosion than its open circuit counterpart. The LPR data revealed the order of corrosion resistance in Singapore offshore seawater is Ti≈SMO254<SS316<70Cu-30Ni < Monel <Mild steel, whereas from the open circuit experiments the Monel was predicted to perform better than the 70:30 cupronickel alloy.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

SPECIFIC EPIBACTERIAL COMMUNITIES ON MACROALGAE: PHYLOGENY MATTERS MORE THAN HABITAT

T. Lachnit, M. Blümel, J. F. Imhoff and **M. Wahl**

IFM-Geomar Leibniz Institute of Marine Science, Germany

Surfaces immersed in the sea become rapidly covered with a biofilm. On non-living surfaces, this is usually followed by colonisation by larger organisms. In contrast, seaweeds remain relatively free from macrofouling and are typically only covered by a thin film of epiphytic bacteria. These microorganisms are an important part of the interface between the alga and its environment. All the molecular components that are released or taken up by seaweed are potentially subject to chemical modification by its biofilm. Through the biofilm's metabolism chemical surface parameters of algae are modified and affect – among other interactions - the resistance of algae toward macrofouling. Epiphytic biofilms are therefore of major importance for the ecology of seaweeds, but their structure and dynamics in nature are nonetheless virtually unexplored. We examined the epibacterial community composition of several algal species, belonging to the taxa phaeophyta, rhodophyta and chlorophyta, by denaturing gradient gel electrophoresis (DGGE). The specimens were collected in the North Sea and Baltic Sea. We could show, that different algal species within one location featured dissimilar epibacterial communities. Bacterial composition of conspecific individuals were most similar, no matter whether the specimen were from the Baltic Sea or the North Sea. Different macroalgal species had dissimilar bacterial communities although they were grown intermingled at one location with similar physical and environmental parameters and were exposed to the same bacterial colonizer pool. This is a strong indication that properties of macroalgae determine the differential settlement and growth of bacteria on their surfaces. North Sea and Baltic Sea differ substantially with regard to bacterial colonizer pool. The observation that conspecifics under these different colonization regimes exhibit more similar biofilms than different algal species under the same colonizer regime strongly suggests that properties of the algal surface and specific interactions between algae and bacteria are the driving agents for this selectivity. Three processes, singly or in combination, may produce algae-specific biofilms. (i) Algal propagules may already carry the specific biofilm. (ii) Algal defences may repel all but the specific strains. (iii) Algal attractants may favour certain strains which in turn inhibit settlement of other strains.. Whatever the underlying mechanism, surfaces of the majority of the algal species studied were colonized by only a selection of available bacterial strains. We may expect that these specific epibacterial films may affect most interactions between the host alga and its environment. Micro- and macrofouling is likely to be influenced by the identity and metabolism of epibiotic bacteria. But also any transcutaneous exchanges (light, nutrients, exudates, signalling molecules and other chemicals) may be affected by the specific surface bacteria. Because epibiotic bacteria are known to metabolize algal exudates and produce own metabolites, chemical signals of the host alga are very likely modified by their biofilms. Interactions with chemically cueing parasites, pathogens or consumers may be modulated by epibacterial biofilms.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

CHEMICAL DEFENSE IN THE RED SEAWEED *LAURENCIA OBTUSA*: DO SURFACE CONCENTRATIONS OF ELATOL INHIBIT HERBIVORE AND FOULING ORGANISMS?

Daniela B. Sudatti[1], Silvana V. Rodrigues[2], Ricardo Coutinho[3], Bernardo A.P. da Gama[1], Renato C. Pereira[1]

[1] Pós-Graduação em Biologia Marinha, Instituto de Biologia, Universidade Federal Fluminense
[2] Departamento de Química Analítica, Universidade Federal Fluminense
[3] Instituto de Estudos do Mar Almirante Paulo Moreira (IEAPM)

The halogenated sesquiterpene elatol, produced by the Brazilian red seaweed *Laurencia obtusa*, has been shown to deter herbivore feeding and to prevent fouling settlement in laboratory and field assays. This compound is known to occur within-thallus in large concentrations, occurring at significantly lower concentrations at the algal surface. Surface concentrations of elatol were tested in laboratory as a defense against herbivory by the sea urchin *Lytechinus variegatus* and as an antifouling defense toward larvae of the barnacle *Amphibalanus amphitrite*. Here we show that this compound, at the concentrations found at the surface of the alga (ranging from 0.5 to 10 ng elatol.cm^{-2}), did not inhibit either the consumption by herbivorous sea-urchins or the settlement of barnacle larvae, unlike within-thallus concentrations of this compound. Although our results clearly show that surface concentrations of elatol did not play an ecological role as defenses against herbivores or fouling, the presumable localization of this compound in within-cell vesicles ("corps en cerise") adjacent to the algal surface strongly suggest that these compounds have a dynamic role to the alga, perhaps being transported to the outer surface of the alga under conditions yet undetermined.

CAPES, CNPq, and FAPERJ supported this research.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

STUDY OF ANTI-SETTLEMENT ACTIVITIES OF MERODITERPENOIDS PURIFIED FROM *HALIDRYS SILIQUOSA*

Gerald Culioli[a], Robert Valls[b], Jean-Philippe Marechal[c,d], Annick Ortalo-Magne[a], Louis Piovetti[a], Anthony Clare[c] and Claire Hellio[c,e]

[a]Laboratoire des Materiaux a finalites Specifiques, Equipe "Chimie des Produits Naturels Marins",Universite du Sud Toulon-Var, Avenue de l'Universite, BP 20132, 83957 La Garde cedex, France.
[b]UMR 6180 CNRS « Chirobiotechnologies : catalyse et biocatalyse », groupe « Separation, Identification et Synthese », Universite Paul Cezanne, Avenue Escadrille Normandie-Niemen, Service 551, 13397 Marseille.
[c]Newcastle University, School of Marine Science and Technology, Ridley Building, Newcastle upon Tyne NE1 7 RU, UK
[d]Observatoire du Milieu Marin Martiniquais (OMMM), 7 avenue Condorcet, 97 200 Fort de France, Martinique, France.
[e]School of Biological Sciences, University of Portsmouth, King Henry Building, Portsmouth, PO1 2DY, UK
Corresponding author: email: claire.hellio@port.ac.uk; phone: +44-239-284-2073 ; fax : +44-239-284-2070

In the course of our studies on the search of new non-toxic antifouling compounds isolated from marine organisms, the chemical content of the Phaeophyceaea *Halidrys siliquosa* (Fucales: Cystoseiraceae) collected in Brittany, France was investigated. This brown alga, found abundantly along NE Atlantic shores, has been previously shown to contain meroditerpenes as well as phlorotannins and aersenosugars.

In this work, six meroditerpenoids have been caracterized: among them, four were new compounds while one known, already isolated from *Cystoseira elegans*, was described for the first time from *Halidrys siliquosa*.

Their structures were characterized on the basis of chemical and spectral evidence including tow dimensional NMR experiments and mass spectrometric techniques.

Antifouling and toxicity tests were conducted on these compounds. For the most active of them, a significant inhibition of the settlement of cyprids of *Balanus amphitrite* was observed at 1 µg/ml while toxicity against nauplii of *B. amphitrite* was only found at higher concentrations.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ANTIFOULING ACTIVITIES OF AVAROL/AVARONE AND THEIR DERIVATIVES AGAINST MARINE BACTERIA, MICROALGAE AND BARNACLES

Jean-Philippe Marechal[a,b], **Claire Hellio**[a,c], **Benoit Veron**[d], **Anthony S. Clare**[a], **Irena Novakovic**[e], **Srdjan Tufegdzic**[e], **Dusan Sladic**[e], **Miroslav J. Gasic**[e], **Maria Tsoukatou**[f], **Constantinos Vagias**[f] and **Vassilios Roussis**[f]

[a]Newcastle University, School of Marine Science and Technology, Ridley Building, Newcastle upon Tyne NE1 7 RU, UK. [b]Observatoire du Milieu Marin Martiniquais (OMMM), 7 avenue Condorcet, 97 200 Fort de France, Martinique, France. [c]School of Biological Sciences, University of Portsmouth, King Henry Building, Portsmouth, P1 [d]Laboratoire de Biologie et Biotechnologies Marines, Université de Caen Basse-Normandie, BP 5186, 14032 Caen cedex, France. [e]Institute of Chemistry, Technology and Metallurgy, Department of Chemistry, Njegoseva 12, 11000 Belgrade, Serbia and Montenegro. 2DY, UK. [f]University of Athens, Department of Pharmacy, Division of Pharmacognosy & Chemistry of Natural Products, Panepistimiopolis Zografou, Athens, GR 15771, Greece.

One of the most promising alternative technologies to heavy metal-based antifouling paints is the development of coatings whose active ingredients are compounds, naturally occurring in marine organisms. This approach is based on the problem of epibiosis faced by all marine organisms and the fact that a great number of them cope with it successfully.

Eight compounds (avarol, avarone, 3',4'-ethylenedithioavarone, 4'-octylthioavarone, 4'-propylthioavarone, 4'-isopropylthioavarone, 4'-*tert*-butylthioavarone and 3'-(*p*-chlorophenyl)avarone) were tested at concentrations from 0 to 50 µg/ml for their anti-settlement activity on cyprid stage as well as their toxicity on nauplii stage of *B. amphitrite*. Avarol was isolated from the marine sponge *Dysidea avara*, avarone is the corresponding quinone, obtained by oxidation of avarol. The other compounds are derivatives obtained by nucleophilic addition of thiols or *p*-chloroaniline to avarone.

From the anti-fouling studies performed on 5 marine bacteria, 5 microalgae and cypris larva of *Balanus amphitrite*, it appeared that avarone and avarol are not good candidates for new antifouling treatment because they exhibited high levels of mortality. 3'-(*p*-Chlorophenyl)avarone and 4'-*tert*-butylthioavarone were active only when used at 25 or 50 µg/ml, in consequence their potential utilisation in the matrix paints would be too expensive. The best compounds were 3',4'-ethylenedithioavarone (active at 10 µg/ml), 4'-octylthioavarone and 4'-isopropylthioavarone (active at 2.5 µg/ml) and 4'-propylthioavarone (active at 1 µg/ml) and showed antifouling activities against all the organisms investigated. The evaluation of toxicity is an important parameter since new laws prohibit the use of toxic antifouling paints. Experiments on nauplii stage demonstrated that avarol (LC_{50}=1.58 µg/ml), avarone (LC_{50}=17.52 µg/ml), 4'-*tert*-butylthioavarone (LC_{50}=39.81 µg/ml) and 3',4'-ethylenedithioavarone (LC_{50}=18.11 µg/ml) were toxic and cannot be used for commercial paints.

The present results showed clearly that among the assayed compounds, the most promising candidates, for new non-toxic antifouling paints, are 4'-octylthioavarone, 4'-isopropylthioavarone and 4'-propylthioavarone.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ANTI-MICROFOULING ACTIVITIES OF TWO INVASIVE MACROALGA EXTRACTS FROM BRITTANY (FRANCE): *SARGASSUM MUTICUM* (FUCALES) AND *GRATELOUPIA TURUTURU* (HALYMENIALES)

Erwan Plouguerné[1], **Claire Hellio**[2], **Olivier Bertrand**[2] **Eric Deslandes**[1], **Benoit Veron**[3] and **Valérie Stiger-Pouvreau**[1]

[1]LEBHAM EA 3877, European Institute for Marines Sciences, University of Western Brittany, Technopôle Brest-Iroise, 29280 Plouzané, FRANCE.
[2]School of Biological Sciences, King Henry Building, University of Portsmouth, Portsmouth PO1 2DY, UK.
[3]Laboratoire de Biologie et Biotechnologies Marines, Université de Caen Basse-Normandie, BP 5186, 14032 Caen cedex, FRANCE.

Any living or non-living surface immerged in aquatic environment faced biofilm formation. The evaluation of the economical cost of this biofouling on a global scale is difficult. Nevertheless, the cost of microbiological corrosion for British and American industries was estimated of several thousands dollars of the GNP. Moreover, microorganisms resistance to common antibiotics led to a crucial need of new antibacterial compounds. Such facts raise the importance of permanently carry on the research of new antifouling compounds.

For our research program, we focused on marine natural products with biological activities. Our model organisms were marine macroalga because they are particularly concerned by biofouling. The colonization of their surface can lead to several perturbations and eventually to the death of the host. In order to protect themselves against other settling organisms, many alga have developed defences against fouling, in producing a wide variety of chemically active metabolites. In our study, two introduced species, *Sargassum muticum* (Phaephyceae) and *Grateloupia turuturu* (Rhodophyceaea) from Brittany coasts (France) were monitored in order to investigate potential antifouling activities with the goal of new ways of valorisation of their biomass. Thus, a complete study of the anti-microfouling activity of extracts (aqueous, acetone, chloroform, dichloromethane, diethyl-ether, ethyl acetate, ethanol 96°, hexane and methanol) of *S muticum* and *G. turuturu* against marine fouling bacteria (5 strains) and biofilm associated phytoplanctonik strains (5) were performed. Our results showed that the most active extracts of *G. turuturu* were the acetone and the dichloromethane fractions, while dichloromethane and chloroform extracts from *S. muticum* showed some very promising results for the research of new bioactive metabolites. We will discuss the potential use of these macroalga for anti-microfouling industrial applications.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

FIELD DEMONSTRATION AND ECONOMIC EVALUATION OF NONTOXIC HULL COATINGS ON PLEASURE CRAFT IN SAN DIEGO BAY, CALIFORNIA

L T Johnson and **J A Gonzalez**

University of California Sea Grant Extension Program, United States of America

During 2002-2003 the University of California Sea Grant Extension Program (UCSGEP) conducted a field demonstration of nontoxic epoxy, ceramic-epoxy and silicone-rubber hull coatings on six pleasure craft in San Diego Bay. In 2002 they evaluated economic incentives for boat owners to switch from copper-based antifoulants to nontoxic hull coatings, in cooperation with UC San Diego Economics Department. They evaluated coatings under typical, operating conditions for pleasure craft and obtained comprehensive information from pleasure craft owners, boat repair/maintenance businesses and marina/yacht club managers. Economic analysis found that long service life was critical for recovering costs to convert to a nontoxic coating and then to clean it in the water twice as often as a copper-based coating. Most nontoxic coatings do not adhere to copper-based coatings. On average, southern California boat owners strip old copper paint after 15 years. The shortest possible time needed to convert all San Diego Bay pleasure craft to nontoxic coatings was seven years, given boat repair yard capacity. Extending regulatory policies to reduce copper antifoulant use over 15 years would allow boat owners to convert to nontoxic coatings when copper paint needed to be stripped, reducing collective conversion costs for San Diego Bay pleasure craft from US$20 million to US$1 million. Contacts with project boat owners in 2004 and 2005 provided longer term evaluation of nontoxic hull coating performance, their satisfaction with the coatings and how they were handling increased in-water, hull cleaning costs. The silicone-rubber coating had to be replaced after one year, so it was not cost effective for a typical boat owner. The epoxy and ceramic-epoxy coatings had been in service for three-seven years by late 2005 and were in good condition. In contrast, copper-based coatings are typically replaced every two-three years in San Diego Bay. Statistical analysis determined that water temperature and interval between in-water cleanings were the most important factors influencing fouling growth accumulation. Coating age and cleaning tool aggressiveness were the most important factors influencing coating condition. Using a gentler cleaning tool was the most important factor for extending coating life. Frequent, in-water cleaning of nontoxic coatings may thus reduce cleaning time and cost, especially when the water is warmer. It may also extend coating life by allowing divers to use a gentler cleaning tool and to clean less aggressively.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

STATISTICAL ADHESION STUDY OF SILICONE COATINGS: THE INTERACTION OF THICKNESS, MODULUS, AND SHEAR RATE ON ADHESION FORCE

Jongsoo Kim*, Bret Chisholm and **James Bahr**

Center for Nanoscale Science and Engineering, NDSU, 1805 NDSU Research Park Drive, Fargo, 58102 USA

Mechanical/physical properties of silicone-based coatings have been extensively studied to evaluate their release performance on marine animals. However, in most cases, the adhesion force was obtained by varying a single parameter, keeping the other parameters constant. The goal of this research is to statistically study the interaction of coating thickness, modulus, and shear rate on adhesion force against pseudo-barnacle (epoxy, Loctite) for a platinum cured silicone coating. The 23 different experimental runs were generated by Design Expert V7 Software (Stat-Ease Inc.) in which combined design method (D-optimal, quadratic model) was used for two mixture components and two process variables. Vinyl-terminated polydimethylsiloxane (PDMS) with two different molecular weights (V21, MW=6 kg/mole and V35, MW=49.5 kg/mole, Gelest Inc.) were mixed at 5 different levels to vary modulus. Coating thickness was controlled by gently pouring a different amount of mixture on a 1"x3" glass slide and dry coating thickness was varied from 200 □m to 800 □m. One week after aluminum studs (D= 7.2mm) were glued to the coatings with the epoxy, the coatings were shear tested at three different shear rates - 2, 12, and 22 □m/sec. For the coatings prepared with 100% of V31 silicone resin, shear stress increases from 0.024 to 0.049 MPa as coating thickness decreases from 800 □m to 200 □m at 2 □m/sec shear rate. Interestingly, the thickness dependence is more pronounced at 22 □m/sec shear rate, showing more significant rate dependence at 200 □m than 800 □m coating thickness. As the amount of V21 increases up to 100%, shear force is more required to detach the pseudo-barnacle from the coatings compared to 100% V35, but thickness dependence on shear stress was not observed.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

SUPERHYDROPHOBIC COATINGS AND FOULING RESISTANCE

A J Scardino[1], H Zhang[2], R Lamb[2], R de Nys[1]

1. Biofouling Research Group, School of Marine Biology & Aquaculture, James Cook University, Australia
2. School of Chemistry, University of New South Wales, Australia

Recent technological breakthroughs have enabled the production of superhydrophobic coatings (SHCs). Hydrophobic materials are combined with extreme roughness to produce surfaces with water contact angles above 160°. The focus on SHCs has been on foul-release properties, however, little is known about the antifouling potential of SHCs. We tested 4 SHCs for fouling resistance against a suite of common fouling organisms; *Amphora* sp. cells, *Ulva australis* zoospores, *Polysiphonia sphaerocarpa* carpospores, and *Bugula neritina* larvae in static bioassays. The 4 SHCs have unique physical architectures that allow a comparison of micro and nano-scale roughness effects. Each SHC was coated onto one-half of a glass petri dish and attachment rates of fouling organisms compared between glass and the SHC. Two of the SHCs displayed no antifouling properties while one SHC deterred some fouling organisms, whilst being preferred by others. The fourth SHC, the only coating with nano-scale surface architecture, significantly decreased settlement by all the tested organisms when compared to glass. All 4 SHCs have similar hydrophobicities but produced markedly different fouling responses with no correlation between surface roughness of the SHCs and fouling resistance. Potential mechanisms correlating surface architectures and fouling resistance are presented.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

NOVEL ANTIFOULING CONCEPTS

D Rittschof [1] and S L M Teo [2]

1 Duke University Marine Laboratory, Nicholas School, USA 2 Tropical Marine Science Institute, National University of Singapore

Classic antifouling concepts use broad spectrum biocides. The commercial solution to regulations restricting use of biocides such as mercury or lead or tributyl tin due to environmental impacts has been to substitute a different broad spectrum biocide. This substitution makes business sense because it requires only minor changes in very complex and otherwise effective polymer systems. The most recent versions of this idea is boosting of copper based anitfouling coatings with broad spectrum organic biocides. It is becoming increasingly obvious that approaches that move away from broad spectrum biocides are needed. The next generation of antifouling solutions could replace broad spectrum biocides with more environmentally benign alternatives.

Such new solutions will present challenges to industry to academia and to governments that would best be solved by joint efforts that take advantages of respective expertise, but that would be a major departure from how global business, academia and governments normally function. The next generation of antifouling coatings must be compatible with existing business models and have known fates and effects. Historically, academic researchers have considered biological activity, not business models or fates and effects or regulatory issues. Similarly governments are not proactive and business has been concerned with the bottom line and meeting the letter of the law. We envision novel coatings based on existing polymer systems containing catalytic amounts of potent antifouling additives engineered for compatibility and to degrade. These molecules will be compatible with coatings processes and to have known fates and effects.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

NOVEL, ENVIRONMENTALLY-FRIENDLY, ANTIFOULING/FOULING RELEASE COATINGS DEVELOPED USING COMBINATORIAL METHODS

Bret J. Chisholm,* David A. Christianson, Shane J. Stafslien, Christy Gallagher-Lein, Justin Daniels, and Dean Webster

North Dakota State University
Center for Nanoscale Science and Engineering
Fargo, ND 58102, USA

Novel, environmentally-friendly, antifouling coatings were prepared by tethering either triclosan or ammonium salt functionality into moisture-curable polysiloxane-based coatings. The biocidal functionality was covalently bound to the coating matrix to prevent leaching of toxic biocide to the environment. High throughput biological assays based on marine bacteria growth and settlement were used to characterize the antifouling character of the coatings and prove that antifouling character was not due to a leaching effect. The minimum amount of tethered biocide required to deter settlement of marine bacteria was determined for two different classes of moisture-curable coatings.

15th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

NOVEL ACRYLIC NANODISPERSIONS IN CONTROLLED-RELEASE SELF-POLISHING ANTIFOULING PAINTS

D M Yebra[6a], T Tanabe[b], A Sánchez[a], Y Iwase[b], M Porsbjerg[c], H Sasaki[b], S Arias[7a], H Tanabe[b], S Kiil[d]

[a]Pinturas Hempel, Carretera de Sentmenat 108, E-08213, Polinyà, Barcelona, Spain
[b]Dai Nippon Toryo Co. Ltd. 1382-12 Shimoishigami, Ohtawara City, Tochigi Pref. 324-8516, Japan
[c]Hempel A/S, Lundtoftevej 150, DK-2800 Kgs. Lyngby, Denmark
[d]Department of Chemical Engineering, Technical University of Denmark (DTU), Building 229, DK-2800 Kgs. Lyngby, Denmark

Ever since the abandonment of tin-containing products, marine paint companies have pursued the development of binder systems yielding a sufficient, sustained, and adjustable release of active compounds. In the last years, Hempel A/S has made an unprecedented effort to utilize a profound scientific understanding of the working mechanisms of its AF products as the main driving force for their optimisation process. Such knowledge will also assure a fast transition to future, more environmentally benign, AF compounds or to lower, but still efficient, release rates of the existing ones.

This paper presents the detailed scientific characterisation of the working mechanisms of a novel tin-free, self-polishing, antifouling paint technology jointly developed by Dai Nippon Toryo Co. Ltd. and Hempel A/S. As in the TBT-SPCs, the polishing mechanism of the new binder system partly relies on the attainment of the adequate number of hydrophilic Na-acrylate monomers at the paint surface (ATR-IR, Pyrolyzer-GC). Nevertheless, and contrarily to most tin-free acrylic-based technologies (e.g. Cu- and Si-acrylates), the attainment of the desired surface composition does not depend on complex hydrolytic reactions, difficult to tailor-make, but on the fast sea water reaction of methacrylic acid monomers. In this paper, we demonstrate how the rate of such reaction can be controlled by limiting the water uptake into the paint through tailor-made hydrophobic acrylate resins, which are also responsible for low and sustained Cu_2O and co-biocide leaching rates (ATR-IR, GC-MS, SEM-EDAX,

mathematical modelling). In the wet paint, and in order to avoid undesired reactions during pigment dispersion, the reactive acid groups are encapsulated by the controlled-release, hydrophobic, acrylate chains, thus forming nano-sized core-shell structures. In this paper, both laboratory data and full paint testing at sea sites are presented in order to demonstrate the excellent performance of this technology both at static and dynamic conditions.

---

[6] Presenting author
[7] Corresponding author. Telephone (+34) Fax: Email: sac@es.hempel.com

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

MICROENCAPSULATION TO CONTROL DCOIT RELEASE FROM ANTIFOULING COATINGS

S. E. Reybuck, Rohm and Haas Company, Spring House, PA, U.S.A.
E. G. Haslbeck, Naval Surface Warfare Center, Carderock Division, West Bethesda, MD, U.S.A.
P. Andreassen, Jotun A/S, Norway

The efficacy of biocides in marine antifouling coatings depends on the concentration and flux of biocide from the coating's surface. Ideally, antifouling coatings are formulated to release biocides at rates above their minimum effective level, but not so high that biocide is wastefully leached from the film. Controlling biocide release over time is desirable in order to optimize the biocide dosage and extend the effective lifetime of marine antifouling paints.

4,5-Dichloro-2-*n*-octyl-4-isothiazolin-3-one (DCOIT: the active ingredient in Sea Nine™ 211N) is an organic biocide which shows efficacy against a wide spectrum of fouling organisms including bacteria, fungi, algae and barnacles. Incorporation of DCOIT in a controlled release system would improve the efficacy, efficiency, and further reduce the environmental exposure of DCOIT. This paper will present results of studies to control the release of DCOIT through microencapsulation within cross-linked polymer shells. Seawater exposure tests and dynamic leach rate studies demonstrate that encapsulation is an effective method to stabilize DCOIT release rates from paint films over time. That is, microencapsulation can provide a level of release control beyond that achieved from the coating formulation alone. A range of release rates has been observed by systematically varying microcapsule structure. Effects of DCOIT encapsulation on field performance, copper release rates, and film polishing rates will also be discussed.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

STENOPROHILURIC COATINGS - THE DAWN OF SUSTAINABLE NON TOXIC MARINE ANTIFOULANTS

Guritza, Dennis A., Baummer, J.C. and Kiefer, Lynda A.

Traditional cuprous oxide based marine anitifoulant coatings rely on an ablative release of toxins to prevent hard-fouling on coated surfaces. Many traditional coatings contain "booster biocides" (herbicides and molluscicides) that add additional toxic impacts to enhance the efficacy of the coating, due to the inherent limits of cuprous oxides in managing different fouling conditions. The coating evaluated in this study takes a revolutionary approach to prevent fouling by creating and sustaining a biofilm that utilizes *metallic* copper in a unique resin system to create an environment that inhibits settling of undesirable organisms. There were two objectives for this study: 1) evaluate the acute toxicity of field exposed and sterile panels to three marine organisms, the opossum shrimp (*Americamysis bahia*), the silverside minnow (*Menidia beryllina)* and the sheepshead minnow (*Cyprinodon variegates*) and 2) to determine the release rate of copper from field exposed panels. Test panels were exposed in a tropical marine bay at Salinas, Puerto Rico. Acute toxicity and copper release from EcoClad™ coating formulation (resin + copper metal) was periodically evaluated from 0 to 297 days. Resin-only panels and copper metal panels (CDA #110) (negative and positive copper controls, respectively) were evaluated for up to 201 days. Sterile panels, immersed in laboratory sterile artificial seawater, were evaluated for acute toxicity and copper release after 14, 63 and 126 days of exposure. Acute toxicity tests completed were 96-hour screening or LC50 assays. Copper release rates were determined using a method derived from the standard ASTM method for measuring copper release from antifoulant coatings.

The EcoClad™ formulation was non-toxic to *A.bahia* and *C. variegates* with 96-hour LC50 values >100 percent sample after 13 days immersion *in situ*. Copper release rates were <10 ug/cm^2/day within 62 days. Resin-only panels (both *in situ* and sterile) were nontoxic to *A. bahia* and *M. beryllina* with 96-hour LC50 values >100 percent sample throughout the test period. No copper release was detected. Copper metal panels (both *in situ* and sterile) were toxic to and *A. bahia* and *M. beryllina* throughout the test period. The copper release rates from the copper metal panels were several orders of magnitude higher than the copper release rates from EcoClad ™ (*in situ* or sterile conditions).

Presenter: John Baummer
EA Engineering
15 Loveton Circle
Sparks, MD USA 21152
jbaummer@eaest.com
410-771-4950 (v)
410-771-4204 (f)

Coauthors:
Dennis A. Guritza
Natural Science Technologies, Inc
Chagrin Falls, Ohio USA

Lynda A. Kiefer
MeadWestvaco Corporation
Laurel, MD USA

12th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

FRICTIONAL DRAG OF SHIP HULL COATING SYSTEMS

Michael P. Schultz

Department of Naval Architecture & Ocean Engineering
United States Naval Academy
590 Holloway Road
Mail Stop 11D
Annapolis, MD 21402, USA
Telephone: (410) 293-6440
Fax: (410) 293-2219
Email: mschultz@usna.edu

Hydrodynamic data from which to compare the performance of silicone ship hull coatings with traditional biocide-based systems are limited. To address this, an experimental study has been conducted to compare the frictional drag of several ship hull coatings in the unfouled, fouled, and cleaned conditions. Hydrodynamic tests were completed in a towing tank using a flat plate test fixture towed at a Reynolds number (Re_L) range of 2.8×10^6 – 5.5×10^6 based on the plate length and towing velocity. The results indicate little difference in frictional resistance coefficient (C_F) among the coatings in the unfouled condition. Significant differences were observed after marine exposure, with the silicone antifouling coatings showing the largest increases in C_F. While several of the surfaces returned to near their unfouled resistance after cleaning, coating damage led to significant increases in C_F for other coatings. The roughness function, ΔU^+, for the unfouled coatings showed reasonable collapse to a Colebrook-type roughness function when the centerline average height was used as the roughness length scale. Excellent collapse of the roughness function for the barnacle fouled surfaces was obtained using a new roughness length scale based on the barnacle height and percent coverage. Predictions of full-scale ship performance based on similarity-law scaling are offered.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ANALYSIS OF THE RELATIVE PERFORMANCE OF MARINE COATINGS FROM 1974-2004: THE EFFECT OF THE TBT-BAN

J C Thomason

School of Biology & Psychology, Division of Biology, Univeristy of Newcastle, UK

A logistic statistical model has been developed that enables the analysis of biofouling on antifouling coatings of different chemical technologies. The model has been derived using 180,000 vessel records for the global marine fleet gathered over the last 30 years. This presentation will demonstrate how coating technologies have changed over the last 3 decades and how they have performed relative to each other. An examination of newer technologies brought to market after the TBT-ban will reveal how efficacious these coatings are and their effect on the operating efficiency of the global fleet.

18th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

TOWARDS ENVIRONMENTAL SUSTAINABLE CLEAN SHIP DESIGN

Associate prof. Dr. **Omar Yaakub**, Prof. Dr. Ab. **Saman Ab. Kadir**, **Oladokun Sulaiman**,

Universiti Teknologi Malaysia,Skudai, Johor, amalaysia

Abstract: Man live in two worlds – the biosphere and the techno sphere world- over the years, time needs, growth, speed, and knowledge and of course scarcity and competition have created demand that necessitated man to build complex institution. Ship design is not left out in this process. Inland water, are under treat from untreated waste that can feed bacteria and algae, which in turn exhaust the oxygen, the ocean cover 70 percent of the globe, many think that everything that run into it is infinite, the ocean is providing us source of freshening winds and current are far more vulnerable to polluting activities that have run off into them too many poisons that the ocean may cease to serve more purpose if care is not taking to prevent pollution- This issue of environment become so sensitive in recently with respect to infrastructure development and most especially in maritime industry because most of the past polluting activities from oil bilge to ballast pumping that has turned into poison have presently had encounter and advert effect on our water, some have choke too many estuarine water where fish spawn. In a nutshell, the two worlds we live are currently are out of balance and in potential conflict and man is in the middle, and since the treat are mostly water related, ship is in the middle too. Historical records of number of calamity that has resulted to heavy lost and pollution has call for environmentally sound ship, which has lead to a number of regulations today that will subsequently affect, policies change and procedures relating to the following and their effect to ship the design of new ships and modification of existing ships. This paper will discuss regulations design, with emphasize on new system design drive towards processing waste and emission on board so that discharge are acceptable, or processed waste can be stored safely on board and given to shore facilities for disposal. And of course design drive towards maintaining ship maneuverability at good efficiency and safety in port.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

MEASURING THE PERFORMANCE OF TODAY'S ANTIFOULING COATINGS

Geoffrey Swain, Brett Kovach, Arthur Touzot, Franck Casse, Chris Kavenagh

Florida Institute of Technology, Melbourne, Florida

The transfer from the self-polishing organotin to tin-free antifouling coatings has created a new learning curve for the shipping industry. Lack of quantitative, side-by-side comparisons among the many new technologies and formulations is the greatest impediment to the selection and management of ship hull coatings. This leads to the potential for penalties in speed, performance and fuel consumption as well as the requirement for unscheduled hull cleaning and dry docking.

This paper presents data from a study that ran side by side comparison of five commercially available coatings applied to 25 x 30cm aluminum test panels under both static and dynamic seawater immersion conditions. The coatings included a self-polishing organotin, a self-polishing copper, an ablative copper and two silicone fouling release coatings. The coatings were monitored for the development of macro and microfouling communities, surface condition and their skin friction properties.

The data showed that each coating type developed its own characteristic fouling community and that there were significant differences in skin friction properties that was further modified by static or dynamic immersion conditions. Under static immersion, the best performing coating was the ablative copper. Under dynamic conditions one of the fouling release systems had the best hydrodynamic characteristics.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

SURFACE ENERGETICS OF FLUORINATED/SILOXANE COPOLYMER FILMS FOR MARINE BIOFOULING RELEASE

G Galli, M Andreucci, E Martinelli, E Chiellini

Dipartimento di Chimica e Chimica Industriale, UdR Pisa INSTM, Università di Pisa
56126 Pisa, Italy, gallig@dcci.unipi.it
A Glisenti
Dipartimento di Chimica Inorganica, Metallorganica ed Analitica
Università di Padova, 35131 Padova, Italy

Fluorinated polymers and siloxane polymers are typical coating materials that exhibit low surface energy properties.[1] In particular, surface segregation and structuring of the low surface energy materials can be tuned to occur at different length scales in appropriately designed polymers and block copolymers.[2]
We are interested in developing architectures of such polymers that can be incorporated into novel coatings with nanostructured surfaces, and in understanding how the chemical composition, topology and order of the nanostructured surface can improve resistance to and release of marine biofoulants.
In this work we prepared new copolymers BCLF10-co-SiMA in order to gain a deeper insight into the surface energetics of polymers that incorporate both fluorinated side groups (BCLF10) and polysiloxane grafts (SiMA) as low surface energy components.
The contact angles θ with different interrogating liquids, both polar and apolar, were used to extract the values of solid surface tension γ_S. Different approaches were used to compare the calculated γ_S. It was found that the polymers were hydrophobic and lipophobic at the same time. This was correlated with the formation of an outermost low energy surface because of a nanostructured surface consistent with creation of an ordered assembly of surface segregated fluorinated chains. However, both low energy side groups were segregated to the outer film surface and its resulting composition and structure depended on the copolymer composition.
The surface elemental composition of the films was determined by angle-dependent XPS measurements. Whilst fluorine was present in very significant proportions in the probed depths, regardless of the polymer film nominal composition, silicon was not detected in the copolymers rich in fluorinated side groups; the higher surface energy polysiloxane grafts were completely hidden in the deeper layers of the film bulk. Thus, the surface composition could be adjusted by properly varying the proportions of the different units in the copolymers. The presence of separated, finely dispersed nanodomains of the individual components was confirmed by AFM.

This work was carried out with financial support from the FP6 project "AMBIO" and the Italian MIUR (2005-03-5277).

1. M. Bertolucci, G. Galli, E. Chiellini, K. J. Wynne, *Macromolecules*, 37, 3666 (2004).
2. G. Galli, E. Martinelli, E. Chiellini, C. K. Ober, A. Glisenti, *Mol. Cryst. Liq. Cryst.*, 441, 211 (2005).

18th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ENGINEERED NON-TOXIC, ANTI-FOULING DESIGNS FOR MARINE ENVIRONMENTS

Anthony Brennan[1,2], **Maureen Callow**[3], **James Callow**[3], **Michelle Carman**[1], **Thomas Estes**[2], **John Finlay**[3], **Michael Hadfield**[5], **Brian Neved**[1], **Ruth Perry**[5], **James Schumacher**[3], **Dean E. Wendt**[1], **Leslie H. Wilson**[4]

[1] Department of Biomedical Engineering, [2] Department of Materials Science and Engineering, University of Florida

[3] School of Biosciences, University of Birmingham

[4] Biological Sciences Department, California Polytechnic State Institute

[5] Kewalo Marine Laboratory, University of Hawaii

In marine environments, substrates become fouled by proteins, algae, barnacles and other organisms, decreasing material strength and increasing fuel consumption for ships. The most effective antifouling coatings are ablative paints which continually release toxic heavy metals. Our research investigates bioadhesion using model non-toxic surfaces with varying topography, surface energy, and surface chemistry. Antifouling and foul release properties are evaluated in laboratory tests with algal spores (*Ulva*), barnacle cyprids (*Balanus*) and tubeworm larvae (*Hydroides elegans*). The topographies investigated include a biomimetic structure called Sharklet AF™ based on skin of fast moving sharks. Across six studies, Sharklet AF™ demonstrated a 70% mean reduction in *Ulva* settlement. Initially it was unclear if this was due to air entrapment at the ultrahydrophobic surface. Triethoxysilane terminated derivatives of polyethylene glycol polysulfone and perfluoropolyether were grafted to the silicone base material changing the captive air water contact angle from 82° to 42°, 71°, and 96° respectively. Acid hydrolyzed silicone (33°) was also studied. Sharklet AF™ was shown to retain its antifouling property when coupled with these chemistries indicating the effect does not rely on trapped air. For barnacles and tubeworms, larger features were investigated to scale with the organism sizes. Channels of varying width/space and depth were generated including 20X5, 20X20, 200X5 and 200X20 (width/space X depth, μm). *Balanus* settlement was significantly reduced by all four dimensions, with the 20X20 providing a 60% reduction in settlement relative to smooth silicone. The channel topographies also tended to inhibit settlement of the tubeworm *H. elegans*, although the 20X20 channels yielded the only significant reduction (paired t-test, $\alpha = 0.05$) of 60% in mean settlement density relative to flat silicone.

A model of the antifouling effects of topography using a scale independent mathematical description will be discussed. The general features are a pattern that has a systematic repeat structure. The repeat structure is hypothesized to destabilize the organism sensing mechanism generally referred to as mechanotransduction. It is of course a function of the organism complexity. Our model addresses the size of the pattern and the sensing organism. Preliminary results demonstrate antifouling effectiveness by a non-toxic mechanism for organisms ranging in sizes from sub-micron to millimeter.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

DEVELOPMENT OF NONFOULING MATERIALS AND COATINGS FOR MARINE APPLICATIONS

Shaoyi Jiang*
University of Washington, USA

Tin-based antifouling paints are being phased out. Non-toxic silicone and fluorinated fouling-release coatings are under development. It is desirable to develop nonfouling materials and coatings, to which biofoulants do not attach. Polyethylene glycol (PEG) is the most commonly used nonfouling material, but unstable. At present, molecular-level nonfouling mechanism is still not fully understood, which obstacles the effort to design new nonfouling materials and coatings.

This talk will cover three topics – (a) recent advances in the fundamental understanding of molecular-level nonfouling mechanism, (b) design of new nonfouling materials beyond PEG to resist nonspecific protein adsorption, bacterial adhesion/biofilm formation, and marine microorganism attachment, and (c) development of non-toxic, non-fouling, and stable coatings with excellent mechanical strengths for marine applications. Two main classes of nonfouling materials (i.e., PEG and zwitterionic-based polymers) will be compared. PEG and zwitterionic chains bind to water molecules via hydrogen bonding and ionic solvation, respectively. It is shown that hydration water is the key to surface resistance to nonspecific protein adsorption. PEG and zwitterionic-based materials effectively resist nonspecific protein adsorption when their surface densities are well controlled. In this talk, zwitterionic-based materials will be highlighted since they not only highly resist nonspecific protein adsorption (adsorbed proteins <0.3 ng/cm^2), but also exhibit superior performance to inhibit bacterial adhesion/biofilm formation. For these studies, zwitterionic polymers are grafted either from a surface via the atom transfer radical polymerization (ATRP) method or to a surface via the physical adsorption of block copolymers containing zwitterionic and hydrophobic moieties. To improve the mechanical properties of a nonfouling material, interpenetrating polymer networks (IPNs) are prepared by the modification of a segmented polyurethane (SPU) with zwitterionic-based polymers. In addition, the development of paint-based nonfouling coatings with self-polishing capabilities will be discussed.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

NOVEL NON-BIOCIDAL HYDROPHOBIC ANTIFOULING COATINGS

H Y Erbil, C E Ozen, I Orkan, E Doganci, M Dandan and **C Hamamci,**

Gebze Institute of Technology, Turkey

Antifouling biocidal coatings containing organometallic compounds are currently being used in most of the commercial vessels and warships to minimize the buildup of marine organisms on ship hulls and submarines; however, these biocides are potentially toxic to marine environments and thus subject to current and future environmental regulations. Environmentally benign polymeric coatings are alternate to these toxic paints from which marine organisms could be easily removed. The selection of such polymers should be done so that the bioadhesion between the foulant and the coating would be weak enough such that the hydrodynamic forces created by the ship's motion or the weight of the foulant would dislodge the marine organisms. This requires a low surface free energy of the polymeric coating as well as the weak interfacial interaction between the coating surface and the microorganism. Algae spores and invertebrate larvae adhere to a surface under water over a wide range of temperatures, salinities and turbulence conditions in order to sustain their life-cycle. It was shown that when a substrate is hydrophobic, the primary adhesion is high, however, the strength of the adhesion is poor as measured by the detachment of the settled spores in a turbulent flow cell simulating the movement of a ship hull in sea. Roughness and surface topography are important for settlement of many organisms (Fletcher & Callow, 1992; Hills & Thomason, 1998; Köhler et al., 1999; Lapointe & Bourget, 1999; Berntsson et al., 2000; Bers & Wahl, 2004; Granhag et al. 2004), however, in most of these studies the surface roughness were in a scale of 20-200 microns. In general, the sea foulants accumulate on such large scale rough surfaces because the increased surface area may offer spores a refuge from shear forces under conditions of water flow. On the other hand, the presence of the surface roughness in the range of 2-5 microns may decrease the total contact area with the algal spores, which are usually 5 microns in diameter, and this will prevent the spores to enter into the cavities of the substrate by simple geometric considerations. The application of this idea requires the precise control of surface roughness which can be determined by contact angle hysteresis (the difference between advancing and receding contact angles), optical microscopy and SEM. Erbil et al, (2003) created superhydrophobic (water drop contact angles of higher than 150°) surfaces from polypropylene using novel solution-casting approaches having micro- and nano-scale roughness with trapped air pockets. However, when such a surface is submerged in seawater, the entrapped air is replaced by water and the benefit of the structured hydrophobicity is lost but the small scale roughness persists. The aim of this study is to test new hydrophobic polymeric coatings as non-biocidal antifouling coatings in seawater. Five new polymers having a definite degree of roughness; polypropylene, polyethylene, cyclic olefin copolymer, ethylene-vinyl acetate copolymer and a fluorocarbon-acrylate copolymer were tested against the fouling of algae spores, invertebrate larvae and sea biofilms in laboratory experiments and the results are presented.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

MALEIC ACID COPOLYMER THIN FILMS- ELECTROSURFACE STUDIES ON A POTENTIALLY FOULING-RESISTANT MATERIAL

C Werner, T Osaki Leibniz Institute of Polymer Research Dresden,

Max Bergmann Center of Biomaterials, Dresden, Germany

The obvious need for alternative coatings to efficiently prevent marine biofouling provokes the evaluation of a variety of polymers for that purpose. Since the physicochemical characteristics of successful coatings have to be carefully adjusted thin film platforms enabling the defined variation of structure and properties are particularly attractive. Alternating maleic acid (anhydride) copolymers carrying different side chains (such as octadecene-, styrene-, or ethylene-) in their comonomers provide a versatile means for the preparation of thin film coatings on various carrier materials. The choice of the comonomers and the reversible conversion of the anhydride moiety into the diacid form -and contrariwise- were demonstrated to permit the adjustment of the polymer coatings with respect to biointerfacial phenomena. As electrostatic interactions largely determine the structure and dynamics of maleic acid copolymers as well as the bioadhesion characteristics of the polymer films electrosurface properties were studied by means of the combined determination of zeta potential and surface conductivity in aqueous electrolyte solutions. The immobilized maleic acid copolymers were found to exhibit a two-step dissociation profile and pH-induced structural transitions in dependence on the comonomer unit. A dramatic increase of the surface conductivity was observed for layers of the more hydrophobic copolymers at alkaline pH values, indicating that electrostatic repulsion of ionized groups controls the extension of the confined layers as long as hydrophobic interactions between the comonomers do not inhibit this effect. Ellipsometric measurements confirmed the corresponding layer expansion. Based on surface charge density data, derived for the investigated set of samples from X-ray photoelectron spectroscopy, the double layer structure, i.e. the interfacial ion distribution and the origin of the surface conductivity, is quantitatively discussed.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

DEVELOPMENT OF SILOXANE-URETHANE FOULING-RELEASE COATINGS: INITIAL SCREENING STUDIES

D C Webster, P Majumdar, A Ekin, R J Pieper, D A Christianson, C Gallagher-Lein, S Stafslien
North Dakota State University, Fargo, North Dakota, USA
F Casse, M Callow, J Callow
School of Biological Sciences, University of Birmingham, Birhmingham, UK

While crosslinked poly(dimethylsiloxane) (PDMS) coatings have shown some promise as fouling-release coatings, they suffer from poor durability due to low toughness and poor adhesion to epoxy primers. Polyurethane coatings are generally tough and durable, and have good adhesion to most substrates. Incorporation of functional PDMS oligomers into a crosslinked polyurethane coating system is expected to result in a self-stratified morphology where the PDMS predominates on the surface. The primary driving force for stratification is the low surface energy of the PDMS. This can result in coatings that have a low surface energy and low surface modulus, but where the bulk coating properties are controlled by the polyurethane composition. By using a crosslinked system, rearrangement upon immersion in water can be suppressed so that the PDMS component largely remains on the surface. A large number of variables can potentially influence the morphology developed and so high throughput methods are employed in order to explore the effect of several of the compositional variables on coatings performance. In one experiment, libraries of organofunctional PDMS and PDMS-polycaprolactone triblock copolymers were synthesized having a range of block lengths, incorporated into polyurethane coatings and screened for their key properties. In addition, libraries of acrylic polyols have also been prepared, and siloxane-urethane coatings prepared and screened. Key properties measured include surface energy and pseudobarnacle pull off adhesion. Most coatings showed low surface energy and there was some variability in the pull off adhesion that could be related to the polymer composition. The coatings also maintained their low surface energy after being immersed in water for 30 days. The acrylic polyol composition served to control the bulk properties of the coating. Coatings were also screened for their interaction with the marine bacterium *C. Lytica* and the green alga *Ulva* and diatom *Navicula*.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

DO WE NEED AN UNCERTAINTY FACTOR FOR PEC?

K. Shibata*, R. Kojima, Y. Yamaguchi, S. Sugasawa, T. Shibata, O. Miyata, T. Senda

National Maritime Research Institute, 6-38-1 Sinkawa, Mitaka,Tokyo 181-0004, Japan
*Corresponding author: Tel: +81422413093, email: kyshiba@nmri.go.jp

The environmental risk of antifouling agent is, in most of the case, evaluated by PEC(predicted environmental concentration)/PNEC(predicted non-effective concentration) ration or MOE(margin of exposure), with uncertainty factor taking into the difference in the sensitivity of target and tested species or other biological perturbation. On the other hand, PEC is calculated based on its environmental loading and fate analysis. It is necessary to model the related phenomena, such as release from ship hull, diffusion and degradation in water column, adsorption to suspended mater and sediment, etc. for the PEC calculation of antifouling agents. However, those phenomena are changeable by time and space. It is necessary to investigate the influence on the concentration of antifouling agents of variation of the release rate, the diffusion and the degradation caused by that of the environmental condition.

Release rate has preliminary effect on the environmental concentration. In this work, the effect of contacting water speed, salinity, pH and temperature has been investigated, using rotating cylinder apparatus with various types of paint. Opposite nature of pH or salinity on the release rate was observed depending on the paints. For example, the higher salinity increases the release rate for one of the paints, but decreases for the other one. Even a standard testing condition is established, actual release rate may far different in real environment.

A simplified model has been developed to predict vertical concentration distribution change with time, taking vertical diffusion, first order photo-degradation kinetics, decrease in sunlight irradiation intensity with depth in water column and seasonal/daily change of sunlight irradiation intensity into account. The calculation result shows daily and yearly periodical concentration change. This concentration change is significant at near the water surface and decreases along the depth of the water column. The decrease in sunlight intensity has been observed according to the absorption and dispersion in the water column, reflecting clearness of the water. In the worst case, photo-degradation rate could decrease to 1/100 at 5m in depth, depending on the wave length effective to the degradation reaction. Such absorption could be almost equivalent effect on the degradation to that caused by the difference in summer and winter in the intermediate latitude. At the same time, diffusion is a big contributor to determine the concentration profile. But, the vertical diffusion rate or mixing could be changeable with time and place, as well.

Evaluation of concentration of the interest should be subjective, when the concentration gradient is observed in special and time scale. The behavior of the antifouling agent is different with sea area. The prediction of the environmental concentration is accompanied by uncertainty. It is necessary to apply the worst case scenario or introduce an uncertainty factor for PEC. The effect of various factors on PEC will be discussed

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

IMPROVED ESTIMATES OF ENVIRONMENTAL COPPER RELEASE RATES FROM ANTIFOULING PRODUCTS

Alistair Finnie

International Paint Ltd, Stoneygate Lane, Felling, Gateshead, Tyne and Wear, NE10 0JY, United Kingdom

A number of alternative experimental and theoretical (calculation) approaches have been used to quantify biocide release rates from antifouling coatings but the current standard laboratory method is the ASTM and ISO 'rotating cylinder method'. This method was not designed to provide 'real-life' data for environmental risk assessment purposes and it is widely perceived that results do not accurately reflect the true release rate of a biocide from an in-service vessel. In contrast, the US Navy's 'Dome method' measures biocide release rates directly from a ship's hull in service and is generally considered to be the most reliable method to-date for quantifying biocide release rates under environmentally relevant conditions. However, the Dome method is not suitable for routine widespread use and so it is recognised that in the absence of reliable 'real-life' data, regulatory authorities may yet use ASTM/ISO release rate data in environmental risk assessments.

In the present study, the relationship between the method-dependent copper release rate and the apparent environmental release rate is established for a number of antifouling coating types using a variety of available laboratory, fields and calculation methods by taking the release rate measured directly from vessel hulls using the US Navy Dome method as a reliable indicator of environmental release rates. Apart from a modified Dome method using harbour-immersed panels, all other laboratory, field and calculation methods significantly overestimate the environmental release rate of copper from antifouling coatings. The difference is smallest for certain erodible/ablative antifoulings, where the ASTM/ISO standard and the CEPE calculation method are seen to typically overestimate environmental release rates by factors of about 10 and 4 respectively, and greatest for self-polishing copolymer antifoulings (SPCs). Where ASTM/ISO or CEPE copper release rate data is used for environmental risk assessment or regulatory purposes, the use of a correction factor is proposed to enable more reliable generic environmental risk assessments to be made. Suitable correction factors may be derived from the available data using a conservative approach based on a realistic worst case and accounting for experimental uncertainty in the data.

It is anticipated that this approach could be extended in future to derive suitable correction factors for other biocides used in the antifouling paint industry, offering a simple solution to determining more realistic release rates from any given antifouling coating for use in a generic environmental risk assessment.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

WATER QUALITY, INVASIVE SPECIES AND TOURISM POLICIES AFFECTING BIOFOULING CONTROL FOR CALIFORNIA AND BAJA CALIFORNIA BOATS IN SALTWATER

L T Johnson and J A Gonzalez
University of California Sea Grant Extension Program, United States of America

Biofouling control in the United States is increasingly affected by environmental policy changes. The State of California has approved a regulatory program for Shelter Island Yacht Basin in northern San Diego Bay, requiring 76% reduction by December 2022 of copper discharged by pleasure craft antifouling paints. California water quality and pesticide regulatory agencies will sample California freshwater and saltwater marinas in 2006 to determine whether to recommend statewide action to reduce copper leached from antifouling paints. These agencies are communicating with United States Environmental Protection Agency, which is reevaluating copper antifouling paint registration at the national level and is considering reducing saltwater quality standards for dissolved copper from 3.1 µg/l to 1.9 µg/l. Concurrently, new California and United States policies are addressing hull transport of invasive species. Ships are believed to bring the majority of new species to a region, where they become established in ports. Commercial fishing, commercial-passenger fishing and recreational boats are implicated in transporting invasive species from ports to smaller harbors and estuaries, as they travel among fishing grounds, cruising destinations and events, such as races and fishing tourneys. Approximately 80% of boats kept in Baja California, Mexico marinas are from the United States, especially California and Arizona. Commercial-passenger boats from southern California often fish in Baja California waters. New, Mexican policies will likely increase cross-border, boat tourism through 2029 by streamlining immigration procedures, renovating existing marinas, improving highways for trailered boats and developing new marinas. Clearly, managing boat-hull transport of invasive species on the North American Pacific Coast will require interstate and international coordination. Boat owners and boating and coating businesses will need education on developing policies and access to cost effective technologies and practices for preventing hull-borne invasive species transport, while protecting coastal water quality. In May 2005, University of California Sea Grant Extension Program (UCSGEP) and California State Lands Commission convened a workshop of experts, stakeholders and policymakers to develop research and educational recommendations for preventing hull transport of invasive species by ships and boats. In 2005 UCSGEP published workshop proceedings; met with Baja California colleagues and with boat repair and environmental stakeholders; and researched a review paper, a policy analysis and an educational poster that will be published in 2006. Following the presentation, interactive discussion of recommendations for research, education and policy will be encouraged.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

FROM LABORATORY TO FIELD: DISSIPATION OF THE MARINE ANTIFOULANT ACTIVE DCOIT

A. Jacobson, I. Guo, Rohm and Haas Company
R.C.A. Steen, F. Ariese, B. van Hattum, Institute for Environmental Studies, Vrije Universiteit, The Netherlands
J. Jacobsen, National Environmental Research Institute, Denmark

4,5-dichloro-2-(n-octyl)-4-isothiazolin-3-one (DCOIT) is the active ingredient in the marine antifoulant Sea-Nine™ 211 Antifouling Agent. In laboratory water and water:sediment studies DCOIT biodegrades rapidly with half-lives of less than a few hours. Metabolism involves cleavage of the isothiazolone ring and the subsequent formation of alkyl metabolites which subsequently undergo extensive oxidation. Several of the metabolites have been tested and are considered to be 'ready' biodegradable. After 28 days of exposure to an inoculum from a waste treatment facility, approximately 90% of the carbon in these metabolites has mineralized to CO_2. Thus, DCOIT is ultimately biodegradable; parent rapidly degrades to compounds which are ready biodegradable. In a field study, the concentration immediately adjacent to a freshly painted boat was approximately 300 ng/L and decreased rapidly so that a short distance from the boat the concentration was less than the level of detection. Evidence obtained indicates that this decrease was due to the rapid biodegradation of DCOIT.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

PHOTOCHEMICAL BEHAVIOR OF ZINC PYRITIONE: DEGRADATION KINETICS AND BYPRODUCT IDENTIFICATION

V.A. Sakkas[1], K. Shibata[2], Y. Yamaguchi[2], S. Sugasawa[2], T. Albanis[1*]

1-Department of Chemistry, University of Ioannina, Greece 45110
2 National Maritime Research Institute, 6-38-1 Sinkawa, Mitaka,Tokyo 181-0004, Japan
*Corresponding author: Tel: +302651098343, email: talbanis@cc.uoi.gr

As a result of the ban introduced by International Maritime Organization (IMO) on antifouling paints containing organotin biocides due to their negative impact on marine environment, new alternative formulations have been developed based mainly on organic booster biocides. Worldwide around eighteen compounds are currently used in antifouling products (the most widely used are: chlorothalonil, dichlofluanid, diuron, irgarol 1051, sea-nine 211, TCMS pyridine, TCMTB, zinc and copper pyrithione, zineb, folpet, mancozeb, thiram, ziram) for amateur and professional use, however, only few data are known about the environmental risks of antifouling coating systems containing such biocides.
Although far from completely understanding the overall threat that they may pose to the aquatic environment, data on the basic mechanisms that regulate environmental fate such as photodegradation should be included.
To elucidate the photochemical behavior of ZnPT, laboratory scale degradation experiments were carried out in aqueous media of different composition under simulated solar irradiation. Moreover the effect of important constituents of natural water that are radical producers and scavengers (dissolved organic matter (DOM), nitrate, bicarbonate) was also examined. It was found that photodegradation proceeds via a pseudo first-order reaction in all cases. The presence of DOM and nitrate ions affect only slightly the photolysis reaction, however in all cases direct photolysis seems to be the dominant process.
Irradiation of the aqueous ZnPT solutions gave rise to several transformation products that were isolated by means of Solid Phase Extraction (SPE) using SDB extraction disks. These byproducts were identified using liquid chromatography-mass spectroscopy techniques and a possible transformation pathway is proposed for the decomposition of ZnPT in aqueous media. Pyridine-2-sulfonic-acid (PSA), is the major photolysis product of the parent compound. Other degradation products formed included pyridine-N-oxide (PO), 2-mercaptpyridine (PS), pyrithione disulfide ($(POS)_2$), pyridine disulfide ($(PS)_2$) and the pyridine/pyrithione mixed disulfide.

Presenting Author: Dr M. J. Waldock
Affiliation: Centre for Environment, Fisheries and Aquaculture Science
Address: Weymouth Laboratory, Barrack Rd, Weymouth, Dorset, DT4 8UB UK
Tel 44 1305 206669
Fax 44 1305 206601
Email m.j.waldock@cefas.co.uk

12th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ARE CURRENT RISK ASSESSMENTS FOR COPPER ANTIFOULINGS APPROPRIATE?

Mike Waldock, Steve Brooks, Bryn Jones and **Thi Bolam**

Centre for Environment Fisheries and Aquaculture Science, UK.

The overwhelming evidence that TBT antifouling biocides are environmentally damaging highlighted the need for regulators to assess the risks of use of the alternatives. For some of these synthetic organic biocides the risk assessment has been relatively straightforward and largely based on comparison of modelled environmental concentrations with predicted no effect concentrations. Where PEC/PNEC ratios are likely to exceed a value of one, many regulatory authorities have moved to ban the use of particular compounds. For copper using the same approach flags up warning signals that environmental concentrations should be dangerously high in enclosed marinas and even in open estuarine waters concentrations may be sufficiently high to cause concern. Are these concerns justified?

Many of these assessments are based on (i) unvalidated models (ii) hazard assessment predicated on total dissolved copper levels in seawater and (iii) risk of effects using laboratory experiments based on exposure of test organisms to copper solutions. The evidence base appears to be huge, but the interpretation belies the excellent understanding we have of speciation and real risk of copper complexes to marine organisms.

This paper provides recent evidence from laboratory tests and from field studies on copper in European coastal waters. Our approach demonstrates that the likely effects of copper toxicity can be determined using a simple speciation method to measure labile (largely toxic species) and by using an experimental exposure system that allows control of the parameters that regulate copper toxicity in the natural environment. The results of the study show that even the most conservative interpretation of the data shows no risk of harm to our study species. Our view is that several regulatory authorities are on the verge of banning copper based on too simplistic a risk assessment; the methods of risk assessment for synthetic organic chemicals cannot be applied to regulate the use of natural elements and the appropriate approach is to take account of speciation of copper.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

THE ROLE OF DERMAL PENETRATION IN OPERATOR EXPOSURE ASSESSMENT FOR ANTIFOULING PAINTS: HOW DO WE MOST ACCURATELY MEASURE SYSTEMIC EXPOSURE?

Gareth Prowse*, Clive Roper§, Nicholas Skoulis†

*. International Paint Ltd, SHERA, Stoneygate Lane, Felling, U.K. NE10 0JY
†. Charles River Laboratories Preclinical Services, Tranent, Edinburgh, U.K. EH33 2NE
§. Arch Chemicals Inc, Toxicology & Regulatory, Cheshire, Connecticut, USA

The legislative environment controlling antifouling paints is currently going through significant changes. The introduction of the Biocidal Products Directive in Europe and the Re-eligibility Evaluation Decision process under FIFRA, enforced by the EPA in the US, has introduced more sophisticated and rigorous assessment of operator exposure in the working environment. Accordingly, the data requirements and testing programmes required to enable credible risk assessment have begun to evolve in order to provide accurate exposure values for Human Risk Assessment (HRA). This paper discusses the results obtained from currently available test methods for assessing dermal penetration values for antifouling biocides and their appropriateness for use in HRA.

The biocide, zinc pyrithione, has many uses, and is commonly incorporated into antifouling and masonry paints. As such generic risk assessments have been made by various authorities (e.g the EPA) to assess the potential exposure of operators to biocides when applying these products. According to the generic nature of these assessments, dermal penetration values have been derived from studies using solutions of the biocide in a solvent. *In vivo* rat studies using applications of zinc pyrithione in aqueous vehicles have provided a value of 3% of the applied dose of zinc pyrithione in the aqueous solution; this value has been accepted for use in HRA. However the validity of using these values in HRA for antifouling paints is dubious as there will be a matrix effect of the paint which may reduce the amount of biocide that is available to penetrate through the skin. *In vivo* studies using rats exposed to antifouling paint containing zinc pyrithione (5%, w/w), gave a dermal penetration value of 0.7% of the original applied dose; an approximate four fold reduction from 3%.

It is widely acknowledged that the permeability of rat skin to chemicals differs to that of human skin, with several references citing that rat skin is three to seven times more permeable to chemicals than human skin. *In vitro* studies, designed according to OECD Test Guideline 428, conducted with the same antifouling paint applied to human skin obtained from reduction plastic surgery, returned a dermal penetration value of 0.08% of the applied dose for zinc pyrithione. This is in line with published data showing that rat skin is significantly more permeable to chemicals than human skin.

It is concluded that dermal penetration values for biocides should be determined for the actual, or realistic surrogate, paint formulations on human skin to ensure that HRAs are conducted with meaningful data in an otherwise already conservative system. This conclusion is in line with recommendations from the OECD (OECD GD No. 28).

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

MARINE PAINT: FROM MULTIDISCIPLINARY RESEARCH TO ENVIRONMENTALLY SOUND ANTIFOULING PAINTS

B Dahlbäck, Programme Director

Göteborg University and Chalmers University of Technology, Sweden

Marine Paint is a multidisciplinary and highly integrated research programme were all competences needed to develop new concepts for sustainable antifouling coatings are represented. The research is funded by The Foundation for Strategic Environmental Research, Mistra, in Sweden.

The first candidate substance from the programme – catemine (medetomidine) – has been proven highly effective against barnacles and with an acceptable ecotoxicological risk profile. The mode of action of catemine, an α_2 adrenoceptor agonist, has been elucidated in the barnacles. Deeper understanding of the barnacle on a genomic, physiological and behavioural level has been established. Developing concepts for paint formulation with catemine has led to several patents filed on controlled release technologies. To date, the most promising is based on using nanoparticles as carriers in the paint.

During the course several new and novel methodologies have been developed: Continuous and reliable barnacle cultivation, bio-imaging technology for understanding the internal of barnacle larvae, computer-based behavioural assay using motion analysis technology to measure the surface behaviour of barnacle larvae, measuring leaching rates of substances from a paint matrix under realistic hydrodynamic flow, ecotoxicological assessment techniques suitable for catemines, methods for measuring surface properties and surface affinities of candidates for antifouling agents.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

THE ECOLOGY OF EPIBIOSIS

Martin WAHL (IFM-GEOMAR, Kiel, D), mwahl@ifm-geomar.de

Epibiosis is a typically aquatic, especially marine, phenomenon. When a substratum organism is colonized by bacteria, diatoms, protozoans and/or multicellular epibionts its functional interface with the environment is replaced by a new epibiont - environment interface. This new 'surface' differs from the old one in many or most aspects: texture, consistency, physiology, optical and chemical appearance. Substantial impacts on physiology and ecology of the host may be expected.

Two major mechanisms contribute to the effect which epibiosis has on the interactions between host and either third species or the abiotic environment. First, the closeness of the association leads to a mingling or masking of signals emitted, and second both host and epibiont may shield each other from effects one is resistant, the other sensitive to. In addition, epibionts and host interact directly. Indirect and direct effects may add up to an overall positive, neutral or negative impact of epibiosis.

The epibiosis effect varies with the biotic and abiotic context. In its turn, this context varies at a genetic, spatial and temporal scale. Consequently, it is not surprising to find that both strength and sign of epibiotic impact may change conspicuously.

Host species react to negative epibiotic effects by deploying specific or general antifouling defenses. These may be expressed either on a constitutive or a regulative basis. By inferring metabolic costs, by pre-empting limiting resources or by possessing multiple functions these defenses may interact with other traits of the host.

Some examples from our research in limnic and marine benthic communities illustrate how these complex interactions may explain the simple but variable ones.

13th International Congress
on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

FOULING AND ANTIFOULING IN AQUACULTURE – A REVIEW

S Dürr, D I Watson, Daniel Beaz, Eivind Bergtun, Rik Breur, Juan Cebria, John Davenport, Donald Fowler, Courtney Hough, John Icely, Alistair Lane, Julie Maguire, Ana Manjua, Manuel Marhuenda, Kjell Maroni, Joe McElwee, Halvor Mortensen, David Murphy, John Murphy, James Newman, Ana Pereira, John Power, Sergio Prieto, John Watters, Peter Willemsen and **Jeremy C Thomason**

University of Newcastle upon Tyne, UK

The aim of this review is, firstly, to identify the type, extent and timing as well as the costs and problems caused by fouling in the European aquaculture industry from the viewpoint of the aquaculture farmer. Secondly, we summarise antifouling strategies already used in aquaculture, and other industries, that can be adapted to the aquaculture sector. This is the basis of the European CRAB (Collective Research on Aquaculture Biofouling) project. The tools of the review were a specifically designed and widely distributed questionnaire, research in peer-reviewed and non-peer-reviewed literature (library and internet sources), farm visits, telephone and personal interviews. In our review, we identify the most important fouling organisms and most significant biofouling problems. Further, we show the most commonly used antifouling strategies, linking them to industry requirements. The main antifouling requirements were determined, allowing us to select the most promising non-toxic antifouling strategies that can be adapted, further developed and modified within the project for use in the European aquaculture industry.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

PATTERNS OF RECRUITMENT AND DEVELOPMENT OF BIOFOULING AT EUROPEAN AQUACULTURE FACILITIES

S Dürr, D I Watson, D Beaz, E Bergtun, R Breur, J Cebriá, J Davenport, D Fowler, C Hough, J Icely, A Lane, J Maguire, A Manjua, M Marhuenda, K Maroni, J McElwee, H Mortensen, D Murphy, J Murphy, J Newman, A Pereira, J Power, S Prieto, J Watters, P Willemsen and **J C Thomason**

University of Newcastle upon Tyne, UK

The aim of this ongoing study is to determine differences and similarities in spatfalls, problematic fouling species and fouling community development on a pan-European scale. This is part of the CRAB (Collective Research on Aquaculture Biofouling) European biofouling baseline study. Recruitment and development of biofouling at 11 aquaculture sites across Europe was surveyed for one complete annual cycle from February 2005 to January 2006. The sites were Val Akva AS (Mid-Norway), Bømlo Skjell AS (S-Norway), Lakeland Marine Farms Ltd (W-Scotland), Curryglass Enterprises Ltd (SW-Ireland), Fastnet Mussels Ltd (SW-Ireland), James Newman (SW-Ireland), Cudomar S.L (E-Spain), Promociones Marsan S.L (E-Spain), Viveiros Ana Manjua Unipessoal Lda (S-Portugal), Sagremarisco-Viveiros de Marisco Lda (S-Portugal), Alevines Y Doradas SA (Canary Islands). As the field component was to be undertaken by aquaculture workers, standardisation of the survey was achieved through central coordination of the survey design, equipment used and analytical procedures undertaken. Monthly recruitment was measured on ten 20x20 cm^2 PVC panels at each site. These were exchanged for new panels after each assessment. Development of biofouling was measured on 50 identical panels at each site. Ten are permanently removed every 6 months (experiments run until 2007). Recruitment of fouling species and development of the biofouling community was assessed on the panels using carefully standardised digital photography plus measurement of wet weight and height of fouling. Digital images were analysed using semi-automated image analysis with a stereological approach, and 3-d aspects were evaluated using the wet weight and height of fouling results. Data have been analysed using multidimensional community analysis, and identification of the patterns and processes of fouling with a pan-European perspective will be presented.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

PATTERNS OF ANTIFOULING DEFENCE IN MUSSELS: ASPECTS OF BIOGEOGRAPHY. PHYLOGENY AND COMPONENT SYNERGY

AV Bers & M Wahl

IFM-Geomar Leibniz Institute of Marine Sciences, Duesternbrooker Weg 20, 24105 Kiel, Germany.
vbers@ifm-geomar.de; tel: +49 431 6004520; fax: +49 431 6001671

Marine organisms seem to rely on defence systems consisting of multiple mechanisms to prevent epibiosis (Wahl 1997). In mytilid bivalves, one defence component is thought to be a distinct microtopography of the periostracum that has previously shown to prevent barnacle settlement (Bers *et al.* 2005). Since mytilid mussels are highly invasive, the question is whether regionally evolved defences are also effective in other biogegraphic regions.

We assessed the antifouling properties of microtopographies of *Mytilus edulis, M. galloprovincialis, Perna perna* and *P. viridis* in various geographical regions. High resolution resin replicas of the shells were exposed in the field to natural fouling in temperate and tropical regions (Australia, Brazil, Chile, Germany, Hong Kong, the UK and the USA) for six weeks. In the majority of cases, microtopography alone did not provide sufficient antifouling protection. All textures were rapidly covered by a thick biofilm layer. Abundances of recruits did not differ considerably between natural microtopographies and smooth or roughened controls.

Subsequently, an additional presumptive defence mechanism, the surface chemistry of the periostracum of *Mytilus edulis*, was investigated. Mussel shells were extracted sequentially with petrol ether, hexane, dichloromethane, diethyl ether, ethyl acetate and methanol. In laboratory based bioassays, the antifouling activity of the resulting six periostracal extracts was tested against representatives of the major groups of fouling organisms, i.e. bacteria, diatoms and invertebrates.
The diethyl ether and ethyl acetate fractions reduced diatom growth significantly at concentrations of 30 ppm; barnacle settlement was significantly reduced by the diethyl ether fraction at 10 ppm.

The results support the concept of a multiple antifouling defence system, where mechanical and chemical antifouling mechanisms target different fouling organisms and act synergistically.

Bers AV, Prendergast GS, Zürn CM, Hansson L, Head RM and Thomason JC (2005): A comparative study of the anti-settlement properties of mytilid shells. *Biology Letters* DOI: 10.1098/rsbl.2005.0389

Wahl, M (1997) Living attached: aufwuchs, fouling, epibiosis. *Fouling organisms of the Indian Ocean: biology and control technology* (eds. Nogabushanam, R. & Thompson, M.), pp. 31–83, New Delhi: Oxford & IBH Publishing Company

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

INVESTIGATION OF MARINE FOULING ON FLOATING STRUCTURES WEST OF DONGSHA ISLANDS, THE NORTHERN SOUTH CHINA SEA

T Yan, W X Yan, Y Dong, H J Wang, Y Yan, G H Liang

(South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China)

The investigation of marine fouling on floating offshore structures west of Dongsha Islands, northern South China Sea, was conducted from April 1988 to October 1990. Two buoy investigation stations were deployed about 110km and 115km west of Dongshadao, Dongsha Islands anchored in water of 325 and 345m depth, and exposed for 8 and 12 months, respectively. The experimental panels on iron frames were placed on the sub-surface metal struts of the buoys and their mooring system and retrieved after 4, 8 and 12 months exposure. Fouling organisms colonizing the buoys themselves and their mooring systems were also sampled following 8 and 12 months deployment.

The results showed that 91 species were collected and identified at these two stations and the fouling community shows a more typical oceanic characteristic. Most of the species were mainly found above –50m depth and a striking vertical zonation of species was also observed with depth. In terms of biomass, the fouling community was dominated by pedunculate barnacles, hydroids and algae with common oysters, pearl oysters and acorn barnacles also important members. Biomass of hard fouling organisms increased over time. Under the influence of hydrological currents propagules of intertidal and sublittoral communities around the Dongsha Islands may also contribute to the development of the fouling communities west of Dongsha Islands.

18th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ANTIFOULING CHEMICAL DEFENSE IN NERITID GASTROPODS *NERITA ALBICILLA* AND *N. ORYZARUM* FROM TUTICORIN, GULF OF MANNAR, SOUTHEAST COAST OF INDIA

M. Santhana Ramasamy # and **A. Murugan**

Suganthi Devadason Marine Research Institute
44-Beach Road, Tuticorin-628 001, Tamil Nadu, India
#Present address: National Centre for Biological Sciences
Tata Institute of Fundamental Research, GKVK, Bangalore - 560065
Email: ram@ncbs.res.in
Fax: +91-80 - 23636662 or 23636862
Mobile: +91-09242183765
Lab: +91-80- 22932337

The negative impact of the toxic biocides used in antifouling paints has necessitated the search for natural, non-toxic and eco-friendly antifoulants. Marine animals are much targeted since they possess characteristic chemical defense strategies and produce novel secondary metabolites. In this context, the marine neritid gastropod molluscs *Nerita albicilla* and *N. oryzarum* were evaluated for antifouling chemical defense. The whole body methanol: water extracts of the two species inhibited the byssus production and attachment in the brown mussel *Perna indica* at 1185 µg/ml and 1625 µg/ml concentration. The observation of low EC_{50} values than the LC_{50} and the 100% recovery of the mussels in the toxicity assay indicated the non-toxic nature of the extracts. The active fractions in the two extracts were localized in butanol phase through bioassay guided gradient partitioning, which indicated their medium polar nature. In the antibacterial assay with the partitioned extracts, the butanol phase of *Nerita albicilla* inhibited all the 40 biofilm bacterial strains. The wide spectral inhibition of biofilm bacteria by the two extracts indicated the targeting of chemical defense against microfoulers.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ANTIFOULING ACTIVITY OF EXTRACTS OF 30 SPECIES OF TEMPERATE MARINE ALGAE AGAINST BARNACLE (BALANUS AMPHITRITE AND SEMIBALANUS BALANOIDES) CYPRIS LARVAE

[1,2]**Jean-Philippe MARECHAL**, [1]**Anthony S CLARE** and [1,3]**Claire HELLIO***

[1]School of Marine Science & Technology, Newcastle University, Ridley Building, Newcastle upon Tyne, NE1 7RU, UK.
[2]Observatoire du Milieu Marin Martiniquais (OMMM), 7 avenue Condorcet, 97 200 Fort de France, Martinique, France.
[3]School of Biological Sciences, University of Portsmouth, King Henry Building, Portsmouth, P1 2DY, UK.
*Corresponding author: email: claire.hellio@port.ac.uk; phone: +44-239-284-2073 ; fax : +44-239-284-2070.

Larvae of many benthic invertebrates settle on surfaces where they metamorphose into juveniles if suitable substrata are available, and are responsible for the major costs of biofouling. One alternative technology to toxic metal-based coatings to control fouling is the development of antifouling coatings with active compounds derived from marine organisms or analogues of the lead compounds. This natural solution to antifouling is based on the principle that marine algae and other basibionts face fouling pressure from epibionts on their own surface and utilise secondary metabolites to keep their surfaces free of fouling. In this study, the antifouling activities of aqueous, ethanolic and dichloromethane extracts from 30 algae from the North East Atlantic coast were investigated for their potential anti-settlement activities against cyprids of two species of barnacle, *Balanus amphitrite* and *Semibalanus balanoides*. Toxicity tests were run using nauplii of the two species. Of the 90 extracts assayed, twenty were very active (<10 μg/ml) at non-toxic concentrations, and as a general trend, these extracts were more active against *S. balanoides* (18) than *B. amphitrite* (2). Only one extract (dichloromethane fraction of *Sargassum muticum*) was effective against both species of barnacle. This result highlights the importance of selecting ecologically relevant species for settlement assays as it is clear that algal extracts from Brittany were more active against larvae from the same environment. From an applied perspective, natural product-inspired antifoulants may have a geographically-restricted relevance.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

MARINE ENDOPHYTES: A SOURCE OF NEW CHEMICAL NATURAL PRODUCTS, A REVIEW

E.B. Gareth Jones, Umpava Pinuran, Aom Pinnoi[1] and Susan J. Stanley

[1]BIOTEC, Central Research Unit, National Center for Genetic Engineering and Biotechnology, 113 Paholyothin Road, Khlong 1, Khlong Luang, Pathum Thani, 12120 Thailand
[2]Department of Ecology & Biodiversity, Hong Kong University, Hong Kong SAR

Endophytes are microorganisms that occur in plants and animals but do not cause disease symptoms. Their role in plants and animals is unknown, but they may inhibit grazing by animals or confer resistance to animals such as insects. Published data on endophytes of marine plants and animals are few, but there is considerable scope for studies on this topic. Studies on marine endophytes have focused on mangrove substrata such as mangrove leaves, wood and roots, or the leaves of marine sea-grasses (e.g. *Zostera* species). Most marine fungal endophytes are generalist species, but many are the source of an array of new or novel compounds of interest to the pharmaceutical industry. However, recent molecular studies suggests there may be truly marine endophytes and this opens up a new approach to their study. Those interested in isolating fungi from marine animals, such as soft corals, bryozoans, refer to such strains as marine derived strains. It is not clear if these are true endophytes or merely spores trapped in the animal tissue.

When searching for new chemical structures from marine animals, it is important to ascertain if these are produced by the animal, and not by fungal or bacterial endophytes. In this talk we will review the fungi isolated from various marine substrata and the use of molecular techniques to identify environmental fungal sequences.

12th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

QUANTITATIVE SURFACE CHARACTERISATION AND FOULING RESISTANCE OF MARINE MOLLUSCS FROM THE GREAT BARRIER REEF

A J Scardino [1], D Hudleston [2], Z Peng [2], R de Nys [1]

1. Biofouling Research Group, School of Marine Biology & Aquaculture, James Cook University, Australia
2. School of Engineering, James Cook University, Australia

Marine organisms provide unique natural models to develop fouling-resistant surfaces. Molluscs are exemplars of natural models, they have a hard surface covered in a three dimensional proteinaceous coating, the periostracum, which is often free of fouling despite strong pressure. In this study a broad range of molluscs from the Great Barrier Reef were characterised for surface features and their fouling resistance measured. The topographical features of 111 species were characterised using light microscopy and SEM. A subset of 36 species with the most unusual surfaces were further characterised using Confocal Laser Scanning Microscopy (CLSM). CLSM was used to generate quantitative surface roughness parameters including mean roughness, mean waviness, skewness of the surface profile, texture aspect ratio and textural fractal dimension. Surface hydrophobicity was also measured. Algorithms used enabled quantification of directionality, randomness and complexity, which are rarely studied in relation to biofouling. Significant differences in surface parameters were discovered at the level of class, family and species. The 36 species characterised were subsequently exposed to fouling in the field for 3 months and fouling quantified. The strength of attachment was also recorded after exposing fouled shell to a known surface water pressure. Surface parameters were correlated with resistance to fouling, and its subsequent removal, to elucidate the key physical parameters associated with fouling resistance in molluscs. Significant positive correlations were found between textural fractal dimension and total fouling cover, and mean waviness and fouling removal. Significant negative correlations were found between skewness and total fouling cover, and hydrophobicity and algal cover. For the first time natural surfaces have been characterized into quantified surface parameters and shown to correlate to fouling resistance. These findings will help to develop foul-resistant coatings and elucidate the mechanism(s) of action of natural foul-resistant surfaces.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ARE MARINE INVERTEBRATE LARVAE SMART ENOUGH TO DISTINGUISH BIOFILMS DEVELOPED UNDER CONTRASTING ENVIRONMENTAL CONDITIONS, AND HOW?

Pei-Yuan Qian

Department of Biology & Coastal Marine Laboratory, Hong Kong University of Science & Technology, Clear Water Bay, Hong Kong

All surfaces submerged in the aquatic environment are rapidly covered with a thin layer of biofilm. Microbes in biofilms are major sources of chemical cues that inhibit or induce larval settlement of marine invertebrates and, thus, have important implications on biofouling phenomena. Previous studies have demonstrated that invertebrate larvae can distinguish the biofilms of different origins, physiological conditions and growth phases, suggesting a strong correlation between larval settlement and the composition of microbe communities in biofilms. However, these studies relied not only on culture-dependent techniques that severely underestimate microbial diversity in nature, but also on rather inaccurate morphological characteristics to describe microbial diversity in biofilms. Despite well-established molecular tools to determine bacterial community profiles in virtually any habitat, there is extremely limited information on the bacterial diversity in marine biofilms. Owing to this paucity of information, the relationship between the microbial diversity of biofilms and their effects on larval settlement remains undetermined. Any knowledge on this issue will improve our understanding of the interaction between larvae and microbes, which is the key determinant in the biofouling phenomena. My laboratory has taken a multi-disciplinary (larval biology, molecular microbiology and chemical ecology) approach to examine the relationship between settling larvae and biofilm dynamics. The specific questions that we have been addressing include: 1) how the microbial community structures of biofilms developed under contrasting environmental conditions affect the bioactivity of biofilms for larval settlement, 2) what kind of inductive or inductive chemical signals are produced by microbes in biofilms, and 3) what kind of molecular mechanisms (or genes) may be involved in chemo-reception and subsequent larval settlement. Our ultimate goal is to bridge the knowledge gap between settlement induction/inhibition activity of biofilms and the microbial community dynamics in biofilms. The knowledge obtained will be applicable for antifouling research.

15th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

POTENTIAL MANAGEMENT APPROACHES FOR INVASIVE SPECIES TRANSPORTED BY VESSEL HULL FOULING

L. Scott Godwin

B.P Bishop Museum, Natural Sciences Department, Hawaii Biological Survey, 1525 Bernice Street, Honolulu, Hawaii 96817-2704, USA
Ph: 808-848-4156, Fx: 808-847-8252
sgodwin@bishopmuseum.org

Presenting Author: L. Scott Godwin
Session: Invasive Species

Ocean-going vessels can be thought of as biological islands for species that dwell in harbors and estuaries around the world. Maritime vessel activity acting as a vector for marine alien species is a complex issue involving ballast water, ballast water sediments, and hull fouling. Ballast water is the pathway that has been the major focus of investigations concerned with marine invasion vectors, and the biofouling that occurs on the surfaces of vessel hulls has been given less attention. Recent compilations of marine alien species in Hawaii include some 343 species, which includes 287 marine invertebrate species. The mechanism of transport for more than 70% of these marine invertebrate species is considered to be hull fouling. Pending administrative rules focused on management efforts for ballast water have recently moved toward mandatory exchange for all United States ports. Hull fouling is a new management issue, and will require expert opinions from various stakeholders connected to maritime shipping, marine resource management, and marine alien species problems. Such an effort was recently undertaken in Hawaii and the goal was to develop initial ideas that could be used to develop a formal management strategy. It was shown that it could be more important to focus management efforts on stochastic events instead of regular arrivals to minimize marine invasive species introductions through hull fouling.

18th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

SHIPS' SEA CHESTS: AN OVERLOOKED MECHANISM FOR SPECIES TRANSFERS

Coutts, A. D. M., and **Dodgshun, T. J.**

Cawthron Institute, Nelson, New Zealand.

Ballast water and hull fouling have been considered the major human-mediated dispersal mechanisms of marine organisms. However, recent studies suggest ships' sea chests are another important mechanism that has largely been overlooked. In this study we describe the occurrence of marine organisms inside the sea chests of vessels visiting or operating in New Zealand.

Since 2000, Cawthron has sampled 53 sea chests from 42 vessels (135 to 13,621 gross weight tonnes) at maintenance facilities around New Zealand. Vessel types included fishing boats, research vessels, bulk carriers, roll-on/roll-off ferries, container vessels, dredges, frigates, cruise ships, tankers and tug boats. Twenty three of the vessels were of domestic origin while the remaining 19 were international. All specimens above 500 µm (dead or alive) within sea chests were identified to the lowest practical taxonomic level.

A total of 151 different taxa have been identified representing one plant species and 12 animal phyla, namely Porifera (4), Cnidaria (13), Platyhelminthes (1), Nemertea (2), Nematoda (1), Mollusca (30), Bryozoa (11), Annelida (19), Sipuncula (2), Crustacea (43), Echindermata (3) and Chordata (21). Of particular interest were the presence of 85 mobile adult taxa in 45 sea chests (e.g. 10 gastropod species, 19 crabs, 4 fish, a sea urchin, a sea cucumber, and a starfish). Sixty one of the taxa were indigenous to New Zealand, 20 introduced (non-indigenous species now established), 15 non-indigenous (not yet established) and 55 were of unknown origin. Most non-indigenous (1 species of isopod, 3 species of amphipods, 6 species of molluscs and 5 species of decapods) were present on vessels operating between the South Pacific and New Zealand.

A wide variety of organisms are capable of surviving inside sea chests, highlighting the potential for sea chests to introduce non-indigenous and disperse native and introduced organisms around New Zealand. The occurrence of adult mobile stages is particularly significant and indicates that sea chests may be of greater importance than ballast water or hull fouling for dispersing certain marine species. These findings illustrate the importance of managing the ship as a whole rather than different mechanisms (i.e., ballast water, hull fouling, sea chests etc) in isolation. Cawthron is currently determining the *en route* survivorship of marine organisms inside sea chests and researching cost-effective treatment methods on New Zealand coastal vessels operated by the Pacifica Shipping Company Limited.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

EN ROUTE SURVIVORSHIP OF BIOFOULING ORGANISMS ON VARIOUS VESSEL TYPES.

Coutts, A. D. M.,Taylor, M. D., Cawthron Institute, Nelson, New Zealand, **Gardner, J. P.A.**, Victoria University of Wellington, Wellington, New Zealand.**Hewitt, C. L.**, National Centre for Marine and Coastal Conservation, Melbourne, Australia.

Biofouling is one of the single most important vectors for the dispersal of non-indigenous marine species (NIMS). However, it is still not known which vessels, vessel routes, and levels of biofouling (e.g., species richness, diversity, abundance, percentage cover, biomass, etc) constitute the greatest biosecurity risk for translocating biofouling organisms to new locations.

The greatest biosecurity risk could lie with slow-moving vessels such as barges, oil exploration rigs, floating dry-docks, decommissioned, specialised, and recreational vessels. Such vessel types typically spend prolonged periods of time stationary, thus they are renowned for accumulating extensive biofouling over the entire hull, including NIMS that are capable of surviving slow voyages to new locations. Alternatively, the biosecurity risk of more active and faster moving vessels such as merchant vessels, tankers, and cruise ships may also be relatively high considering high levels of biofouling, including NIMS, have been observed within anomaly areas of the hull (e.g., dry docking support strips, bow thruster tunnels, around bilge keels, rope guards, sea chests, and rudder posts) as a result of variation in hydrodynamic flows and in the effectiveness of the anti-fouling paint.

The authors have undertaken a study to identify, for a range of vessel types, key factors (e.g. hull location; voyage speed; and voyage duration) which determine the *en route* survivorship of biofouling organisms. This firstly involved the development of a novel method (i.e., MAGPLATEs) for attaching per-fouled settlement plates to the hull of different vessel types. MAGPLATEs were used to attach pre-fouled settlement plates to nine different vessels visiting or operating in Picton, New Zealand (e.g., recreational vessels, towed and motorised barges, and RO/RO ferries) representing three arbitrary speed categories: slow (3-6 knots); medium (8-10 knots), and fast (14.5-22 knots).

Prior to vessel departure, divers attached three replicate MAGPLATEs at three different hull locations: 1) bow region (exposed area); 2) within a dry docking support strip in the middle of vessels (areas where anti-fouling coatings are old/ineffective); and 3) the stern region (protected area). A further three replicate MAGPLATEs were attached to a metal plate underneath a local wharf for control purposes.

Photographs were taken of all 12 MAGPLATEs, including a further three undisturbed control settlement plates, immediately after each vessel's return. All MAGPLATEs were then removed and reattached underneath the same wharf where the settlement plates accumulated the biofouling. All plates were photographed seven days later to determine the post voyage chronic survivorship of biofouling organisms after the trials and all plates removed and preserved to assist with the positive identification of biofouling organisms. A further set of settlement plates were redeployed and another set of replicate trials undertaken on the same nine vessels and voyage routes. The results from these trials will be revealed in the presentation.

18th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

THE DEVELOPMENT OF RECOMMENDATIONS FOR THE PREVENTION OF SPECIES INTRODUCTIONS THROUGH MERCHANT VESSEL FOULING IN CALIFORNIA

L. Takata and **M. Falkner**

California State Lands Commission, USA

Passed in 2003, California's Marine Invasive Species Act renewed and expanded the state's program to prevent the introduction of non-indigenous species from merchant vessels. In addition to its existing ballast water management responsibilities, the California State Lands Commission (CSLC) was charged with the tasks of evaluating the risk posed by non-ballast vessel based vectors (essentially vessel fouling), and recommending action to reduce the discharge from NIS through this mechanisms. The risk evaluation and formulation of recommendations were to be conducted in consultation with a technical advisory group (TAG) that included, but was not limited to, shipping and port representatives and the U.S. Coast Guard. Final recommendations were to be provided to the state legislature by the spring of 2006.

Though vessel fouling is thought to be an important mechanism for introductions, little recent research has been conducted on the risk posed to U.S. waters. To the knowledge of this author, the only research conducted in California during recent decades consisted of a single survey of 9 container ships in the Port of Oakland. The challenge, therefore, for the CSLC and the TAG was to evaluate the fouling risk for California, and to formulate scientifically sound recommendations with a limited knowledge base, and within a restricted timeframe.

The TAG, composed of scientists, shipping and port representatives, non-governmental organizations, and regulatory agencies, began discussions in May 2005 with a workshop in San Francisco, CA. There, invited speakers provided background aimed towards informing subsequent discussions, and breakout discussion sessions were held to scope preliminary management considerations. Presenters included invasive species experts and fouling researchers from the U.S. mainland, Hawaii, and New Zealand, and vessel maintenance professionals from the commercial shipping industry. Subsequent meetings continued the information sharing process, and meetings late in the process shifted towards discussions on potential management frameworks for California. Wherever possible, analyses and qualitative surveys were completed using existing resources, and considered during the development of recommendations.

This presentation will provide insights into the advisory group process, the recommendations put forward by the California State Lands Commission to the California State Legislature, and the rationale behind them.

12th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

IS THE INVASIVE POTENTIAL OF A FOULING COMMUNITY A FUNCTION OF ITS DIVERSITY? FIRST RESULTS FROM A GLOBAL EXPERIMENT

M Lenz and **M Wahl**

Leibniz Institute of Marine Sciences at the University of Kiel (IFM-GEOMAR), Duesternbrooker Weg 20, 24105 Kiel, Germany

In the world's oceans, drifting objects and shiphulls provide a mobile habitat for fouling organisms. Generally, they are not only harbouring single species but rather serve as a vector for entire assemblages. Communities or fragments of them have a potential for invasion that differs from that of isolated organisms: they form microhabitats which are stabilized by interspecific interactions and should therefore be more resistant towards the fluctuations of environmental parameters inevitably associated with a translocation. Additionally, when introduced communities contain several sexually mature conspecifics reproduction and spread are substantially facilitated. However, though our knowledge about the ecology of invasions is steadily growing, the aspect of whole-community introduction was very rarely considered in former studies.

We conducted field experiments at 8 different stations in four regions of the southern hemisphere to investigate which community characteristics determine the invasive potential of fouling assemblages. Communities, grown on artificial hard substrata, of two different successional stages and therefore of different biomass, cover, diversity and complexity were transplanted between habitats on an intra-regional scale. We monitored them during the following 8 to 12 weeks and assessed their structural convergence towards reference resident communities of the same age. The rate of convergence, measured by the increase in similarity between resident and transplanted assemblages, served as an inverse indicator for the ability of the latter to persist in a new abiotic and biotic environment. We regard this as a measure for the communities' invasive potential. In this contribution, we will present the first results of this modular experimental approach that is conducted within an international network of marine research institutions.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

EVERY NOOK AND CRANNY: NICHE BIOFOULING AS A POTENTIAL VECTOR FOR INVASIVE MARINE PESTS

John A Lewis[1] and **Angela Gillham**[2]

[1]Defence Science & Technology Organisation, Australia
[2]Australian Shipowners Association, Australia

Modern antifouling paints can prevent the attachment and growth of macroalgal and invertebrate fouling species on the underwater hull of a ship for up to 5 years. However, not all submerged surfaces and equipment on a ship hull are protected in this way. These fouling "niches" can become heavily fouled and provide a refuge for the translocation of exotic species. Examples of niche areas include: seachests, seawater inlet and outlet pipes and grates, internal seawater piping systems, propellers and propeller shafts, bilge keels, anodes and docking block support strips. Several projects are underway in Australia to identify these fouling niches, to determine the composition of fouling communities growing within these niches, to assess the risk posed by niche biofouling for the translocation of invasive marine pest species, and to develop management strategies to minimise the risk of such translocation. In one project, in-water dive surveys were conducted on more than 30 Royal Australian Navy ships, while in a second project commercial ships were inspected on an opportunity basis when they dry-docked for hull maintenance. Some findings from these projects will be presented to illustrate the occurrence and composition of niche biofouling communities and possible strategies to minimise the risks they pose in regard to invasive marine pest translocation discussed.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

PEDICELLARIAE OF THE CROWN-OF-THORNS SEA STAR AS A NATURAL DEFENCE AGAINST FOULING: AT A PINCH!

J Guenther and **R de Nys**

Biofouling Research Group, School of Marine Biology and Aquaculture, James Cook University, Townsville QLD 4811, Australia

Sea stars have surfaces that are remarkably free of fouling organisms, although they face the same fouling pressure as any other immersed hard substratum. Asteroid pedicellariae, which are forcep- or pincer-like appendages made of calcareous ossicles, have repeatedly been suggested as a mechanism to prevent the settlement of fouling organisms and foreign materials. However, the structure and distribution of asteroid pedicellariae and their role in keeping the surface free of any macro-fouling organisms is unclear. To investigate the role of asteroid pedicellariae in fouling control, this study examined the presence of macro-fouling organisms on the sea star *Acanthaster planci*, the morphology and distribution of its pedicellariae and their defensive role against fouling. All examined specimens (n=41) were free of macro-fouling organisms on the surface, while the commensal shrimp *Periclimenes soror* was observed on the aboral surface of one specimen. The straight pedicellariae of *A. planci* had a mean length of 0.7 ± 0.03 mm with a mean distance of 2.6 ± 0.1 mm between pedicellariae. There was a weak positive correlation between the number of pedicellariae and the surface area of *A. planci* ($P = 0.001$, adjusted $R^2 = 0.328$). To determine whether pedicellariae respond to settling larvae, randomly selected pedicellariae were mechanically stimulated by dropping silica beads (<106 μm, 150-212 μm, 212-300 μm and 425-600 μm, density: 2.5 $g.ml^{-1}$) and zirconium/silica beads (200 μm and 500 μm, density: 3.7 $g.ml^{-1}$) over the pedicellariae. The percentage of responding pedicellariae increased proportionally with increasing size of the silica beads. However, the percentage also increased when zirconium/silica beads of similar size but higher density were used, indicating that the weight, not size, of the beads is the driving factor. Pedicellariae were also stimulated by placing larvae of the bryozoan *Bugula neritina* of varying ages (0-2 h, 6-8 h) close to a pedicellaria and dropping fragments of the fouling alga *Chrysocystis fragilis* of varying sizes (150-200 μm, 550-600 μm and 950-1,000 μm) over the pedicellaria. However, the response was consistently low, with only 15% and 11% of the pedicellariae responding to 0-2 h and 6-8 h old larvae of *B. neritina*, respectively, and none of the pedicellariae responding to the fragments of *C. fragilis*. The results suggest that asteroid pedicellariae are not as effective in fouling control as previously implied. Potential physical and chemical antifouling properties of sea stars need to be further investigated to determine the mechanism of action of fouling deterrence in sea stars.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

EPIBIONT COMMUNITIES ON SEA STARS: ONLY SPECIALISTS NEED APPLY

J Guenther and **R de Nys**

Biofouling Research Group, School of Marine Biology and Aquaculture, James Cook University, Townsville QLD 4811, Australia

Anecdotal evidence suggests that sea stars have surfaces devoid of fouling organisms. To determine the presence of fouling-resistant surfaces on sea stars, field surveys were conducted in the intertidal and subtidal zones of the northern part of the Great Barrier Reef, Australia, during the dry and wet season in 2005. A total of twelve sea star species were identified and examined for both micro- and macro-fouling organisms. To quantify the abundance of micro-fouling organisms, five specimens per species were collected. Samples were taken from various positions of the aboral surface, stained with 4',6-diamidino-2-phenylindole and observed under a fluorescence microscope. Numbers of bacteria across sea star species ranged between 0.5 to 11.8 x 10^4 bacteria.cm^{-2}. There were significant differences in numbers of bacteria between sea star species, however there were no marked differences between seasons. To quantify the abundance of macro-fouling organisms, ten specimens per species were visually examined and no macro-fouling organisms were found. However, there were a number of species-specific parasitic or commensal gastropods, shrimps, polychaetes and copepods living on the surfaces of the sea stars. The parasitic gastropod *Parvioris fulvescens* was found exclusively on the aboral surface of the sea star *Archaster typicus*, while the gastropods *Asterolamia hians* and *Granulithyca* sp. were only found on the aboral surface of *Astropecten indicus* and *Nardoa pauciforis*, respectively. The gastropod *Thyca crystallina* was found on the oral surface of *Linckia laevigata* and the commensal shrimp *Periclimenes soror* between spines of the aboral surface of *Acanthaster planci*. An unidentified polychaete species was found in the adambulacral groove of *Archaster typicus*, whereas unidentified copepods were found on the aboral surface of both *Linckia laevigata* and *Echinaster luzonicus*. As no macro-fouling organisms were found on sea stars, they offer an exceptional model to investigate and understand the mechanisms driving general fouling-resistant surfaces and the selective settlement of specialist invertebrates.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

PROXIMITY TO ANTIFOULING TREATMENTS AFFECTS THE ECOLOGY OF INVERTEBRATE ASSEMBLAGES

K A Dafforn[1], T M Glasby[2] and E L Johnston[1]

1. School of Biological, Earth and Environmental Sciences, University of New South Wales, Sydney, NSW 2052, Australia
2. NSW Department of Primary Industries, Port Stephens Fisheries Centre, Private Bag 1, Nelson Bay, NSW 2315, Australia

While hull fouling has been identified as the primary vector for marine invasion in most regions of the world, few studies have examined the different opportunities for invasion presented by commercial and recreational vessels. For the past two decades in Australia, the type of antifouling paint used by commercial and recreational boats has differed. Commercial ships have generally used tributyltin (TBT) on their hulls, while recreational vessels have been restricted to copper-based paints. We investigated the effect of different antifouling paints used on commercial and recreational vessels on the development of sessile invertebrate assemblages at four embayments in Port Jackson, NSW, Australia. The perimeter of settlement panels were painted with copper or tin antifouling paint and recruitment to the central unpainted area recorded. The plates were deployed in multiple embayments receiving primarily recreational or commercial vessel traffic, and were sampled photographically after five and ten months. Organisms showed similar responses at both times of sampling, although the effect of the copper was reduced after ten months, while the effect of tin remained constant. Copper-treated plates were found to enhance recruitment of several introduced species. In contrast, the TBT-based antifouling paint was highly effective at preventing recruitment of almost all fouling organisms. The only exception to this being turfing algae, which was more abundant in proximity to organotin paints, and also showed increased settlement on plates deployed in commercial embayments. Recruitment of several endemic species was greatly reduced by both copper and tin-based antifouling paints. The increased use of copper antifouling paints on vessels and the accumulation of copper in recreational embayments may be directly facilitating the transport and establishment of pollution-tolerant invasive species into disturbed native habitats.

13th International Congress
on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

SHORT TERM TESTING OF ANTIFOULING SURFACES: THE IMPORTANCE OF COLOR

Emily Ralston, **Melissa Tribou** and **Geoffrey Swain**

Florida Institute of Technology, Melbourne Florida

Short term testing of antifouling coatings through static immersion is frequently used to down select candidate systems. However, the coatings to be tested are often formulated in different colors and we were interested to discover the effect this had on the development of biofouling. Two experiments were designed, one investigated the effects of black and white and the other the effects of black, white, blue, green, yellow and red. Clear acrylic was used to provide a uniform surface for fouling organisms and the color was created at the back of the acrylic. The test sections were suspended in the Indian River Lagoon for up to one month , after which they were analyzed for fouling. It was found that there was a significant difference in fouling pressure both based on color and the direction the panels faced. These experiments demonstrate that color has a strong effect on the short term biofouling community development. At the Florida test site it was found that organisms show a strong, and significant preference for dark colored substrates. This preference can last up to 1 month or more, and as such, color must be considered when using short term assays to determine effectiveness of antifouling surfaces.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

INITIAL BACTERIAL ADHESION IN MARINE ENVIRONMENT

C Wang, Q. Zhao*, Y L Liu and **S Wang**

Division of Mechanical Engineering, University of Dundee, DD1 4HN, UK

Pipelines and heat exchangers using seawater as coolant suffer from biofouling. Biofouling not only reduces heat transfer performance significantly, but also causes considerable pressure drop, calling for higher pumping requirements. Since initial microbial adhesion is a prerequisite for biofouling formation, prevention of microbial adhesion on the equipment surfaces will have a major impact in preventing biofouling. Another approach to reduce cooling water biofouling is to make the surfaces less attractive for the microorganisms, so that they can be removed easily from the surfaces by flowing water. The surface energy of a solid surface gives a direct measure of intermolecular or interfacial attractive forces. Over the past two decades, marine bacterial adhesion to surfaces with different surface energies has been investigated with different or even contrary conclusions. In order to investigate the effect of the surafce energy of the substrates on bacterial adhesion, we developed Ni-P-PTFE nanocomposite coatings with various surface enerergies. The surafce chemisties and roughness are very similar for these coatings. We performed bacterial adhesion tests on these coatings with *Pseudomonas fluorescens*. We observed that the surface energy has a significant influence on the adhesion of *Pseudomonas fluorescens*, and that there exists an optimum surface energy (about 25 mN/m) for which the adhesion of *Pseudomonas fluorescens* is minimal. The results are consistent with famous Baier' curve. The bacterial adhesion mechansims in water as well as the Baier' curve were well explained with the extended DLVO theory.

This work was supported by EC FP6 AMBIO project.

* Corresponding author. Tel.: +44-1382-385651; fax: +44-1382-385508.

E-mail address: q.zhao@dundee.ac.uk (Q.Zhao).

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

THE INTERACTIONS OF SEASON, SURFACE TEXTURE, FLOW REGIME AND GLASS TRANSITION TEMPERATURE ON THE DEVELOPMENT OF MARINE BIOFILMS

C M Zürn, J C Thomason

University of Newcastle upon Tyne, UK

A number of physical, chemical and biological factors influence the development of marine biofilms. Experiments were undertaken to examine the interactions between season, glass transition temperature (Tg), flow regime and texture on their development in both the field and laboratory. Glass slides, coated with three different experimental polymers, modified to only vary in Tg, and epoxy resin tiles were used as substrata in the different experiments. Biofilm community diversity was enumerated using fluorescent microscopy (DAPI and LIVE/DEAD staining techniques) and image analysis. Different morphological bacterial groups and other micro-organisms enumerated included: Bacterial consortia, rods, cocci, spirilla, chain-rods, filamentous bacteria, cyanobacteria and diatoms. Results showed that there were complex interactions of all four factors on the development of marine biofilms in the field. Laboratory experiment showed that there were significant three-way interactions between surface texture, flow regime, and Tg on the development of the marine biofilm forming *Pseudomonas* strain NCIMB 2021.

18th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

DOES POLLUTION EFFECTS THE SEAWEEDS FOULING ACTIVITY TO ARTIFICIAL SUBSTRATE PLACED IN GUANABARA BAY, RJ, BRAZIL?

J Torres, **L M S Gestinari** and **Y Yoneshigue-Valentin**

Universidade Federal do Rio de Janeiro, Instituto de Biologia, Departamento de Botânica, Av. Brigadeiro Trompowisky, s/n°, 21941-590, Cidade Universitária, Ilha do Fundão, Rio de Janeiro, RJ, Brazil - Phone number: (21) 2280-7893; Fax number: (21) 2225-3390
jutorres99@yahoo.com

Environments under artificial eutrophication influence are usually known to be represented by few species. It may occur due to the different seaweeds responses to different pollutants, encouraging for the growth of some species and harmful for many others. The Guanabara Bay is an estuarine ecosystem located in the Rio de Janeiro city and for many decades has been progressively compromised by severe environmental conditions, such as those related to the urban development and the wastes from industries, harbors, airports, agriculture activities and untreated domestic sewage from millions of houses, all dumped together into this bay affecting the marine biota. The aim of this study was to evaluate the Guanabara Bay water quality based on the seaweeds fouling activity to artificial substrate placed in three sample sites in the bay. These sites (Inner Beach, Gragoatá Beach and Paquetá Island) were chosen in regard to the distance from the entrance of the bay in order to verify the influence of ocean water and pollution on the seaweeds communities from these sites. The artificial substrate consisted of a kind of dough used in swimming pools repairs, commercially known as "Tubolit". Plastic Pètri dishes were used as moulds for this dough. The intention of the experiment was to follow the seaweeds fouling activity along the four seasons of the year. Thus, in each site, 12 disks disposed in horizontal lines represented the months of the year and six disposed in vertical lines represented the replicates (a total of 72 disks). The analysis of seaweeds densities suggests that abiotic and biotic factors are intimately related and are extremely important to the structure of the seaweeds communities and its companion fauna. Factors such as tides and water flows (characterized by different temperatures and salinities) seem to have the same effect on the three different communities from the chosen sites. Nevertheless the nutrients, directly related to eutrophication, may be determining the density and composition of the three communities. In Paquetá Island (far away from the Guanabara Bay entrance) the density is high, but in Inner Beach (entrance of the bay) the density is low. In Gragoatá Beach intermediate values are found. Three taxonomical groups of seaweeds may indicate the environmental degradation level in the Guanabara Bay. The ephemeral green algae are characteristic from environments under sewage influence and are found in great amounts in Paquetá Island. The coralline algae are not tolerant to high concentrations of phosphorus, one of the most common nutrients in environments under eutrophication influence, and are found in Gragoatá and Inner Beach, but not found in Paquetá Island. And the most complex brown algae are the first to disappear when the environment shows higher levels of degradation. Some plants from this group were observed only in Inner Beach. These results indicate that there is still a water quality gradient in relation to the entrance of the Guanabara Bay.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

THE SECRET HISTORY OF A PAINT FLAKE: USING SEM AND EDX ANALYSIS TO INVESTIGATE THE COATINGS CYCLE OF A COMMERCIAL VESSEL AND ASSESS POTENTIAL POINT SOURCES

D J Howell and B Behrends

University of Newcastle Upon Tyne, UK

Due to the ban on tributyltin (TBT) as an active antifouling (AF) biocide by the IMO in 2003, a number of new, tin-free antifouling coatings have been developed. These coatings are being used to seal in the old TBT coatings after their in-service period of five years has elapsed, temporarily hiding the TBT problem, but not disposing of it. This study uses scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) on a paint flake taken from a dredge in a repair shipyard to get to investigate the structure of the layers and to assess the tin content of those layers. Ten layers of coating could be distinguished in the paint flake using SEM. It was shown that together, SEM and EDX can be used as a qualitative indicator of TBT. Layers of coating containing high levels of Sn were found, confirming that paint flakes such as this one that originate from shipyard wash-down water are a potentially significant source of TBT pollution.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

STUDY OF EXPLORATION BEHAVIOR OF ALGAE USING DIGITAL IN-LINE HOLOGRAPHY

M. Heydt, A. Rosenhahn, M. Grunze

Heidelberg University, Germany

Presenting author: Matthias Heydt
Affiliation: Applied Physical Chemistry, Heidelberg University
Address: Im Neuenheimer Feld 253, 69120 Heidelberg
Telephone: +49-6221-545064
Fax: +49-6221-545060
e-mail: m.heydt@uni-heidelberg.de

To study three dimensional processes under water we are using a novel microscopy technique: Digital in-line holography. Digital in line holography is based on the original idea of D.Gabor's "new microscopic principle" [1]. An interference pattern of the so called "source wave" and the so called "object wave" is recorded and contains all three dimensional information of the object. Using computers, real space information about the objects can be restored from these holograms applying a reconstruction algorithm [2, 3]. By focusing coherent LASER light onto a pinhole, a divergent radiation source is produced which can be used to track objects with submicron resolution. For a conventional microscope it is not feasible to focus under water. The holographic instrument has the great advantage that the focusing can be done subsequently later on a computer to obtain all the three dimensional information's about the object of interest. [1, 2, 4] To study the motion and exploration behavior of marine organisms towards different antifouling surfaces we are using an underwater digital in-line holographic microscope. [5] While recording the three dimensional path of marine organisms we gain more detailed understanding about the early attachment stages. These experiments are complementary to general screening biological experiments performed within AMBIO [6].

[1] D. Gabor, Nature 1948, 161, 777-778
[2] W. Xu, M.H. Jericho, I.A. Meinertzhagen, and H.J. Kreuzer, PNAS 2001, 98 (20), 11301
[3] W.Xu, M.H. Jericho, H.J. Kreuzer, Opt. Lett. 2003, 28(3), 164
[4] J. Watson, S. Alexander, G. Craig, D.C. Hendry, P.R. Hobson, R.S. Lampitt, J.M. Marteau, H. Nareid, M.A. Player, K. Saw, K. Tipping, Meas. Sci. Technol. 2001, 12, L9
[5] S.K. Jericho, J. Garcia-Secerquia, W. Xu, M.H. Jericho, H.J. Kreuzer, submitted
[6] Ambio : Advanced Nanostructured Surfaces for the control of biofouling, FP6 EU integrated project, http://www.AMBIO.bham.ac.uk/

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ENZYME ACTIVITIES AND IMPOSEX LEVEL IN *HEXAPLEX TRUNCULUS* AS BIOMARKERS OF TBT IN MEDITERRANEAN SEA

F Garaventa[1], A Jemec[4], M Faimali[1], A Ramsak[3], K Stopar[3], K Sepčić[2], G Greco[1], C Corrà[1], L Lipej[3], A Malej[3]

[1]CNR - Institute of Marine Sciences, Department of Marine technologies, Via de Marini, 6, 16149 Genova, Italy - [2]Department of Biology, Biotechnical Faculty, University of Ljubljana, Večna pot 111, 1000 Ljubljana, Slovenia - [3] National Institute of Biology, Marine Biological Station, Fornače 41, SI-6330 Piran, Slovenia - [4]National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

The aim of this study was to assess the effects of TBT and other contaminants on neogastropod *Hexaplex trunculus* along the Slovenian coast. The level of imposex (the superimposition of male sex organs - penis and vas deferens in a female gastropod) and enzyme activities (acetylcholinesterase (AChE)), glutathione S-transferase (GST) and catalase (CAT)) were measured. Imposex is widely attributed to the exposure to tributyltin (TBT) compounds, used world-wide in antifouling paints for ships. Thus, imposex has been widely used as a highly sensitive biomarker of tributyltin pollution in a large number of environmental surveys. On the other hand, selected enzymes are usually not used to indicate TBT pollution. The activity of AChE is generally proposed as an indicator of organophosphorus and carbamate pesticides exposure, whereas induction of GST can be suggestive of exposure to organochlorine compounds. Catalase is induced after the incidence of oxidative stress (e.g. imbalance between oxidants and antioxidants leading to damage) due mainly to metal pollution.

Specimens of the neogastropod *Hexaplex trunculus* were collected in 8 stations along the Slovenian coast. Sampling stations were chosen on the basis the marine activities impact on them. One is a marine protected area, two are natural monuments and the others are subjected to an increasing impact of contaminants. Organisms were morphologically analyzed to assess the degree of imposex, and were subjected to a multibiomarker analysis to determine the effects of pollution on the biochemical parameters in *H. trunculus*. The activities of AChE, GST and CAT were measured in both viscera and muscle samples (5 repetitions per sample).

The results indicate that the imposex level is very high starting from the level of 4.6 (measured by Vas Deference Sequence Index, from 0 to 5) and 22% (measured by Relative Penis Size Index, from 0 to 100%) registered in the population from the marine protected area. In animals taken from polluted sides, the VDS index and penis length were significantly higher compared to less polluted ones. Among enzymes, CAT proved to be the most affected biomarker. Activities of CAT in both viscera and muscles from nearly all polluted sites were significantly increased compared to protected areas. AChE activities in both viscera and muscles were significantly decreased in animals from one site located in the port. GST in viscera was induced only at one site loaded with wastewater from chemical industry and treatment plant and GST in muscle was increased at two polluted sites. These three sites also had significant effect on imposex biomarkers.

The results indicate that the differences in enzyme activities measured in samples from different sites are correlated with the imposex level trend and with the antropogenic impact that presses different sampling sites. The results of this multibiomarker approach seem to be a very promising tool towards a more realistic characterization of the contamination at a certain area, and enable to fully understand the effects of certain environment on selected organisms. Furthermore, the correlation between enzyme activity and the imposex level could suggest that imposex is not only due to TBT pollution.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

BIOMONITORING OF THE ENVIRONMENTAL CONTAMINATION BY TBT (TRIBUTYLTIN) IN THE MEDITERRANEAN SEA: NEW IMPLICATIONS IN THE USE OF IMPOSEX AS A SUITABLE TOOL.

F Garaventa[1], **M Faimali**[1], **A Terlizzi**[2], **S Fiorini**[1], **E. Centanni**[3] and **B Pavoni**[3]

[1]CNR - Institute of Marine Sciences, Department of Marine technologies, Via de Marini, 6, 16149 Genova, Italy
[2]Dept. of Biological and Environmental Science and Technology, University of Lecce, CoNISMa, 73100, Lecce, Italy
[3]Dept. of Environmental Sciences, University of Venice Calle Larga S. Marta 2137, 30123, Venice, Italy

The use of biomarkers and biological indicators for environmental monitoring has been advocated on the basis of ecological relevance, and such tools have often played a leading role in environmental management as well as in controversies which may arise there from. One case in point is the use of imposex in neogastropods as indicator of tributyltin (TBT) contamination of coastal waters.

Tributyltin (TBT) and its derivatives have been defined as the most toxic compound deliberately released into the marine environment by man. The presence of these chemicals in marine environments is mainly due to a massive use of antifouling paints incorporating TBT as a biocide. The negative effects that organotin compounds cause to marine environment have forced many governments to forbid their use. To limit the impact of organotin pollution, since January 1st 2003, the International Maritime Organization (IMO) has enacted a global ban on the use of organotin compounds in antifouling systems.

Imposex - the superimposition of male sexual organs (penis and vas deferens) onto female Neogastropods such as *Hexaplex trunculus* (Linné, 1758) - is used world-wide as indicator of ecological impact of organotin based antifouling paint (TBT and TPhT).

In this context, the first part of this work deals with a monitoring program performed in the Mediterranean sea. The concentration of organotin compounds in organisms tissues was analysed by Gascromatography in order to assess the presence of a clear correlation between the imposex level and the TBT concentration that is essential to consider imposex a reliable bioindicator.

The results of the biomonitoring program, besides their intrinsic value, pointed out an anomaly in the correlation between imposex and organostannic compounds tissues concentration, generating doubts on the reliability of this biomonitoring tool. For this reason the work developed into two following step: the imposex analysis in specimens of *H. trunculus* coming from Natural History Museums collected before the 1965 (years of the first patent for the use of TBT in antifouling paint) and a laboratory experiments of imposex induction by the controlled injection in the organisms of TBT and of another class of endocrine disruptors (PCB). We found clear sign of imposex in Museums specimens and the induction experiment pointed out that other chemicals (PCB and $MgCl_2$) are able to induce imposex in *H. trunculus*.

The results of both these two steps suggested that the level of imposex, at least in this species, could be not considered as a specific biomarker for TBT contamination but, instead, as a non specific response to stress stimuli; these results could be the basis for further researches on mechanisms regulating sexual development in gastropods and their response to environmental pollution.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

IN VITRO ANTIBACTERIAL AND ANTIMICROFOULING ACTIVITY OF SOME SYNTHETIC DERIVATIVES AND NATURAL POLYMERIC 3-ALKYLPYRIDINIUM SALTS PURIFIED FROM THE SPONGE *RENIERA SARAI*

E Chelossi[1], I Mancini[2], K Sepčić[3], T Turk[3], F Garaventa[1] and M Faimali[1]

[1] Institute of Marine Sciences – Section of Marine Technologies – CNR, 16149, Genoa, Italy
[2] Laboratorio di Chimica Bioorganica, Università di Trento, I-38050 Povo- Trento, Italy
3 Department of Biology, Biotechnical Faculty, University of Ljubljana, Večna pot 111, 1000 Ljubljana (Slovenia)

Recently, water-soluble 3-alkylpyridinium salts (poly-APS), isolated from the Mediterranean sponge *Reniera sarai* (Pulitzer-Finali), and their structurally related synthetic analogues were screened for their antimacrofouling activity, showing good inhibitory effects on cyprids larvae of *Balanus amphitrite*. The formation of a bacterial biofilm is usually foreword for the development of a complex fouling community, thus prevention of bacterial growth and attachment is of primary importance.

The aim of this work was to investigate the antibacterial and antimicrofouling potential of these compounds, comparing the efficacy of natural poly-APS with their synthetic analogues. Ten synthetic analogues including neutral 3-octylpyridines and monomers, dimers and tetrameric oligomers of 3-octylpyridinium salts, as well as the natural poly-APS, were assayed against a wide collection of marine bacteria, including *Vibrio*, *Aeromonas*, and *Bacillus* species. The Minimum Inhibitory Concentration (MIC) of each compound was determined using the broth microdilution method. The growth inhibition of a natural seawater biofilm under laboratory conditions was detected by scanning electron microscopy (SEM) only for the natural poly-APS. Glass samples (1×1 cm^2, three replicates) were immersed in unfiltered natural seawater for a period of 10 and 20 days at temperature of 20°C, in presence of poly-APS at different concentrations (0, 0.01, 0.1, 1, 10 $\mu g \times ml^{-1}$). Inhibition of biofilm formation was evaluated by counting the microorganisms (bacteria, protozoa, diatoms and fungi) at 5000X magnification (field of view = 400 μm^2). Results showed that considerable antibacterial activity towards both Gram positive and Gram negative bacteria was displayed by dimeric and tetrameric oligomers, with MIC values ranging from 1.0 to 28.3 μM. Natural poly-APS showed low-medium efficacy against all target bacteria (MIC ranging from 0.9 to 6.9 μM). In terms of structure-activity relationship, our data showed that higher antibacterial activity of synthetic analogues might be related to relative increased molecular complexity and/or presence of bromine atom in the structure. Results of biofilm growth inhibition showed a reduction of total number of settled microorganisms, that was closely related to increase in poly-APS concentration. Following the observed ability of poly-APS to inhibit the biofilm growth, it could be worthy to test the efficacy of the synthetic analogues to inhibit the development of natural seawater biofilm. Moreover, based on the natural origin of alkylpyridinium compounds, their chemical stability and water solubility, as well as the easy access by organic synthesis, the novel compounds emerging bioactive from the present study may be good candidates for various applications, such as potential new drugs against microbial pathogens or as natural biocides in development of new antifouling paints.

13th International Congress
on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

MEASUREMENTS OF THE ADHESION STRENGTH OF PERMANENTLY ATTACHED CYPRIDS AND NEWLY METAMORPHOSED BARNACLES (*BALANUS AMPHITRITE*) USING A FULLY TURBULENT FLOW CHANNEL

A Cavaco[1], **A S Clare**[1], **M J Downie**[1], **A Beigbeder**[2], **Ph Dubois**[2] and **Ph Degée**[2]

[1]University of Newcastle upon Tyne, England
[2]Université de Mons-Hainaut, Belgium

The present generation of commercial foul-release coatings offer impressive performance for a number of applications but foul in low-flow environments. Ideally future improvements in such coatings would include better release characteristics. Adult barnacles have been a natural focus of attention for efforts to understand adhesive failure on silicone elastomers and the colonising form - the cypris larva - has largely been overlooked. Consequently, while coating thickness, elastic modulus and surface energy are known to be important to the performance of foul-release coatings against adult barnacles, comparable knowledge for cyprids is essentially absent. In part this deficiency reflects the relative difficulty of working with larvae compared to adults, particularly in relation to adhesion. Here we describe a fully turbulent flow channel designed to measure the adhesion strength of cyprids under flow conditions similar to those existing on the wetted surface of a large high speed ship. The apparatus is capable of a maximum bulk velocity of 13.4 m s^{-1} with a wall shear stress of 224 Pa; roughly equivalent to a 140 m vessel operating at 40 knots.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

UNDERWATER HULL GROOMING AS A MEANS OF IMPROVING SHIP HULL COATINGS PERFORMANCE

Melissa Tribou and **Geoff Swain**

Florida Institute of Technology, Melbourne Florida

Underwater cleaning of ship hulls is routinely performed to remove fouling. This improves ship performance and reduces the frequency of dry-docking cycles. The traditional cleaning methods developed for biocide based coatings are vigorous and they remove much of the coating, causing unwanted input of biocides into the water and roughening of the surface. The adoption of the silicone fouling release coatings has prompted the development of less aggressive cleaning methods; however, cleaning is only implemented once fouling has become established on the surface. This research investigated the feasibility of using frequent underwater grooming of ship hulls as a method to maintain and prolong ship hull coatings in a smooth and fouling free condition. The concept is to deploy several low power autonomous underwater vehicles when the ship is in port that continually grooms the surface, removing microbial and juvenile fouling with only minimal impact to the coating surface.

This study investigated the frequency of grooming required to maintain coatings free from fouling. Four surfaces, including a foul-release coating, ablative copper, an epoxy, and Teflon, were tested. The coated test panels were immersed under caged conditions at the Florida Institute of Technology static immersion site for 120 days. The surfaces were subjected to 3, 6, 12, and 24-day grooming intervals. Pre-groomed and post-groomed fouling conditions on each test surface were assessed and maximum required lateral forces at each grooming event were measured. Our results show that foul-release coatings that were groomed at the 3 and 6 day intervals remained free from fouling. All groomed ablative copper coatings maintained foul-free surfaces. Both the epoxy and Teflon surfaces became fouled at all grooming frequencies, but fouling was reduced for the 3-day grooming frequency. The lateral forces required to groom the surfaces, with the exception of the foul-release coating, increased with time. The results demonstrated that frequent grooming can have prolonged, positive effects on the antifouling performance of coatings. Future research will look at grooming methods and different coating types.

15th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

MARINE BIOCORROSION: THE INFLUENCE OF MACROFOULING IN THE CARBON STEEL API 5L X65 CORROSION BEHAVIOR

L V R Brito – Messano [1,2], R Coutinho[2] and E H S Cavalcanti[3]

[1]Programa de Pós-Graduação em Biologia Marinha,/Universidade Federal Fluminense, [2]Instituto de Estudos do Mar Almirante Paulo Moreira and [3]Instituto Nacional de Tecnologia, Brazil

Seawater is a complex corrosive system, and biofouling is one of the factors that influence corrosion processes. In this study, we investigated the behavior of corrosion associated with the development of macrofouling in carbon steel plates, along the first 6 months of the successional process. An experimental design was developed from June to December/2002, in Cabo Frio Island, Arraial do Cabo, Brazil (42°W, 23°01'S). Electrical contacts were fixed to six carbon steel plates (API 5L X65; 150x200x20mm), that were attached to four structures suspended by rafts. Different treatments were applied to the plates: (1) the "control" (in which plates were covered with *nylon* meshes to observe what happened in absence of macrofouling); (2) "community" treatment (in which macrofouling community was analyzed) and (3) "barnacle" treatment (where other macroorganisms were excluded using brushes to induce the dominance of barnacles). Along 6 months, the cover of organisms in the "community" and "barnacle" treatment was estimated weekly using a 10x10 cm quadract with 30 intersection points. Free corrosion potential against an Ag/AgCl $_{(KCl)}$ electrode was the electrochemical parameter monitored in parallel with the biofoulers percent cover. We registered 28 taxa: 17 belonging to the macroalgae taxa and 11 related to macrofauna taxa, both classified into 7 functional groups. In the "community" treatment, the dominant organisms were filamentous macroalgae (23.73%), barnacles (17.51%), hydrozoans (16.96%) and encrusting bryozoans (9.58%). In the "barnacle" treatment, cover varied between 39.38% and 62.50%. Corrosion potential ranged between -665.75 mV(Ag/AgCl $_{(KCl)}$) and –517. 50 mV (Ag/AgCl $_{(KCl)}$), remaining around the free corrosion potential for ferrous alloys in seawater. This variation could not be related to fouling community development. After 24 weeks, the plates were removed to calculate uniform corrosion rate and to observe if localized attacks could be found in each treatment. The highest uniform corrosion rate was found in the control treatment suggesting that macrofouling provides a protection against mass loss. Despite the low percent of localized attacks found, what is expected in case of carbon steel, the community treatment showed the highest values. This fact suggests that not only the barnacles induced localized corrosion, what is frequently reported in literature, but also other biofoulers influenced in this process.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

VESSELS' HULLS AS INTRA-REGIONAL VECTORS OF SPECIES

F B Mostacato[1] and **R Coutinho**[2]

[1]Programa de Pós-Graduação em Biologia Marinha,/Universidade Federal Fluminense and
[2] Instituto de Estudos do Mar Almirante Paulo Moreira, Brazil

Recent studies demonstrate the importance of the intraregional transport of species, particularly through the hulls of domestic vessels. Vessels with ballast water navigate on international routes predominantly, and so they have received much attention as species' vectors mainly in the interregional transport mode. However, domestic vessels represent an underestimated threat in the species' transport via hulls. Thus, the fouling on vessels' hulls can act as far in the homogenization of native and cryptogenic species as in the increase of distribution range of exotic species already established in port regions. The aim of the present study was to evaluate the role of vessels' hulls in the regional transport of marine species. Two vessels, the bulk carrier Frotargentina and the sea marker Tubarão were used in 4 experimental campaigns. The potential of vessels' hulls in the transport of marine species, the effect of vessels voyages in the population densities of sessile and vagile species/groups, and the distribution of these populations along the hull were evaluated with percentage cover and relative density data. Sessile organisms such as *Balanus amphitrite*, the macroalgae *Enteromorpha* sp. and *Ulva* sp. demonstrated a large potential of being transported to other regions through the hulls of vessels. On the other hand, the bryozoan *Bugula neritina* and the ascidian *Styela plicata* had a significative reduction of their densities after voyages, mainly of adult populations. Regarding to the vagile organisms, the isopod *Sphaeroma walkeri* presented a large potential of transport, probably by its habit of sheltering within dead barnacles' carapaces. It was also verified that some parts of the vessels' hulls were preferentially occupied by organisms such as *Ulva* sp., *B. neritina*, and *Obelia dichotoma*. Exotic species such as *Megabalanus coccopoma*, *Perna perna*, *Isognomon bicolor* and *Styela plicata* were also transported on the vessels' hulls of this study.

... 16th International Congress ... on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

INTERACTION BETWEEN ENVIRONMENT FACTORS AND LARVAE DENSITY UNDER EUTROPHIC AND OLIGOTROPHIC CONDITIONS IN THE RIO DE JANEIRO COAST, BRAZIL

J E A Gonçalves[1 2]*, R Coutinho[1] and I R Zalmon[2]

[1]Instituto de Estudos do Mar Alte. Paulo Moreira, Brazil - *arrudagoncalves@yahoo.com.br
[2]Universidade Estadual do Norte Fluminense, Brazil.

The paper "Supply-Side Ecology (Lewis, 1986) showed that the amount of larvae and propagules in the water column is a key factor of the benthic succession process. Afterwards, several papers pointed out that environment factors can influence this process as well. Based on these informations, a 75 months larvae, α chlorophyll, nutrients (PO_4 - NO_2 - NO_3 - NH_4), pH, temperature, salinity and O_2 monitoring was performed in a eutrophic (Guanabara bay, RJ) and in a oligotrophic environment (Arraial do Cabo, RJ). These two environments of the Brazilian Southeast coast are 164 km distant each other, and have several equal benthic species or similar groups. In both areas 14 larvae types were identified, and Cirripedia was the group with major larvae concentration. The groups Decapoda, Bivalvia, Ascidiacea e Mytilidae had lesser but significant concentrations. In Guanabara Bay, the greatest Cirripedia larvae concentrations occurred in autumn and winter, with means varying from 2.000 to 6.000 larvae/m³. Other groups with significant larvae concentrations were the Polychaeta, D larva, and Mytillidae, reaching concentration peaks of 180, 163 and 140 larvae/m³, respectively. The abiotic data were analyzed in the same time scale used for larvae, and showed that the phosphate values were higher during winter and spring. Corelated to the increase of phosphate and the increase of some larvae availability, the nitrito, nitrate and amonia monitoring also made evident the abundance peaks in these same seasons, indicating an effect in the increase of plankton community. Even though this pattern had not been constant along the whole years monitored, such periods might be indicated as critical to fouling on hard substrata. Temperature, salinity and oxygen showed little seasonal variation, on the contrary to nutrients (phosphate, nitrito, nitrate and amonia) and α chorophyll that oscillated significantly along time. In Arraial do Cabo, the Cirripedia larvae had the highest concentrations with a peak of 1000 larvae/m³ during spring and winter. Polychaeta and Mytillidae larvae also showed significant concentrations reaching means above 100 larvae/m³. The temperature, salinity, dissolved oxygen and pH data had values with low seasonal variation. Conversely, the nutrients and α chorophyll varied enough along time.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

SUCESSION OF BIOFOULING UNDER EUTRÓPHIC AND OLIGOTROFIC CONDICTIONS ON THE RIO DE JANEIRO COAST, BRAZIL

J E A Gonçalves[1 2]*, R Coutinho[1] and I R Zalmon[2]

[1]Instituto de Estudos do Mar Alte. Paulo Moreira, Brazil *arrudagoncalves@yahoo.com.br
[2]Universidade Estadual do Norte Fluminense, Brazil

The goal of this study was evaluate successional process of fouling organisms in a eutrophic (Baía de Guanabara, RJ) and oligotrophic environment (Arraial do Cabo, RJ), apart 164km along southest brazilian coast. Four 20 x 25 cm steel plate tests were submerged until 2 meters heigth, tied to floats, in each study site between april 1997 and march 1998. Fouling percentual cover was monitored every two weeks using pontuation method. At Arraial do Cabo, 41 fouling habit taxa was identificated. Between them was occurred 19 algae, 6 sponges, 6 ascidians, 3 bryozoans, 3 moluscs, 1 hydrozoan, 1 annelid, 1 crustacean, 1 anthozoan, 1 echinoderm and biofilm. Total cover percent of fouling organism was over 100% since first monitoring month, because species overllaping. After one to three submerged months there was significative percent reduction of organisms cover, with slowly raising during following months until obtaining relative stability. The most thickness of test plates was 6,5 cm. During first 4 months, thickness inceased oly 0,6 cm, having *Hincksia* and hydrozoan like dominant organisms. After that, *Schizoporella* and, mainlly, barnacles had dominated quite all substrate during agost and september 1998. This raising helped number and size increase of *Schizoporella,* and, later, *Perna perna* settlement. At Baía de Guanabara, 15 taxa were identificated and one third of that was ascidians. The first increase of test plates thickness has occurred by the presence of small organisms like polichaets and hydrozoans, or in initial development stage like barnacles and *Styela* settlers. With *Bugula* arrive in december 1998 and growing of two last organisms, significative thickness raise until 9,5 cm in january 1999. Results showed that eutrophic ecosystem, i.e. Baía de Guanabara; had lower diversity, but has an ecological succession faster and bigger biomass than oligotrophic ecossystem, i.e. Arraial do Cabo.

18th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ANTIFOULING ACTIVITY EVALUATION OF THE GLYCEROPHOSPHOLIPIDS ISOLATED FROM MARINE ORGANISM FROM ARRAIAL DO CABO REGION – RIO DE JANEIRO – BRAZIL.

William Romão Batista[1], Cláudio Cerqueira Lopes[2], Rosangêla Sabbatini C. Lopes[2], Maria Hèlena C. Baeta Neves[1] ,Jari Nóbrega Cardoso[2] .

[1]Instituto de Estudos do Mar Almirante Paulo Moreira (IEAPM) and [2]Instiuto de Química, Universidade Federal do Rio de Janeiro (UFRJ).

One of the great problems faced when any structure is placed in the sea, is the natural action known as biofouling, also called incrustation, which is the process of settling and growth of bacteria, algae and invertebrates sessil organisms, developed on natural or artificially submerged structures. Aiming to clarify up this problem, man has used products that have the effect to hinder or delay the evolution of biofouling in the structures placed in the seas and oceans. Amongst the products used so far, TBT (tributil-tin) was the substance which presented greater effectiveness, however due to evidence of its harmful effect in the environment the society opted for its banishment.

This work evaluated the use as a natural antifouling of substances of the glycerophospholipid group. For this, one commercial available glycerophospholipid and eight lipid extracts of four marine organisms, including three species of sea sponges and one species of marine mollusk, which could possibly contain analogs of these substances, have been used in microbiological fouling assays, where microscopy blades unilaterally covered with agar-agar contend such extracts, had been fixed in four acrylic panels and submerged in a tank containing sea water. Each panel was removed at different moments and evaluated with respect to the type and amount of adhered microorganisms. The results indicated an antifouling effect against the bacteria present in the biofilm, the early stage of biofouling formation, serving in this way to subsidize futures work and possible applications of these products, for industrial purposes, aiming at the TBT substitution.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

SEMIOCHEMICHALS: INFLUENCE OF CO-SPECIFIC FACTORS ON THE SETTLEMENT OF CIRRIPEDS ON ROCKY SHORES

M Ballesté[1,3], **L M Lage**[2,3] and **R Coutinho**[3]

[1]Universidade Santa Úrsula, [2]Universidade Estadual do Norte Fluminense, and [3]Instituto de Estudos do Mar Almirante Paulo Moreira, Brazil

Complex biochemical, physical, and ecological factors influence the development of fouling communities. Semiochemicals are biochemical signals responsible for different behavioral and physiological responses of organisms. The goal of this study was therefore to analyze their effects on the settlement of cirripedes to verify whether they facilitate larvae settlement on substrate. Seven by five centimeter granite plates were submitted to two treatments: A carapace macerate and a living barnacle macerate. A control group without any treatment for three barnacle species (*Chthamalus bisinuatus*, *Tetraclita stalactifera*, *Megabalanus coccopoma*) was used to verify the origin (carapace vs. live animal) and the effects of semiochemicals. Plates were placed on the upper and lower midlittoral of the rocky shore of Ponta da Fortaleza – Arraial do Cabo, RJ. All barnacle species showed similar results, suggesting that the action mechanism of the semiochemicals can be applied to mostly all cirrepedes. ANOVA and post-tested with Tukey (ANOVA, α=0.05) statistical results demonstrated a strong influence of semiochemicals on barnacle settlement and also showed that living organisms must be present so that semiochemical release can take place. Therefore the hypothesis of their presence in the carapace was discarded. The results of this study helped to understand the biofouling process and also provided a better understanding of the dynamics of barnacle settlement on rocky shores.

METALS OF ANTIFOULING PAINTS ARE TRANSFERRED TO MARINE ORGANISMS OF GUANABARA BAY ?

W C Paradas & G M Amado Filho

Instituto de Pesquisas Jardim Botânico, Brazil

In order to determine the contribution of antifouling paints (AFP) to metal concentration in organisms from Guanabara Bay (GB), levels of metal were compared in two main fouling algal species, *Ulva flexuosa* and *Ulva fasciata* and one isopod species - *Sphaeroma serratum* from sites of artificial substrate covered by AFP and sites of natural substrate. In addition, experiments (in triplicates) with one plate (36 cm^2) covered with 100 mg of AFP Renner AF10 fixed in aquaria (4000 ml of seawater) were maintained during seven day in the following conditions: 1 - aquarium with algae (250 mg of *U. flexuosa*); 2 - aquarium with algae and isopod (300 individuals of *S. serratum*); 3 - aquarium with isopod. Concentrations of Cd, Cr, Cu, Pb and Zn were determined by Atomic Absortion Spectrophotometry. Significantly higher concentrations of Cu and Zn were detected in samples collected over artificial surfaces covered by AFP than natural substrate from GB. For example, Cu concentration in *U. flexuosa* was 148 $\pm$ 2 $mg.g^{-1}$ of dry weight in artificial substrate and 19 $\pm$ 2 $mg.g^{-1}$ in natural substrate; and in *S. serratum* Cu concentration was 199 $\pm$ 3 $mg.g^{-1}$ in artificial substrate and 120 $\pm$ 3 $mg.g^{-1}$ in natural substrate. Results of AFP metal concentrations revealed elevates Cu and Zn levels: Cu, 324,785 $\pm$ 57,000 $mg.g^{-1}$ and Zn 145,232 $\pm$ 12,400 $mg.g^{-1}$. Metal accumulation by organisms under experimental conditions showed that Cu was accumulated in the following concentrations: *U. flexuosa* accumulated 3,856 $\pm$ 328 $mg.g^{-1}$ in experiment 1, 2,539 $\pm$ 198 $mg.g^{-1}$ in experiment 2; and *S serratum* accumulated 349 $\pm$39 $mg.g^{-1}$ in experiment 2 and 215 $\pm$ 32 $mg.g^{-1}$ in experiment 3. The increase of metal concentration on *S. serratum* in experiment 2 in relation to experiment 3 revealed that metals accumulated by algae were thereafter transferred to isopods by feeding. Our data showed that the leaching of metals by antifouling paints present on decks and boats are the main source of Cu and Zn in marine areas and that these metals were transferred to both primary producers and primary consumer.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

BARNACLE SETTLEMENT BEHAVIOR ON THE MICRO-TEXTURED METAL SURFACE

R Horiuchi[1], Y Kameyama[1], J Komotori[2], S Kobayashi[3] and I Katsuyama[3]

[1]Graduate School of Science and Technology, Keio University, Japan
[2]Department of Mechanical Engineering, Keio University, Japan
[3] Japan NUS Co. Ltd., Japan

It is known that the cypris larvae of barnacles swim around and explore with their first antennas for a surface to settle on. We focused on the relationship between the surface texture and their behavior of settlement.0This study investigates the barnacle settlement on three micro-textured surfaces manufactured by FPB (Fine Particle Bombardment) treatment. FPB treatment is a method which shoots out particles of several ten micrometers in high speed and bombards them on to a material surface. SUS316L steel discs were used as the substrate. Three different types of the FPB treated specimens with the micro-textured surfaces and polished surface (P) were prepared as follows: 1) specimen with a surface segmented half of polish and of high-speed tool steel particles treatment (P-HI) 2) specimen with a segmentation of surface half polished and the other half alumina particles treated (P-AL) 3) specimen with 3 types of surface areas; polished, alumina particles treated and glass beads treated (P-AL-GL). All of the modified surfaces possessed a microscopic surface roughness. The attachment of barnacles *Balunus amphitrite* on micro-textured surfaces and polished controlled surface was observed in laboratory environment.

In both P-AL and P-HI, barnacles settled on the treated surfaces but not on the polished surfaces. The cypris larvae settled only on to the treated surface and not on to the mirror-finished surface in P-AL specimen. However settlement of few cypris larvae was observed on the surface of P specimen.

In the case of the P-AL-GL specimen, the surface which the cypris larvae settled on to most was the AL surface, and the least was the P surface. From the surface analysis, the AL surface had a similar surface roughness to the GL surface but the former possessed a relatively dense texture.

These results indicate that cypris larvae examine the surface for a more suitable settling place but then they will eventually settle on even to a less suitable surface if they have no choice. In addition surface roughness under the submicrometer scale, the larger the surface roughness was and the less the texture density was, more cypris larvae settled.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

A NEW AUTOMATED METHOD TO MEASURE THE ADHESION STRENGTH OF ADULT BARNACLES TO SURFACES AND ITS COMPARISON TO ASTM D5618

S.L.Henry[1], **A.S.Clare**[1], **R.J.Mutton**[1], **M.J.Downie**[1], **D.Willaims**[2] and **P.Willemsen**[3]

1 School of marine Science and Technology, University of Newcastle, England
2 Akzo-Nobel (International Paints Ltd) Newcastle, England
3 TNO, Den Helder, Holland

The need for effective non-biocidal replacements for organotin-based paints has focussed attention on foul-release technology and an underlying need to understand the adhesion mechanisms of fouling organisms. The economically-important barnacle, *Balanus amphitrite*, is a well established model for such studies. Previous investigations have used a standard method, ASTM D5618, to evaluate the efficacy foul-release coatings under development by measuring the adhesive strength of adult barnacles with hand-held force gauges. Recently, however, our laboratory commissioned a custom-built, computer-controlled, automated instrument (Advanced Analysis and Integration Ltd, Manchester) to facilitate intensive, laboratory-based screening of foul-release coatings. Here we evaluate the new automated system with adult *B. amphitrite* grown on test surfaces in our laboratory and compare the force measurement results with those obtained using ASTM D5618.

Funded by the EU Integrated Project, AMBIO

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

BIOFOULING ZONATION IN FOTONEGATIVE ENVIRONMENT AT MACEIÓ COAST, ALAGOAS, BRASIL

M. D. Correia, H. H. Sovierzoski, A. G. A. Borba Jr & V. R. Cedro

Universidade Federal de Alagoas, Setor de Comunidades Bentônicas, LABMAR/ ICBS, Rua Aristeu de Andrade, 452, 2° andar, Maceió, Alagoas, Brazil. 57.021-090. tel./fax.: (82)3221.2501 email mdc@fapeal.br

The biofouling zonation according to the environmental variations occur accentuated alterations in the species composition. The biofouling seasonality in a negative environmental at the tide region was characterized. The study area situated in the coast of Ponta Verde, Maceió city, Alagoas State, northeast of Brazil, among coordinates 9°39'S - 9°40'S and 35°41'W - 35°42'W. In the decade of 60 was built Alagoas Yacht Club, extending since the beach line until the beginning of the coral reef platform, with support structures formed by concrete pilasters, with bases of $1m^2$. In this area, at the tide region, it formed a negative environmental, where the incidence of the solar light is very reduced, mostly in the winter's months, however with water great circulation in the high tides. During low tides these pilasters remain completely outside water for two hours, staying the fouling organisms totally exposed. The work was accomplished in June 2005 (winter) and in January 2006 (summer) and were chosen 20 pilasters considered only one side of each bases for analysis. Quadrats method were used and the data transformed in coverage percentage. The organisms identification was accomplished in the own environment and when necessary were collected samples for confirmation in laboratory, until the minor taxonomic level possible. In the whole 16 taxa were registered, with the more diversity for 13 taxa of Porifera, besides the presence of Polychaeta Serpulidae, Cirripedia *Tetraclita* sp and Hydroidea *Sertularia* sp. In the winter Hidroidea *Sertularia* sp and Porifera *Tedania ignis* were considered dominant with percentages above 50%. Porifera *Haliclona curacaoensis* and Cirripedia *Tetraclita* sp were frequent with occurred between 4 and 26%. Variations of 2 and 8% of occurrence were to rare organisms that represented by 4 species of Porifera *Chalinula molitba, Haliclona manglaris, Haliclona melana* and *Cinachyrella alloclada*. The summer's period had a reduction in the number of species, being registered in the whole 14 taxa, with just 10 species for Porifera. Polychaeta Serpulidae, Cirripedia *Tetraclita* sp and Rhodophyta *Gelidium* sp were dominant organisms with accentuated variations, however in some occurred above 50%. Hydroidea *Sertularia* sp and Porifera *Tedania ignis*, were frequent both with occurrences between 5% and 32%. *Chalinula molitba* and *Haliclona manglaris* were rare organisms which ones presented values lower than 10% of occurrence. Besides taxa above mentioned other organisms were registered at the studied pilasters, however they went of occasional occurrence, because had small number of samples and with few percentages. The Phylum Porifera had the more elevated biodiversity at the negative environmental studied, with occurrence preference for the winter's period, when the percentages were high significant.

12th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

THE EFFECTS OF MARINE NATURAL PRODUCT EXTRACTS IN A PAINT SYSTEM

Lily D. Chambers, Frank C. Walsh, Robert J.K. Wood & Keith R. Stokes*

Surface Engineering & Tribology Group, School of Engineering Sciences,
University of Southampton, Highfield, Southampton SO17 1BJ, UK.
*Physical Sciences Department, Dstl Porton Down, Salisbury, Wiltshire SP4 0JQ, UK.

Biofouling has a negative effect on the hydrodynamics of a ship's hull, increasing the fuel consumption and giving rise to materials degradation through biocorrosion. The requirement to control fouling in an environmentally acceptable manner, over a variety of operational profiles, is needed to replace the toxic antifouling paints currently used. One potential method is to use naturally derived marine metabolites. Marine natural products have been investigated as alternative antifoulants for over two decades with research concentrating on the isolation of products which function as a natural deterrent to other organisms colonising and biofouling their surfaces. The efficacy of these products within coating systems has, however, received relatively little attention.

If the application of such compounds into coatings can be better characterised, the use of a natural antifouling product has the potential to provide an effective bio-compatible, non-toxic antifouling solution. Such a coating strategy would also comply with future demands and legislation while allowing a reduction in an engineered vessel's through-life cost.

In this presentation, crude extracts of the coastal algae *Chondrus crispus*, as well as the commercial booster biocide Chlorothalonil, were incorporated into a commercial binder/rosin paint system using a high shear mixer. The coatings were applied to mild steel with a dry film thickness between 30 and 100 μm. Three different coatings will be discussed, one having an ethanolic algal extract, another containing a commercial biocide and a control system with no antifoulant additive. These coatings were characterised to determine the influence of the additives and to assess their potential as future antifouling systems for ship hulls. Experiments were conducted to investigate water permeation using electrochemical techniques and to establish the effect of surface roughness on the substrate and coatings using profilometry. Initial stages of biofouling on the coating surfaces were determined using nucleic acid staining and fluorescence microscopy together with scanning electron microscopy.

12th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ORGANOTIN ANTIFOULINGS EFFECTS ALONG THE BRAZILIAN COAST AS INDICATED BY IMPOSEX IN MARINE NEOGASTROPODS

Ítalo Braga de Castro [1] & **Marcos Antonio Fernandez**[2]

Programa de Ecotoxicologia Marinha, (1) LABOMAR/UFC, (2) Dep. Oceanografia/UERJ

Organotins were used globally as biocides in antifouling paints from the late 70´s to late 90´s. Their recognized toxicity on non-target organisms, persistence in sediments and transference to high trophic levels in the marine food webs led their application to be progressively restricted in the most European countries, the USA, Japan, Australia and New Zealand, and pollution effects were reduced in these areas accordingly. This is not the case, however, of most developing countries, where this class of compounds application is not controlled. Recently, effects of these compounds were reported in Brasil, Argentina and Chile, as well as in India, South Africa, Malaysia, Thailand, Hong-Kong, Taiwan and Korea. This work reports the results of several biomonitoring studies along the Brazilian coast. Imposex development in two species of muricid gastropods was used as biomarker of organotin exposure and the results are reported. Studied areas, from N to S, were Pecém harbor and Mucuripe harbor (CE), Natal harbor (RN), Cabedelo Harbor (PB), Recife and Suape harbors (PE), Jaraguá harbor (AL), Aracaju (SE), Salvador and Aratu harbors (BA), Forno Harbor and Guanabara, Sepetiba and Ilha Grande bays (RJ), São Francisco do Sul and Paranaguá (PR), Itajaí (SC) and Rio Grande (RS). Sampling periods extended in some instances from 1997 to 2006. Imposex response was classified as high (sterility found in females in at least one station), moderate (females with developed penis and vas deferens at least one station) and low (only initial imposex development observed in all stations in the area). Imposex was observed in all studied areas, and was classified as high in 6, moderate in 5 and low in 7 out of the 18 areas, with 214 stations sampled. A comparative study carried out in parallel revealed that *S. haemastoma* is more sensible than *T. rustica* for imposex induction, indicating that in some cases this evaluation was less effective, and organotin pollution is more pronounced. These results are strong evidence that antifouling pollution could be a treat to marine communities in Brazil, including in areas considered to be well preserved from pollution. They also indicate that more studies are required both on organotin compounds effects and on the new organotin-free (but not biocide-free) antifouling compounds effects on brazilian species in particular and tropical ones in a general sense. Tropical, developing countries are within the most critical areas for antifouling pollution today, as both generations of antifoulings are being used simultaneously and without control in their case, and sinergic effects in the toxicity of combined antifouling biocides have been demonstrated in laboratory studies.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

THE EFFECT OF HYBRID SOL-GEL FILMS AND (NANO)STRUCTURING ON ANTIFOULING AND FOULING RELEASE

J. van Zanten, C.H.A. Rentrop, P.R. Willemsen

TNO Science and Industry, The Netherlands

Fouling organisms have traditionally been controlled by antifouling paints that contain biocides (toxic compounds). Regulations now require that antifouling paints must not cause adverse effects on the environment.. The AMBIO project aims to develop new environmentally benign coating technologies that will balance societal concerns for Safety, Health and the Environment with industrial competitiveness in the global market by (nano)structuring of marine coatings. TNO Science and Industry is therefore looking at the effect of (nano)structuring of coating surfaces on antifouling and fouling release properties by introduction of nanosized particles to generate nanocomposite coatings.

In this project (nano) clay particles are modified with different additives to give surface structuring and hydrophobicity. Two important contradictory properties have to be taken into account to generate this effect. The (organically modified) clay particles have to be dispersed in the coating medium on a nanoscale, which can only be realized by making the particles compatible with the coating system. In a second step the particles need to migrate to the surface to generate a surface roughness and hydrophobicity. The morphology and chemical state of the (nano)structuring was determined with confocal microscopy in a dry and immersed state and with the captive bubble test.

The effect of the (nano)structuring of coatings was evaluated in a hybrid sol-gel coating system with and without surface structuring by determining the antifouling and fouling release properties. Thereto the attachment and removal under hydrodynamic shear of three marine bacteria; *Cobetia marina, Marinobacter hydrocarbonoclasticus* and *Vibrio alginolyticus* and a fresh water bacteria *Pseudomonas fluorescens* was determined. Furthermore the foul-release properties of the test chemistries with respect to sporelings of the fouling algae *Ulva linza* is investigated and the antifouling properties of these coatings is tested by settlement (and metamorphosis) of barnacle cyprid larvae in droplet assays. The hybrid sol-gel coatings with and without structuring were found to inhibit settlement of barnacle cyprid larvae and show promising results with respect to foul-release properties.

18th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

A THREE-YEAR BIOMONITORING STUDY ON ORGANOTIN POLLUTION IN MACEIÓ, ALAGOAS STATE: IMPOSEX DEVELOPMENT IN *THAIS RUSTICA*

M A Fernandez[1]; I B Castro[2]; J P Quadros[1] & E Camillo Jr[1]

Programa de Ecotoxicologia Marinha, (1) Dep. Oceanografia/UERJ, (2) LABOMAR/UFC

Imposex response in neogastropods populations is a widely used biomarker for organotins pollution. This kind of study was only performed, however, in most developing countries since a few years, and in these countries organotins application still lack regulations today. Imposex have been reported in many places of the brazilian coast, as also in Chile and Argentina, always in the vicinities of harbors, shipyards or marinas. As chemical determinations of organotins are expensive and time-consuming, imposex is a very useful tool for screening studies in areas suspected of organotin pollution. In this study, *T. rustica*, was tested in a three year study along Maceió coast, Alagoas State. This area was choosen because it is located in an open shore with good water circulation, and has two well-defined point-sources of organotin compounds. This condition was considered adequate to investigate the variation in the response of gastropods populations in an annual basis. Samplings were carried out in the summers of 2002, 2003 and 2004. Sampling stations (total of 10), sample size (30 adult specimens per sample) and analytical protocol was rigorously the same. Imposex intensity was determined by % imposex females, RPLI (Relative Penis Lenght Index), RPSI (Relative Penis Size Index) and VDSI (Vas Deferens Sequence Index). Results have showed that imposex intensities declined in the order City harbor (S5) > Emissário (S6) > Terminal Triken (S7) > Saco da Pedra (S8) in all sampling periods. As main organotin sources were located at S5 and S7, and local water circulation is from N to S (S1 to S10), this pattern of imposex results was expected. With the exception of S6, the year 2003 results indicate a lesser response on the populations, and thus, reduced pollutand load or better pollutant flushing. Indeed, imposex was not even detected at one station (S8), in this year. As S6 was closer to the main organotin source, S5, city harbour, and have some indexes (VDSI) with even greater values, the last hypothesis seems a better way to explain this observation. Observed variations within results of each station, however, in the considered time period, were much less pronouced that the variations found between the results of each station, when mean values were considered. These results indicate that the variation of environmental parameters as organotin loads and current intensities were probably small along this experiment time period, while the sampling size was sufficient to produce reprodutive results. These observations confirm imposex development as a reliable tool for monitoring organotin pollution in Brazil.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

A NEW, NON-DESTRUCTIVE IMPOSEX INTENSITY EVALUTION PROTOCOL FOR BIOMONITORING ORGANOTIN POLLUTION IN THE BRAZILIAN COAST

M A Fernandez; F M Pinheiro; J P Quadros; E Camillo Jr; A R de Rezende; F Ostritz; S C da Silva; D O Folha e T Veloso.

Programa de Ecotoxicologia Marinha, Dep. Oceanografia/UERJ

Imposex response in neogastropods populations is a widely used biomarker for organotins pollution. The recognized toxicity of these compounds led to controls on their application in most developed countries, beginning in 1982 in France. In some cases, as Japan, their application have been banned. This is not the case, however, of most developing countries, where this class of compounds application is not controlled. Recently, effects of these compounds were reported in Brasil, Argentina and Chile, as well as in India, South Africa, Malaysia, Thailand, Hong-Kong, Taiwan and Korea. As the global ban on organotins compounds, scheduled by IMO to begin in january 2003 have not been enforced yet, problems with these compounds are still likely to occur in the third world countries. This is the case of Brazil. Being probably the first country among the developing ones to partialy ban the use of TBT antifouling paints (Brazilian Navy, 2003), and also to include limits on organotins concentrations in water (CONAMA resolution 357, 2005), Brazil is also one the most studied countries in third world in this aspect. Monitoring studies, bioassays and chemical analysis of sediments and biota have been conducted and are being published in recent years. A national-wide monitoring effort has been propposed, and have been made in a preliminar form, as reported elsewhere in this meeting. Imposex in neogastropods is indicated as the better screening tool to do this. Traditional methods of imposex evaluation have been used following the general approach developed by Gibbs and collaborators in England in the eighties, and improved by Fioroni and Stroben and collaborators in Germany in the nineties. The application of these methods, however, depends on internal anatomical features of imposex development for the evaluation, and thus requires the sacrifice of the analysed specimens. Our group have been developing and testing successfully an alternative, non-destructive protocol to avoid sacrificing animal lives. This new protocol is based in a reversible narcotization and in statistical, instead of anatomical, inference. The original study cases and results from ongoing studies are reported to support our propposal of using this protocol instead of the conventional one in a national monitoring programm of antifouling pollution.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

MODEL SENSITIVITY ANALYSES OF BENTHIC INVERTEBRATES DYNAMICS AS EXPERIMENTS TO REGULATE POPULATION ABUNDANCE

Mariana Alves de Guimaraens[1], Dinair Cristina Pinheiro da Costa[1], Michel Iskin Silveira da Costa [2].

1 Universidade de Pernambuco, Instituto de Ciências Biológicas, Departamento de Biologia, Rua Arnóbio Marques 310, Santo Amaro, Recife – PE, 50100-130, Brazil.
Fax/Phone: (21) 2285-3471
E - mail: mguimaraens@hotmail.com
2 Laboratório Nacional de Computação Científica (LNCC).

The simulation models used for the sensitivity analyses were based on the logistic model: ***dN/dt=(c-m) *N*(1-N/K)***. Where *c* is the growth function, *m* the mortality function, *N* number of individuals in the population and *K* the carrying capacity. The growth function includes daily recruitment values as inputs to the model and the mortality function the mortality rate. Recruitment daily values, mortality rate, *K* and initial condition were changed to calibrate the model and evaluate the recovery capacity of the population. In addition parameters were changed one at a time + and– 10% to evaluate the stability of the population models. The results were compared with the baseline runs using the following equation: **(100/(n*Savg) * [S1-S2])**. Where *n* is the number of simulation days, *Savg* is the average of the baseline run values. *S1* are the baseline run values and *S2* are the values of each sensitivity experiment. Basic simulation experiments allowed values of invertebrates that oscillated between 900 and 450 individuals in 100 cm2. With further simulations showed values bellow 500 individuals and population crashes followed by values that showed recovery. Indicating populations management possibilities, through control of recruitments values, mortality rates and levels of invertebrate initial conditions of the model. Preliminary experiments with + and - 10% parameters values changes showed variations of less than 10 %, attesting the stability of the system. However the decrease of the mortality rate can cause the system to crash, leading to variability greater than 90% between baseline runs and systematic sensitivity experiments results.

18th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

DEVELOPMENT OF ANTI-FOULING SOLUTIONS FOR USE IN MARINE COATINGS

J B Kristensen*° 1, K V Gothelf*, F Besenbacher*, T Rand° and **C H Poulsen°**

*)iNANO, University of Aarhus, Denmark and °)Danisco A/S, Denmark

The need for environmentally friendly anti-fouling agents in the commercial as well as recreational ship coating segments has prompted two leading companies in their respective fields to join the bioscience know-how of Danisco A/S and the paint technology of Hempel A/S in an effort to fight biofouling without the hazard of having damaging substances accumulate in the sea and harbours.

While the paint technology is developed by Hempel, Danisco has initiated an Industrial PhD project with the Interdisciplinary Nanoscience Centre (iNANO) at University of Aarhus, in which state-of-the-art know-how and technology in the fields of biochemistry, biotechnology, nanoscience and nanotechnology will be used to develop an anti-fouling solution with optimal paint compatibility, outstanding performance and minimal environmental issues.

The hope is to achieve solutions with high efficiency against biofouling combined with a high degree of safety in handling and rapid biodegradation, as well as facilitated approval and registration for coatings. The sometimes difficult and slow transition from prototype to commercialized paint product is expected to improve significantly by the use of agents that have already undergone strict toxicological and environmental evaluation.

15th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ANTIFOULING PAINTING EFFECT ON 1-12 MONTHS BENTHIC COMMUNITY SUCCESSION ON AN ARTIFICAL REEF

W Krohling, D S Brotto and **I R Zalmon**

Universidade Estadual do Norte Fluminense, Brazil

To evaluate the functional role of the epibenthic community on an artificial reef (21°29S, 41°00W) it was created an exclusion fouling area through the application of antifouling paint (Tritão Cooperkote - Akzo Nobel Coatings) on half of the 36 concrete reef modules while the other half remained natural. Concrete panels with the same treatments were attached to the external surface of each module. Four panels of each treatment were taken to the laboratory monthly and the fouling community was quantified by point-intersection technique. In the non-painted reefs, the initial stages (1st to 3rd months) were characterized by the dominance of empty space and balanids up to 20% cover. Subsequently, they were colonized by the hydroids *Bougainvillia* sp and *Obelia* sp and the bivalve *Ostrea* sp. On the antifouling panels no species was registered until the 8th month and afterwards the few resistant were *Megabalanus tintinabulum*, *Balanus trigonus*, *Balanus* spp and *Ostrea* sp. The empty space was superior to 70% even at the 12th month. The average number of taxa on non-painted and painted panels varied from 4 to 16 (from 1st to 12th months) and from 2 to 4 taxa (8th to 12th months), respectively. The turnover rate and community structural difference index were highest on non-painted panels. The initial colonization process was similar on both treatments with a decreasing on empty space and an increasing tendency on species richness, diversity and *Ostrea* sp recovery. The differences between treatments are partially accepted, since both successional trajectories were distincts when we consider the first submersion month as the beginning of fouling colonization. However, when it is considered the 8th month as the initial development stage on painted reefs, the community succession process was very similar to the non-painted.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

SCALING UP TO AVOID THE NOISE: THE TOOL OF GLOBALLY REPLICATED EXPERIMENTATION

M Lenz[1], M Molis[2] and M Wahl[1]

[1]Leibniz Institute of Marine Sciences at the University of Kiel (IFM-GEOMAR), Duesternbrooker Weg 20, 24105 Kiel, Germany; [2]Biologische Anstalt Helgoland, Foundation Alfred-Wegener-Institute for Polar and Marine Research, Marine Station, Kurpromenade 201, 27498 Helgoland, Germany

Ecologists, like researchers in any other field of natural sciences, seek to formulate general concepts which are applicable to a multitude of natural systems. In this process, the interaction between theoretical reflections and empirical testing has proven to be a powerful tool. The verification of ecological concepts in field studies can reveal their weak points and helps to improve their coherence, but *in situ* experiments are largely influenced by the variability inherent in the system under investigation. This is reflected by unexplained noise in the results that hinders their interpretation and obstructs the view on general aspects. Here, the replication of experiments in space or time is considered as one way to overcome this problem. The international research program GAME (Global Approach by Modular Experiments), located at the IFM-GEOMAR in Kiel, Germany, initiated a worldwide network of marine research institutions that allows to replicate ecological experiments on a global scale. In these studies fouling communities grown on artificial hardsubstrata serve as a model system, since their properties make them perfect for comparative ecological studies on large spatial scales. Fouling organisms are present in all costal marine habitats, while they establish and form complex communities on time scales ranging from weeks to months. Moreover, they respond quickly to manipulations, while the principle components of the communities are the same in all ecosystems. We present projects of the GAME program as examples for the successful use of fouling communities in basic ecological research.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

EVOLUTION OF OXYGEN REDUCTION CURRENT AND BIOFILM ON CATHODICALLY POLARISED STAINLESS STEELS IN SEAWATER

A Mollica, M Faimali, E Chelossi, F Garaventa, C Corrà and **G Greco**

CNR - Institute of Marine Sciences, Department of Marine technologies, Via de Marini, 6, 16149 Genova, Italy

The high corrosiveness of seawater towards Stainless Steels (SS) and similar active-passive alloys is often considered as a result of electrochemical effects induced by biofilm growth. In particular it is accepted, even if mechanisms are not understood, that biofilm induces a faster oxygen reduction rate on the underlying metal surface. Aim of this work, partly supported by the European Community[1], was to validate the correlation between biofilm growth and faster oxygen reduction rate on SS cathodically polarised in seawater as a preliminary step in view of the comprehension of the involved mechanisms.

Therefore several SS samples were exposed, at the same time, to natural seawater and polarised at different fixed potentials chosen in between -300 ÷ +100 mV Ag/AgCl.

At each imposed potential, cathodic current was repeatedly measured during SS exposure and specimens were periodically taken and analyzed by epifluorescence microscopy to evaluate the density of settled bacteria.

Two models were hence applied to fit, independently, the data describing the evolution of cathodic currents and bacterial population on SS polarised at each imposed potentials.

The first model, developed to describe the evolution of cathodic current, assumes that on SS polarised at a fixed cathodic potential two oxygen reduction currents, a slow and a fast one, can concurrently run on complementary surface fractions. In addition, it is assumed that the "active" surface fraction, on which the fast reduction kinetics runs, increases during SS exposure to seawater following a logistic expression completely defined once the values of an incubation time t_0 and of a "duplication time for the current" τ_c are fixed.

The second model describes the evolution of bacterial population by two parameters, the probability p that a planktonic bacteria settles on surface and an "apparent duplication time" τ_b, defined as the time necessary for a settled bacteria to generate another bacteria which settles in turn.

Afterwards, values of the parameters of the two models obtained from the best fit of the relevant experimental data were compared.

The main conclusions reached with the mentioned procedure are:

- the two "duplication times" τ_c and τ_b (for cathodic current and settled bacteria, respectively) if measured on SS samples polarised at the same potential, are equal. It means that, in the first phase of the biofilm growth, cathodic current and bacteria settlement proceed in time with the same evolution law: the increase of cathodic current is, hence, directly proportional to the amount of settled bacteria.
- τ_c and τ_b depend on the imposed potential; in particular these two duplication times strongly increase when potential is increased above a critical value close to -150 mV Ag/AgCl. Through capacitance measurements (Mott-Schottky approach), a change in the electronic properties of the passive layer, from a conductor to an n-type semiconductor, when imposed potential overcomes the same critical value, was also observed.

[1]Project "Electrochemical Actives Biofilms", NEST508866, 6th European FP.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

FIELD EXPERIMENTS OF TRIAL ANTIFOULING PAINTS USING ISOCYANO COMPOUNDS

Y Nogata[1], **Y Kitano**[2], **E Yoshimura**[3], and **I Sakaguchi**[1]

1 Central Research Institute of Electric Power Industry, Japan
2 Tokyo University of Agriculture and Technology, Japan
3 Seres Inc., Japan

A variety of natural products with antifouling activity have been isolated from marine organisms. Particularly interesting antifoulant candidates are isocyanoterpenes and its related compounds, such as isothiocyanates and formamides, which inhibit larval settlement of barnacles at very low concentrations without toxicity.

To develop efficient and environmentally benign antifouling agents, attempt has been made to synthesize isocyano compounds based on structure of 3-isocyanotheonellin, which isolated from nudibranches of the family Phyllidiidae. A number of derivatives were synthesized and examined for their settlement inhibitory activity against cypris larvae of the barnacle, *Balanus amphitrite*, and some of which, despite their simple structures, showed a high ability for antifouling against barnacle larvae compared to antifouling active natural isocyano compounds.

In this study, we investigated whether these promising compounds prevent the settlement of fouling organisms in the field. A large amount of 4 candidates was synthesized, incorporated into 8 types coatings, and tested their antifouling activity in the field. A total of 32 trial paints was made and placed at two field sites, Odaiba in Tokyo and Miyajima in Hiroshima for one year. In both field experiments, many test paints showed antifouling effect comparable to commercial antifouling paints for a few month. However, their antifouling effect did not keep for one year; especially, their surfaces were easily covered with bio-films and seaweeds. These results suggest that icocyano compounds show antifouling activity against invertebrate settlement in the field conditions, but their antifouling activity against algae is lower.

The development of antifouling paints using isocyanides will require a number of issues to be addressed including coating compatibility, controlled release and further field testing. With respect to environmental acceptability, it will be necessary to examine whether the compounds biodegrade to inactive products and effect of non-fouling organisms. Nevertheless, the promising results obtained with initial trials suggest that isocyanides are useful model compounds for the development of environmentally benign antifouling paints.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ANTIFOULING COMPOUNDS FROM JAPANESE ALGAE

T. Okino[1], T. Kamada[1], T. Ishii[1], E. Yoshimura[2], and Y. Nogata[3],

[1]Hokkaido University, [2]Ceres, Inc., [3]Central Research Institute of Electric Power Industry JAPAN

Natural products are possible sources and potential leads of environmentally safe antifoulants. As a port of our screening program of antifouling compounds from marine organisms, lots of Japanese algae showed potent settlement inhibitory activity against epiphytic diatoms *Nitzchia* sp. and *Cylindrotheca closterium* and spores of the brown alga *Ectocarpus siliculosus*. These diatoms were selected for inhibition assay of microfouling and algal spores were used for macrofouling inhibition. Bioassays were performed by modification of the Avicel method using cellulose TLC aluminum sheets. Test samples were applied to a sample zone of the TLC sheets in Petri dishes. Diatoms and algal spores were incubated in the Petri dishes for 1-2 weeks. The antifouling activity of test samples were easily obsereved.

As a result of screening program, we found the extracts of brown algae *Dictyota* spp. and red algae *Laurencia* spp. inhibited settlement of both diatoms and algal spores. Several extracts were purified to obtain antifouling compounds by silica gel column chromatography and preparative-TLC. Structures of antifouling compounds from the algae were determined by NMR and MS analyses. Well known terpenoid class compounds were proved to be antifoulants of both microfouling and macrofouling. Furtheremore, our natural products bank from *Laurencia* spp. were examined for antifouling activity. Total of more than 40 compounds were estimated for inhibition of algal settlement. For example, the brominated sesquiterpenoid bromolaurinterol inhibited settelement of *Nitzchia* sp. at a low concentration of 1 □g/cm^2. Another example was laurinterol which inhibited settlement of algal spores at a low concentration of 3 □g/cm^2. Interestingly, a well known antifoulant of barnacle larvae, elatol showed weak inhibition of microfouling (both diatoms) at 10 □g/cm^2.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

LIFE IN THE SLIP-LANE: THE EFFECT OF MOLECULAR LEVEL FRICTION ON ALGAL CELL ADHESION

M. E. Pettitt[1*], J. Bowen[2], M. E. Callow[1], J. A. Callow[1], J. A. Preece[2], G. J. Leggett[3]

[1]School of Biosciences, [2] School of Chemistry - University of Birmingham. [3]Department of Chemistry - University of Sheffield.

The anti-fouling and foul release properties of a surface are ultimately determined by its structural chemistry at the molecular level. Surface friction/lubricity is one aspect that has been discussed frequently in relation to fouling release performance. This paper describes the influence of surface friction, a molecular level phenomenon, on the adhesion of algal cells to model surfaces with varied frictional properties.

Self-assembled monolayers (SAMs) are ideal systems for investigating molecular level phenomena such as friction as their structural properties can be systematically tailored by altering chain-length and adsorbate terminal groupings. Here straight chain alkanethiols of varying chain length (C_8-C_{18}) were used, as they provide surfaces with different frictional and lubricative properties whilst minimising the change in surface energy. Friction coefficients were determined by Friction Force Microscopy (FFM), and had been previously found to decrease with increasing alkyl chain length as the SAM changed from a disordered liquid-like to a regular crystalline packing structure.

The release properties of the SAMs were determined for two types of algal cell viz. zoospores of the green fouling alga *Ulva linza* (syn. *Enteromorpha*) and the diatom *Navicula perminuta*, a single celled alga. Cell removal was effected by hydrodynamic wall shear stress in a water channel apparatus. The degree of release of both species was found to correlate with the length of the SAM over a particular range of friction coefficients. Results are discussed in relation to the tribology of the SAMs and the implications for foul-release coatings are considered. This work was carried out with financial support from the EC Framework 6 Project 'AMBIO', The University of Birmingham, 'ACORN', EPSRC and the RSC Analytical Chemistry Trust Fund.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ADVANCED NANOSCALE CHARACTERIZATION OF MARINE BIOFOULING INTERFACES

I Y Phang[1], N Aldred[2], A S Clare[2], G J Vancso[1,*],

[1]University of Twente, The Netherlands
[2]University of Newcastle upon Tyne, United Kindom

Tin-containing antifouling paints have been used in the shipping industry for several decades in the fight to prevent adhesion of natural organisms on e.g. ship hulls. However, the toxicity of tin paint also affects other marine organisms and is becoming a major environmental concern. A new EU legislation will be introduced to eliminate tin containing toxic paints by 2010. Thus new formulae for coatings will be needed in the near future to achieve the desired antifouling action. In order to support the development of this process, we started a program focusing on fundamental understanding of the interaction of marine organisms as "adhering" organisms and substrate-biological organism interactions from different points of view. The aim of this study is to use AFM-based single molecule force spectroscopy to investigate the *Balanus amphitrite* adhesion proteins. Firstly, the body of a settled cypris larvae of *Balanus amphitrite* was amputated and the permanent cement was exposed. A series of AFM force-distance curves were captured to probe over permanent cement to monitor its curing behavior. The detectable events show decreases over time but no significant trend in maximum pull-off force. However, the pull-off length (corresponding to the molecular stretching) decreases over time. This shows that the cement undergoes curing (cross-linking), with protein chains interdigitating with other chains over time.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

PRIOR SETTLER DENSITY OVERRIDES TEXTURE AND ORIENTATION CUES IN SETTLING *SEMIBALANUS BALANOIDES* CYPRIDS IN THE CLYDE SEA

Gabrielle S. Prendergast*[1] Constanze M. Zurn[1], Lars J. Hannson[2], Ritchie M. Head[3], A. Valeria Bers[4], Jeremy C. Thomason[1]**

*Corresponding author/presenter g.s.prendergast@ncl.ac.uk
** j.c.thomason@ncl.ac.uk, (+44)191-222-7890
[1] School of Biology, University of Newcastle upon Tyne, Newcastle NE1 7RU, UK.
[2] Danish Institute for Fisheries Research, Kavalergården 6, DK-2920 Charlottenlund.
[3] Materials Technology Division, TNO Industry, Bevesierweg (Harssens), PO Box 05, 1780 AM Den Helder, The Netherlands.
[4] Institute for Marine Research, Duesternbrooker Weg 20, 24105 Kiel, Germany.

When choosing a suitable settlement site, cyprid larvae of the acorn barnacle *Semibalanus balanoides* respond to a wide range of biological, chemical and physical cues. Cues may have positive or negative effects and may vary in effect spatially, temporally, and according to cyprid physiology. The focus of the present study was on three factors influencing settlement: orientation (O), texture (T), existing settlers (E); data on larval supply (S) and settlement period (day or night, P) were also recorded. The settlement of over 200,000 cyprids over 17 tides on textured tiles with two orientations was digitally photographed and quantified using computer image analysis techniques. A multifactorial GLM provided a general idea of cause and effect relationships. Removal of non-significant interactions from a series of step-down anovas yielded a fully significant reduced model:
settlement $min^{-1}cm^{-2} = T + P + E + (T*O) + (T*P) + (O*P) + (T*P*E) + (O*P*E) + \varepsilon$.
Estimations of effect size (ω^2) determined the magnitude of effect of each factor on cyprid settlement. A formula was created to rank factors influencing settlement and a limited theoretical probability model of the best (optimum) and worst 'settlement niche' for this species was created. A regression analysis to look at the relationship between the presence of conspecifics and new settlement showed that gregariousness had a negative density-dependent effect. Additional regressions informed the development of a series of path analysis models, in order to graphically represent a series of complex causal relationships in terms of a best-fit model hypothesis.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

A MONOLAYER FOR ANTIFOULING WITH ENZYMES AS THE BIOACTIVE COMPONENT.

Ib Schneider (speaker), **Fadhil S. Kamounah**, **Knud Allermann** (1) and (2) **Kjeld Schaumburg**, (1) BioLocus A/S, Agern Allé 3, DK-2970 Hoersholm, Denmark, Phone: +4535550959, e-mail; ibs@biolocus.com and (2) CISMI, University of Roskilde, DK- 4000 Roskilde, Denmark.

COATZYME – AN ENZYME BASED, WATER BORN, SELF POLISHING COATING FOR ANTIFOULING.

Ib Schneider and **Knud Allermann**
BioLocus A/S, Agern Allé 3, DK-2970 Hoersholm, Denmark. Phone: +4535550959, e-mail: ibs@biolocus.com

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

USE OF MARINE INVERTEBRATE LARVAE AS INDICATOR OF ENVIRONMENTAL IMPACT ON FOULING PREVENTION: THE BRAZILIAN NUCLEAR POWER PLANT CASE

Skinner, L.F.[1], **Silva, S.H.G.**[2], **Lavrado,H.P.**[2]; **Viana,M.S.**[2] & **Junqueira,A.O.R.**[2]

1. Universidade do Estado do Rio de Janeiro – Departamento de Ciências. R. Francisco Portela 794, Paraíso, São Gonçalo, RJ. CEP: 24435-000. lskinner@uerj.br
2. Universidade Federal do Rio de Janeiro- Dept. Biologia Marinha. CCS, Bl. A, S. 089, RJ, RJ. CEP 21949-900

* Financial support by CNPq and FAPERJ

Nuclear power plants usually are located close to coastal regions due to its water use for cooling systems. So, sea water are pumped and released for this. Perhaps, with this water, larvae of marine invertebrates are also pumped to this system and fouling prevention is very important. At Angra dos Reis nuclear power plant, Brazil, chlorine is used as antifouling and water discharge is located in a different site of pumping. In this region, sea water temperature could reach values as high as 35 °C on summer months. So, in discharge site, three main impacts are due to power plant activities: thermal increase, chlorine concentration and water flow. Between may 2002 and February 2003, plankton samples are performed to evaluate the impact of effluent on larval availability and transport. Plankton samples were collected using electric pumps (5700 $L.h^{-1}$) for 5 minutes and mesh size of 110 µm at surface and 3 meters deep in 6 sites, 4 inside the impacted area and 2 control sites at pumping region and away from any impact of power plant. Water-analysis were also performed (temperature, salinity, chlorine, flow velocity) at both profundities. As a result, the main factors influencing larval availability were chlorine concentration (higher closest to effluent discharge) and temperature (higher on summer months) and larval availability was negatively correlated with both variables. No trend on larvae vertical distribution was registered. The highest richness of invertebrate larvae were registered at pumping and discharge sites, indicating that larvae are then transferred from one bay to another. The decrease on larval density and richness with increasing distance from discharge also indicates the effect of water flow, chlorine and thermal impact that could prevent larval entrance on this small bay.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

FIELD SETTLEMENT INDUCTION OF THE MUSSEL *PERNA PERNA* IN RESPONSE TO NATURAL PRODUCTS FROM THE BROWN SEAWEED *STYPOPODIUM ZONALE*

A R Soares, B A P da Gama, C L Teixeira, R C Pereira and **V L Teixeira**

Universidade Federal Fluminense, Brazil

The culture of marine organisms of commercial interest, such as macroalgae, oysters and mussels, is generally limited by the difficulties inherent to obtaining sufficient amounts of biological material to initiate or maintain the culture. Moreover, the exploitment of matrices from natural beds threatens the populations from these species. In mussel culture, mussel spat collectors made of several materials are usually employed, being many times not efficient. The aim of this study was to test the efficiency of natural products from one seaweed (*Stypopodium zonale*) as inducers of the settlement of mussels *Perna perna* in artificial spat collectors made from two materials (sisal and silk nylon ropes), as well as using phytagel^{tm} (as a reducer of the diffusion rate of extract in contact with seawater). For that purpose, 80 ropes made of sisal and silk nylon (50 cm each) were treated with combinations of *S. zonale* (Phaeophyta, Dictyotales) crude extract and phytagel^{tm}, generating 8 types of collectors with 10 replicates each. Collectors were submerged in a long-line system at Urca inlet (Guanabara Bay, Rio de Janeiro) for 3 months, being sampled fortnightly to count the number of recruited mussels. The recruitment was detected continuously after 45 days of immersion, and was significantly higher on treatments with *S. zonale* extract ($p < 0.001$). Spat collectors made of silk nylon were always more efficient than the sisal ones, and the presence of phytagel^{tm} had an effect opposite to the expectation, reducing recruitment. Our results suggest that the combined use of silk nylon and *S. zonale* extract can increase significantly the efficiency of mussel spat collectors, enhancing culture productivity and preserving natural mussel beds.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

DEGRADATION OF BOROCIDE® P TRIPHENYLBORON-PYRIDINE IN THE MARINE ENVIRONMENT

R L Amey[1] and **C Waldron**[2]

[1]INVISTA USA
[2]Arch Chemicals, Inc., USA

The commercial applications of Borocide® P triphenylboron-pyridine, which include hull coatings, fishnet protection, and as a starting material for the formation of other triphenylboron-amine biocides, have been known in Japan since 1995 and the product is also currently registered for use in Korea and China. Borocide® P triphenylboron-pyridine, a non-metal biocide for anti-fouling coatings, undergoes decomposition in the marine environment to ultimately form boric acid, pyridine, and phenol. Competing hydrolytic, thermolytic, photolytic, and biotic pathways initially produce diphenylborinic acid [$(C_6H_5)_2BOH$] from triphenylboron, which subsequently decomposes into phenylboronic acid [$C_6H_5B(OH)_2$], the immediate precursor to boric acid and phenol. Hydrolysis is relatively slow in natural seawater when compared to either photolysis or the biological decomposition of Borocide® P triphenylboron-pyridine. Soluble copper ions, such as those produced by cuprous oxide-based coatings, catalyze the hydrolysis and increase its rate by as much as 4X. The exclusive formation of phenol as the final organic degradation product, even in the absence of oxygen, is suggestive of an ionic pathway, rather than a free radical one, and which is strongly influenced by the solvent effect of the seawater medium. Borocide® P triphenylboron-pyridine and its combinations with zinc and copper *Omadine*® antifoulant inhibit both the settlement of *Balanus amphitrite* barnacle larvae and the growth of other marine fouling organisms such as the diatom *Amphora*. Inhibitory concentrations, the various effects of sediment and sunlight on efficacy, the general aquatic toxicity, and the leach rate from commercial coatings will be discussed in more detail.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

EVALUATION OF ANTIFOULING ACTIVITY OF THE CRUDE ORGANIC EXTRACT OF SEAWEED *Laurencia flagellifera,* COLLECTED FROM PENHA (SC-BRAZIL).

J Benvenutti, K N Kuroshima, K R S Sauer-Machado, L L Valle de Lacerda, M A B Barreiros, L Lacava.

CTTMar - UNIVALI – Universidade do Vale do Itajaí, Brazil.

Recently, there is one considerable interest in exploring marine habitats to search compounds with biological and ecological activities. It still knows, that exists one direct relationship between the natural defense of marine organisms against biofouling and the prevention of the biofouling in artificial structures. On the other hand, the development of antifouling agents with low toxicity is essential to prevent environmental problems. Therefore, this work was developed to investigate the antifouling activity of the seaweed *Laurencia flagellifera* (Rodophyceae) collected from the Paciência Beach, Penha, S.C. (Brazil), through field assays. The extracts were prepared in three concentrations: natural volumetric concentrations, and two others with 3 and 5 times this values; all with 5 replicates. These extracts were incorporated into the gel and molded in plastic Petri dishes. Five dishes corresponding to replicate from each concentration and another one to control were fastened in aluminum structures and had been kept in the sea at 1 meter deep, during 35 days. Weekly four of these aluminum structures had been removed from the water to evaluate the settlement of the fouling. The percentage of cover by micro and macroorganisms, the number of organisms and identification of main groups were evaluated. Parallel tests in tank contend filtered seawater had been carried out through to evaluate the diffusion of extract to seawater. All of the concentrations tested showed a decrease in its extract contend during the time. In the end of assay, it was verified that about 60 to 70% of the initial extract remained in the dishes. No relationship was observed between the loss of the extract and its concentration. In the first week, the biofilm was responsible by the main percentage of cover of fouling, after than, the presence of macroorganisms was registered. This cover and number of organisms showed an increase through time. However, in the high concentrations, the amount of seaweed settled showed a decrease indicating that this extract has a probable antifouling activity. The bactericidal activity of this extract was evaluated against *Bacilus thurigiensis* and two marine bacteria isolated from the same beach where the seaweed was collected. These bacteria had been characterized as gram negative, oxidase positive and small bacillus. The MICs to *Bacilus thurigiensis* was 23mg/ml and two marine bacteria were at 57µg/ml. These results showed the potential of this seaweed as source of natural products with antifouling activity and it is being excellent material for future studies and applications of technologies to prevent biofouling.

12th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

SUBSTRATUM PREFERENCE DURING RECRUITMENT OF TWO INVASIVE ALIEN CORALS ONTO SHALLOW SUBTIDAL REEFS

J C Creed and **A F De Paula**,

Universidade do Estado do Rio de Janeiro & Laboratório Museu Nacional-Universidade Federal do Rio de Janeiro, Brazil

Two species of azooxanthellate coral, *Tubastraea coccinea* Lesson, 1829 and *T. tagusensis* Wells, 1982 are alien to the rocky shores of Brazil. The influence of substratum types wood, granite, concrete, steel and ceramic tiles on their recruitment was investigated experimentally. On the artificial plates the mean density of *T. tagusensis* varied from 202 to 512 colonies.m^{-2} and *T. coccinea* varied from 187 to 233 colonies.m^{-2} after 17 mo. The density of recruits of *Tubastraea* spp. was similar to those found in coral reef environments worldwide. A strong coupling between local adult density and recruitment density was found at a scale of < 1m. Substratum type and species were important in determining density and size of the recruits of the alien corals. The density of *T. tagusensis* on cement was higher than on ceramic tiles or steel but *T. coccinea* density did not differ significantly between substratum types. The size of *T. tagusensis* recruits did not differ between materials but *T. coccinea* recruits were smaller on steel than on granite or cement. The density of recruits also depended on the density of adults on the reef. No differences in cover or biomass of the associated biological community were found between substrata. *T. coccinea* and *T. tagusensis* didn't exhibit very strong selection for specific substrata and ably recruited to all materials. Such opportunistic and fecund species demonstrated that they are generalists in substratum utilization and this explains how they successfully travel on and invade areas consisting of different substratum materials.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

STEREOLOGICAL ANALYSIS OF BIOFOULING

S Dürr and **J C Thomason**

University of Newcastle upon Tyne, UK

We demonstrate a new way to apply stereological principals in the analysis of digital images of marine biofouling that increases robustness and precision of the results compared to the common random dot technique. The aim was to enable us to analyse digital photographs taken by field workers of non-scientific background in a pan-European project studying biofouling in the aquaculture industry. For our analysis, we use the freeware Image J. As well as no-set-up cost, ImageJ has an enormous user base, on-line support, and is platform-independent. Further, it can easily be customised to specific needs by the user. Our method is based on stereology in the form of random systematic sampling by applying random grids on systematically selected fields of views. This method increases robustness and precision of the results while using the same number of dots as the common random dot technique that analyses the complete image.

12th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

PERFORMANCE OF BENZOATE -BASED EPOXY COATINGS UNDER SIMULATED MARINE CORROSION CONDITIONS

[1,2]G. Blustein, [1,2]R. Romagnoli, [1]A. Di Sarli and [1]B. del Amo

[1]CIDEPINT – Centro de Investigación y Desarrollo en Tecnología de Pinturas. (CICPBA-CONICET), Calle 52 e/ 121 y 122, (B1900AYB) La Plata, Argentina
[2]UNLP – Universidad Nacional de La Plata
e-mail: pintprotec2@cidepint.gov.ar

From 1970 on, two major goals were achieved in the field of paint technology: the replacement of toxic inhibitive pigments and the progressive elimination of solvents in paint formulations to fit VOC's regulations. Traditional anti-corrosive paints contain lead or hexavalent chromium compounds as active pigments, which contaminate the environment and, at the same time, represent a risk to human health. In this sense, it is believed that benzoates as anticorrosive pigments for paints could match environmental concerns with proved anticorrosive efficiency.

The inhibitive properties of soluble benzoate compounds were known from many years ago and were studied employing sodium benzoate and benzoic acid, in different media, still those containing chloride.

The employment of soluble compounds (benzoic acid, sodium benzoate, etc.) in anticorrosive paints is limited by the fact that their lixiviation by water penetrating the pores of the coatings would greatly increase coating permeability with the concomitant loss of the protective properties of the paint. However, it is possible to prepare insoluble metallic benzoates with certain cations (e.g. zinc, aluminium, iron, etc.) whose compounds are widely used in paint technology.

The objective of this investigation was to study the inhibitive properties of zinc basic benzoate-based paints in simulated marine corrosion condition (3% NaCl solution). The anticorrosive properties of lab-prepared pigment were investigated by means of electrochemical techniques in pigment suspensions. In a second stage, anticorrosive paints containing zinc basic benzoate were formulated and their performance was evaluated by accelerated (salt spray chamber) and electrochemical (EIS) tests.

Experimental results show that zinc basic benzoate is adequate to formulate epoxy anticorrosive paints with improved anticorrosive performance in aggressive conditions, especially with the water-borne binder.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

APPROACHES TO THE CONTROL OF GOLDEN MUSSEL SETTLEMENT

[1, 3,4]M Pérez, [1,2]M García, [1, 3, 4]R Romagnoli, [1,3]M Stupak

1CIDEPINT – Centro de Investigación y Desarrollo en Tecnología de Pinturas.
Calle 52 e/ 121 y 122, (B1900AYB) La Plata, Argentina
2CICPBA- Comisión de Investigaciones Científicas
3CONICET – Consejo Nacional de Investigaciones Científicas y Técnicas
4UNLP – Universidad Nacional de La Plata
e-mail: biofouling@cidepint.gov.ar

In Argentina, studies on biofouling control were carried out principally in the marine environment due to heavy fouling colonization and, as a consequence, the great economic impact on submerged man-made structures. However, the introduction of golden mussel, *Limnoperna fortunei*, into South American freshwaters from Asia, just over fifteen years ago, and their spread through inland waters have resulted in a major economic problem to rawwater- dependent infrastructures, including power generation facilities. Currently, there is great interest in devising new non-toxic methods to control the mussel settlement. In this paper, results obtained by application of cathodic protection currents and the effect of two tannin solutions on *Limnoperna fortunei* were investigated.

The application of a potential difference across an interface generates an electric field and the flow of current. When the interface is cathodically polarized its pH increases as a consequence of hydroxyl generation. Organisms do not resist abrupt pH changes as those that take place in a polarized interface. In this way, cathodic protection is a useful method to control fouling settlement. The main problem is to decide the optimum current density level to avoid fouling settlement. In the particular case of *Limnoperna fortunei*, it was found that very low cathodic current densities are capable of influencing the behaviour of these mussels; these current densities are too low to protect steel against corrosion. So, cathodic current densities required to protect steel are high enough to avoid *Limnoperna fortunei* settlement.

On the other hand, the probable antifouling effect of two different tannins on *Limnoperna fortunei* was studied. Tannins are naturally occurring phenolic compounds with high relative molecular weight (>500) which precipitate proteins. Low concentration solutions of tannins, quillaja and quebracho, were employed in this research and its action compared with that of saturated solutions of cuprous oxide, a common biocide pigment used in antifouling paint formulations. Results obtained showed that mussels close hermetically their valves when they are exposed to quillaja and quebracho tannin solutions, at concentrations of 1g/L and 0,5 g/L.

After 120 minutes exposition they neither had their siphons extended and nor byssal threads were produced. Similar behaviour was observed in experiments carried out with cuprous oxide saturated solution. However, when organisms exposed to test solutions were transferred to freshwater they ould recover. In control crystallizing vessels (filtered freshwater only), *Limnoperna fortunei* showed a normal behaviour, i.e. they maintained their siphons extended, made byssal threads and reattached themselves. Thus, it was concluded that tannins may be employed as active pigment to formulate effective antifouling paints.

Application of cathodic protection systems and the development of antifouling coatings containing tannins as active pigment are two promising methods to control golden mussel settlement.

12th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

INHIBITION OF MARINE BIOFOULING BY NATURAL TANNINS

M C Pérez*, M T García, G Blustein, M E Stupak
CIDEPINT (Centro de Investigación y Desarrollo en Tecnología de Pinturas), La Plata, Argentina, * e-mail: biofouling@cidepint.gov.ar

Paints containing organotins were used to protect marine structures by reducing biofouling. However, increasing concerns about the negative effects of these compounds on marine non target organisms and environment have led to a ban on TBT-containing coatings. An alternative to toxic compounds is the use of natural products that are non-toxic but have antifouling properties.

Tannins, natural water soluble complex polyphenolic substances, have high relative molecular weight (>500) and are common in most of the higher plant species. They precipitate proteins such as gelatin from solution (astringency), and are also important in industry, food and environmental sciences. In the last fifty years the anticorrosive properties of tannins were known. Subsequently a number of tannin-based products appeared on the market and found a certain amount of success as pre-treatment primers for use of rusted steel without requiring complete removal of the corrosion product. On the other hand, tannins show anticarcinogenetic and antimicrobial activities due to their antioxidative in protecting cellular components from oxidative damages, and due to they inhibit the growth of some kinds of fungi, yeasts, bacteria and viruses.

The aim of this study is to test the effect of quebracho tannin as probable antifouling pigment in both laboratory and in the sea.

Because of tannins have a high solubility in aqueous media and consequently they would leach rapidly, they were precipitated as aluminium tannate, which has an adequate solubility in sea water.

In the lab, it was evaluated the effect of decreasing dilutions from a 1 g/L quebracho tannin solution and aluminium tannate saturated solution on *Balanus amphitrite* and *Polydora ligni* larvae. For field trials, plates of inert gels (PhytagelTM) containing aluminum tannate were exposed in Mar del Plata harbour, Argentine. Exposure of larvae to dilutions as low as 1:16 for quebracho tannin and 1:8 aluminum tannate saturated solution produced a loss of phototactic response and a reduction in appendage activity up to complete immobilization; as the concentrations were increased the effects were more evident. In all cases, when larvae were transferred to fresh artificial sea water they could retrieve their movements and follow their development.

In field trials, after 28 days exposure in the sea, aluminium tannate was effective in inhibiting settlement ($p < 0.05$ by ANOVA test using STATISTICA program). A great decrease in microfouling diversity was observed, the green alga *Enteromorpha intestinalis*, the tube-worm *Hydroides elegans* and the sand-tube building *Polydora ligni* shown a significant decrease in growth and density in relation to controls ($p<0.05$ through ANOVA and contrast LSD test).

The present study suggests that natural tannins could be employed as bioactive pigment for new antifouling technologies.

15th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ENVIRONMENTAL ASSESSMENT OF THE EFFECTS OF A NUCLEAR POWER PLANT EFFLUENT ON THE FOULING ASSEMBLAGES OF ANGRA DOS REIS (RJ) BRAZIL

S H G Silva; M Mayer-Pinto; B L Ignacio; M S Viana; E P Vilanova; H P Lavrado; A O R Junqueira; M T M Széchy; M P Curbelo Fernandez
Universidade Federal do Rio de Janeiro, Brazil

Thermal pollution caused by a power plant effluent can reduce biomass and diversity in fouling assemblages. In Brazil, Almirante Álvaro Alberto Nuclear Power Plant (CNAAA) is located at Angra dos Reis, in the southeast region of Rio de Janeiro State. The present study has evaluated the development of fouling assemblages transplanted from non-impacted areas (away from the influence of the power plant discharge) to areas under the effects of the nuclear power plant effluent. In the latter, the discharged water has higher temperatures, higher flow velocities and higher chlorine levels than surrounding areas. In May 2003, 20 granite panels (20 x 20 cm) were immersed at a 0,5m depth in the control area. After 40 days, 4 panels were withdrawn for the analysis of fouling cover before transplant (control 0). Twelve panels were transferred to sites in the discharge area (four of them at a distance of 100m from the discharge point, four at 600m and four at 1400m). The remaining four panels were kept immersed at Brandão Island as control (control 1). After the transplant, panels have remained immersed for more 40 days. The panels at 100m far from the effluent outflow had a significant reduction in richness (from 31 to 8 taxa). The only algae that have prevailed in that site were *Enteromorpha flexuosa*, *Dyctyota cervicornis*, *Jania* sp. and *Polysiphonia subtilissima*, although many of them showed some thallus abnormalities. Multivariate analysis (n-MDS) showed that the sites to which panels were transplanted formed significant distinct groups from the two control sites (global $r= 0.673$; $p<0.05$). Only panels at the 1400m site did not differ from the controls ($r=0.297$; $p>0.05$). However, the former ones presented a higher percentage cover of red algae and a lower cover of stoloniferan bryozoans than control 1, pointing out that the effluent may still have influence on the abundance of some fouling organisms even at 1400m far from the discharge point. The results showed that the nuclear power plant had a clear influence on the local fouling assemblages, and also that the transplant technique can be used as an important tool in environmental impact assessment studies.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

IRON BENZOATE AS ENVIRONMENTALLY-FRIENDLY PIGMENT FOR PAINTS TECHNOLOGY: CORROSION AND FOULING CONTROL

1,2**G Blustein**, 1**M García**, 1, 2**M Pérez**, 1,2R **Romagnoli**, 1**B del Amo**, 1**M Stupak**
1CIDEPINT – Centro de Investigación y Desarrollo en Tecnología de Pinturas.
(CICPBA-CONICET), Calle 52 e/ 121 y 122, (B1900AYB) La Plata, Argentina
2UNLP – Universidad Nacional de La Plata
e-mail: biofouling@cidepint.gov.ar

Traditionally, paints designed to protect metallic structures from corrosion and fouling have been formulated with high toxic pigments. For instance, lead or hexavalent chromium are used for anticorrosive paints and organotin compounds for antifouling paints. Although these active pigments are highly effective inhibitors, their use has been declining because they contaminate the environment and, at the same time, represent a risk to human health. International regulations concerning the protection of both the environment and industrial workers have prompted paint manufacturers and end users to desire replacements for these pigments.

The anticorrosive properties of soluble benzoate compounds were known from many years ago and were studied employing sodium benzoate and benzoic acid in different media, included those containing chloride. The employment of soluble benzoate compounds in paint technology is limited by its high lixiviation which takes to the loss of the protective properties of the paint. However, it is possible to prepare insoluble iron benzoate to incorporate within paint film.

One of the goals of this investigation was to study the inhibitive properties of iron benzoate-based paints in simulated marine corrosion condition (3% NaCl solution). The pigment anticorrosive properties were investigated by way of electrochemical techniques in pigment suspensions. In a second stage, anticorrosive paints containing iron benzoate were formulated and their performance was evaluated by accelerated (salt fog chamber) and electrochemical (corrosion potential and ionic resistance) tests.

On the other hand, the effect of iron benzoate in the laboratory and in the sea as probable antifouling agent was studied. Iron benzoate pigment in seawater is hydrolyzed and consequently it produces a pH decrease. In this sense, the effects of the pH on nauplii and the anion benzoate dissolved in seawater and leached from an antifouling paint were evaluated. Although anion benzoate has an intense narcotic effect on *Balanus amphitrite* nauplii, the results clearly demonstrated that the combined action of this compound and a pH decrease produce a pronounced antifouling activity, i.e. the synergic effect is greater than separate effects. Field trials confirmed laboratory assays; paints containing iron benzoate were effective in inhibiting organism settlement.

Results show that iron benzoate pigment has successful anticorrosive and antifouling properties; the high levels of inhibitory activities suggest a potential for novel active ingredient in paint formulations.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

EFFECTS OF THE THERMOCLINE GENERATED BY A NUCLEAR POWER PLANT EFFLUENT ON THE RECRUITMENT OF THE FOULING ASSEMBLAGE AT ANGRA DOS REIS (RJ) BRAZIL

M S Viana; H P Lavrado; S H G Silva
Universidade Federal do Rio de Janeiro, Brazil

Nuclear power plants, such as the Almirante Álvaro Alberto Nuclear Power Plant (CNAAA), are located in coastal zones to use seawater in their cooling systems. In Brazil, water is taken at Itaorna Beach and discharged at Piraquara de Fora Cove in high flow velocities, heated and with the addition of chlorine for preventing biofouling in the heat exchangers. This hot effluent induces the formation of a thermocline in the discharge area, generating a maximum of 5ºC difference between surface and bottom waters. In summer, mean temperature of surface waters can reach approximately 36°C, which is considered stressful to the majority of marine organisms. The objective of the present study was to evaluate the monthly recruitment of the fouling assemblage in areas under the influence of the nuclear power plant, looking for differences between the surface and bottom waters in impacted and non-impacted areas. Therefore, three wooden panels were immersed in two depths (0,5m e 2,5m), in seven sites: four of them near the discharge area and three in control areas. Panels were changed monthly during one year.

There was a significant interaction among the three factors analyzed: depth, site and season (ANOVA, $F=1,939$; $p<0,05$) regarding taxonomic richness. In general, the discharge area sites presented significantly higher richness in bottom panels than in surface ones, regardless of the season. On the other hand, reference sites did not show significant differences between the two depths, throughout the year. Biofilm cover, which indicates the absence of recruitment by other organisms, presented a significant interaction between site and season ($F=3,511$; $p<0,001$) and between depth and site ($F=23,260$; $p<0,001$). Reference sites differed only from the site under the direct influence of water flow in the discharge area, where biofilm cover reached almost 100%. In the latter, due to the intense water flow, there is no formation of a strong thermocline. Hence, no significant differences were observed in biofilm cover between the depths. In sites distant 200m, at most, from the effluent discharge point, where the thermocline is present, there was a significant difference between the two study depths, with a higher biofilm cover on surface panels. However, this effect appears to be spatially limited since the furthest site from the discharge point (650m) had similar results to the ones found in the reference areas. The presence of a thermocline, due to the discharge of the heated effluent, interferes in the recruitment of fouling organisms in points under the influence of surface water, but has no significant effects in depths below 2,5 meters.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

TANNIN CAPSULES: A PROMISING ANTIFOULANT

L Deladino1, **A Navarro**1, **M Martino**1,2, **R Romagnoli**3,4, **M García**3, **M Stupak**3 and **M Pérez**3,5

1Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA), CONICET, Fac. Ciencias Exactas. 2Dpto. de Ing. Qca. Fac. Ingeniería, (UNLP), 47 y 116, La Plata (1900), Buenos Aires, Argentina.3Centro de Investigación y Desarrollo en Tecnología de Pinturas (CIDEPINT, CIC-CONICET). 4 Fac. de Ciencias Exactas (UNLP). 5 Fac. de Ciencias Naturales y Museo (UNLP)
e-mail: biofouling@cidepint.gov.ar

Protection of ship-hulls from marine fouling organisms is essential for efficient operations and energy conservation. For this reason, ship hulls have been coated with antifouling paints that contain toxic compounds, such as copper and organotin, and create an environmental hazard due to continuous release of toxic materials. New strategies are being developed which use non-toxic or natural compounds to control fouling growth.

Encapsulation provides protection against environmental conditions like pH, temperature and chemical substances. It is one of the most suitable methods for controlled release of a wide spectrum of active compounds. The objective of this work was to encapsulate *Quillaja saponaria* tannins and to study their release in sea water. Capsules were obtained by ionic gelification between sodium alginate (2% w/w) and calcium chloride (0.05 M); the alginate solution contained 0.01 g/ml of tannin. Then, the formed calcium alginate beads were immersed in a chitosan solution (2% w/w). Interaction between the chitosan, a cationic polysaccharide, with the negatively charged alginate resulted in the formation of a membrane. Different immersion times (30 and 60 min) in CaCl2 and in chitosan (30 and 60 min) solutions were analyzed. Then, the beads were dried at room emperature. Release assays were

performed sinking twenty dry capsules in test tubes containing 10 ml of sea water. The tanninconcentration released was determined by UV spectrophotometric measurements at 280 nm (Beckman DU 650 USA) during 30 days. Percentages of tannin release in sea water were 29% w/v (30 min in CaCl2 + 30 min in chitosan) and 31% w/v (60 min in CaCl2 + 60 min in chitosan); the rate of tannin release was 0.01 mg/ml.day in both cases.

The action of *Quillaja saponaria* tannin on *Polydora ligni* was evaluated in lab trials employing: a) tannin solutions, b) tannin capsules and c) tannin capsules into hard, stable gels (PhytagelTM). For field trials, gel replicates were suspended from floating docks at Mar del Plata harbour (Argentina), for 28 days. Bioassays shown that *Quillaja* tannin solution and tannin capsules affected *Polydora ligni* larval survival. When organisms were in contact with tannin solutions, a rapid immobilization of appendages and loss of phototactic response occurred, these effects were faster as tannin concentration was higher. On the other hand, larval response was similar for all cases, i.e. no difference was observed between different times of capsules preparation. In addition, it was proved that both alginate and chitosan had no effect on larvae activity. Field trials shown similar results, i.e. *Polydora ligni* did not build tubes on gels.

In conclusion, 1) encapsulation is an excellent method to evaluate antifouling properties of high soluble compounds and 2) *Quillaja* tannin has an inhibitor effect on *Polydora ligni* settlement.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

EVALUATION OF ANTIFOULING PAINTS IN THE GUANABARA BAY AND ARRAIAL DO CABO, RIO DE JANEIRO, BRAZIL

J E A Gonçalves[1] *, C E L Ferreira[2], D L de F Menezes[3] and R Coutinho[1]

[1]Instituto de Estudos do Mar Alte. Paulo Moreira, Brazil *arrudagoncalves@yahoo.com.br
[2]Universidade Federal Fluminense, Brazil
[3]Diretoria de Engenharia Naval, Brazil

An experiment with ten new paints without TBT was carried out for two years to select the most suitable ones to be used on the Brazilian Navy ship hulls. Chemical formulas were developed by 6 companies. Paints were used on 20 x 25 cm steel plates (N = 6 for each paint + control) submerged at 2m deep in two distinct sites: Guanabara Bay (RJ) and Arraial do Cabo (RJ). The former is characterized as an eutropic environment that receives a great amount of organic matter from domestic sewage; most of the Brazilian ships are harbored at this site. The latter is an oligotrophic environment. Foulers were collected fortnightly, identified, and their fouling thickness and percentage of coverage estimated. A "Biofouling Index" (BI), ranging between 0 and 1, was created based on fouling thickness and percentage of coverage. Paints ranking "1" during two years were used on Brazilian Navy ship hulls. Poliquets, hydrozoans, and bryozoans were dominant among 16 organisms found on the plates in Guanabara Bay. Four paint formulas lead to <1 cm fouling thickness at the end of a two-year period in that site. As for percentage of coverage, one formula was an efficient antifouling paint as the percentage of fouling was 8.7% by the end of the second year. Plates painted with three other formulas showed 50% fouling. The remaining paints showed 100% coverage in just three months, which showed a low fouling efficiency. One formula showed excellent antifouling efficiency (BI = 0.2). Five others also have a good performance (BI between 0.4 and 1). In Arraial do Cabo, 43 taxa were identified during the 2-year monitoring. Plates that were covered by another formula showed the presence of biofilm and a 0.05 cm fouling thickness. Fouling growth was also low (1.4 cm thickness at the most) on plates painted with the remaining 8 formulas. The percentage of coverage given by all formulas were <100% in two years. Eight paint types showed a BI < 1 and therefore a good antifouling efficiency in oligotrophic environment. We conclude that paints used on Guanabara Bay ships need a high antifouling performance compared to the ones used on substrates in oligotrophic environments (i.e., Arraial do Cabo).

18th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

HEAVY METAL CONCENTRATIONS IN ARTIFICIAL REEF WITH ANTI-FOULING PAINTING

C E Rezende, Gobo A. R, Almeida M, Gobo R R, Rangel T P, Krohling W and Zalmon I R

Universidade Estadual do Norte Fluminense, Brazil

Artificial reefs with anti-fouling paint were investigated at 9 meters deep, 3.0 miles north coast of Rio de Janeiro, Brazil (21°29'S, 41°00W) in order to determine heavy metal concentrations incorporated by fouling organisms even after the painting validity time. Two species, a coral Carijoa and an oyster *Ostrea equestris* were scratched separately from concrete reef balls painted (Tritão Cooperkote - Akzo Nobel Coatings) and non-painted. Biological material was dried, grained and dissolved with acid mixture in hot plate. The heavy metals Fe, Mn, Zn, Cu, Ni and Cd were determined by atomic absorption spectrophotometer in oyster soft tissue and in coral total tissue. The results show that the absolute concentration distribution in oysters for both types of substrates with and without anti-fouling paint showed the same distribution (Fe>Zn>Cu>Mn~Ni>Cd), whereas in coral tissue was observed a different distribution for all elements except Fe and Cd. Oyster tissue presented major concentration for Fe, Mn and Ni in substrates without antifouling painting; Cu was enriched five times in antifouling painting substrate, and Cd and Zn had similar concentrations on both substrates. Coral tissue showed enrichment for Mn (3x), Cu (14x), Ni (2x) and Cd in antifouling painting substrates; Fe and Zn presented a similar concentration for both substrates. Comparing heavy metal concentrations for the two different benthic organisms, we could reinforce the combined use of these species once coral response for Mn, Ni and Cd was better than on oyster; the latter showed a better response for Fe, Zn and Cu. However, it is necessary to consider heavy metal transport forms since oysters mainly reflect the transference among suspended particulate matter despite the coral is a better indicator for dissolved forms.

18th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

EFFECTS OF BIOFOULING (EPIBIOSIS) ON THE SUSCEPTIBILITY OF MACROALGAE TO GRAZING

G Jackson[1,2], R Coutinho[1], L M Lage[1,3], and R C Pereira[2]

[1] Instituto de Estudos do Mar Almirante Paulo Moreira
[2] Universidade Federal Fluminense
[3] Universidade Estadual do Norte Fluminense, Brazil

The impact of grazing vs. biofouling in chemical defense selection in marine habitats has not been determined yet. It has been demonstrated that high levels of grazing influence populations and communities of marine macroalgae, but the effect of epibiosis has been overlooked. Therefore the goal of this study was to determine whether the production of chemical defenses in basibiont seaweeds is induced by the presence of biofouling (macroalgae epiphytes). Six genera of seaweeds (*Ulva*, *Dictyota*, *Dictyopteris*, *Osmundaria*, and *Pterocladiella*) with and without epiphytes were collected at Rasa Beach, Armação dos Búzios, Brazil. In the laboratory, epiphytes were removed (but seaweeds were considered as "with epiphytes" for late comparison purposes) and basibiont seaweeds were dried. Half of dry algae with and without epiphytes (treatment and control, respectively) were turned into powder (comprised of all algal chemicals). The other half was used to obtain extracts comprised of secondary metabolites that theoretically would protect the algae against epibiosis and would also reduce algae palatability to potential herbivores. The correspondent extracts were obtained using dichloromethane. Each algae extract was incorporated into carragenan-based food to test for chemical deterrence against different species of generalist fish (mainly the territorialist damselfish *Stegastes fuscus*) in Forno Bay, Arraial do Cabo, Brazil. Consumption rates (measured as percentage) of food prepared with powder of seaweeds with vs. without epiphytes were equally consumed (t-test; $p > 0.05$). Among food containing seaweed extracts, *Dictyopteris* and *Osmundaria* with epiphytes were more consumed (t-test; $p = 0.006$ and $p = 0.001$, respectively). One large fish bite was observed on most artificial foods prepared with those seaweeds compared with several small bites on other foods prepared with different seaweed genera, suggesting that *S. fuscus* "tasted" *Dictyopteris* and *Osmundaria* and released them promptly. So they may not be palatable due an increase of defense substances. *Pterocladiella* showed a higher percentage of consumption when food was prepared using extracts without epiphytes (t-test, $p = 0.031$), which suggests that the presence of epiphytic algae may enhance their production. Percentage of food consumption with and without epiphytes prepared with *Ulva* and *Dictyota* extracts showed similar results (t-test, $p = 0.222$ and 0.578, respectively). *Ulva* is generally considered free of chemical defenses, while defenses in *Dictyota* may not affect herbivory in fish. We conclude that the induction and (or) increase in chemical defenses due to the presence of epiphytes depend(s) on algae genera. Results obtained in this study will be compared to the ones from ongoing studies using the sea urchin *Lytechinus variegatus* and the same seaweed genera (with and without epiphytes).

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

AQUATIC ECOLOGICAL RISK ASSESSMENT FOR PYRITHIONE ANTIFOULANTS BASED ON LABORATORY AND FIELD STUDIES

J C Ritter, N P Skoulis, R J Fenn

Arch Chemicals, Inc., U.S.A.

Zinc and copper complexes of pyrithione are finding growing acceptance as booster biocides in antifoulant paint formulations designed to replace those based on the recently banned tributyltin. As a consequence, increased attention has been focused on these compounds and many papers have been recently published on their environmental effects. While these studies provide valuable information, there is in addition a large collection of unpublished work in the form of environmental fate and aquatic toxicity studies conducted or sponsored by Arch Chemicals. The results of these studies will be presented and compared with those published in the recent literature. An ecological risk assessment, which demonstrates that photolysis and biodegradation rapidly convert pyrithione in the aquatic environment to species that are less toxic by several orders of magnitude, will also be presented. Risk quotients of less than one may be obtained all realistic scenarios.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

MAM-PEC
A COMPUTER MODEL TO PREDICT ENVIRONMENTAL CONCENTRATIONS OF ANTIFOULING COMPOUNDS IN ESTUARINE AND COASTAL ENVIRONMENTS

M B Pereira[1], **B van Hattum**[2] and **A Baart**[3]

[1]Hempel A/S, Lundtoftevej 150, DK-2800 Kgs. Lyngby, Denmark. [2] Vrije Universiteit, De Boelelaan 1115, 1081 HV Amsterdam, The Netherlands. [3] WL/Delft Hydraulics, P.O. Box 177, 2600 MH, Delft, The Netherlands

With increasing legislation on antifouling products on national and regional level, reliable tools to assess the exposure for the environmental risk assessment are in demand. During the 90'ies a number of new antifouling agents were introduced to the market due to the increased awareness of the effects from the use of organotin compounds. In 1999 the first version of a model to predict the concentration of antifouling agents in the marine environment (MAM-PEC) was released. The model was developed by the Delft Hydraulics Institute and Vrije Universiteit, Amsterdam, under the auspice of an EU sponsored project commissioned by the Antifouling Working Group under the European Paint Manufacturers Association, CEPE. The model has since been improved and MAM-PEC version 2.0 is ready to be released incorporating several new features.

The fate of the antifouling agents in the marine environment is the result of many complex and interacting abiotic and biotic transformation and transport processes. The MAM-PEC model is a multi-dimensional hydrodynamic and chemical fate model based upon existing models on chemical fate in the water compartment (DELWAQ) and in the sediment compartment (SILTAR), developed by Delft Hydraulics. MAM-PEC predicts the concentration of antifouling compounds in the water column and in the sediment in 5 generalised "typical" marine environments (open sea, shipping lane, estuary, commercial harbour, and pleasure craft marina). The environmental and hydrodynamic parameters such as silt concentration, DOC, POC, salinity, temperature pH, tides, currents, and the dimension of harbour/marina may be chosen by the user. Version 2.0 also includes the possibility to include wind and current driven water exchange for use in areas with limited water exchange due to low or no tides. The compound characteristics such as partitioning, sorption, biotic and abiotic degradation in water and sediment, and speciation are included in the model and a photolysis module is added in version 2.0. The model includes a number of default compounds (*e.g.* Copper, Irgarol, Dichlofluanid, Zinc Omadine, Sea-Nine) with the possibility for the user to add new ones. The estimation of the emission of the antifouling agent is based on the leaching rate from the paint, area of painted underwater hull, shipping intensity and other parameters. Version 2.0 incorporates the emission scenarios based upon MAM-PEC scenarios, developed by OECD and adopted by EU as the standard environmental emission scenarios to be used for evaluation of the biocides under the Biocidal Products Directive. The user-friendly menu-screens and the possibility to adapt it to local scenarios makes MAM-PEC a valuable tool for regulatory authorities as well as antifouling biocide producers and paint manufacturers. The model has been validated for a number of compounds and is today recognised by regulatory authorities in EU and USA.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

EPIBIOSIS ON THE RED SEAWEED *Cryptonemia seminervis* (HALYMENIACEAE): EFFECTS ON HERBIVORY AND FOULING

R P de A Santos, B A P da Gama, J H S Miyamoto and **R C Pereira**

Programa de Pós-Graduação em Biologia Marinha, Universidade Federal Fluminense

Benthic marine macroalgae are particularly susceptible to biofouling (epibiosis) because they are sessile and restricted to the photic zone, where conditions for the growth of fouling organisms are optimal. Epibiosis may provide a "protective coating" to the basibiont alga, but generally seems to be detrimental: the negative effects of fouling on host plants have been extensively documented in marine systems, and include a decrease of light and nutrient availability, a loss of flexibility resulting in increased brittleness, mechanical damage of host surfaces, changes of surface pH, and changes in drag which can cause breakage during storms. Host plants can also be fouled by higher preference epibionts, thus suffering not only the direct negative effects of being fouled, but also experiencing increased rates of grazing. Epibiosis may also induce the production of antifouling defenses. The seaweed *Cryptonemia seminervis* (Rhodophyta, Halymeniaceae) is usually collected with a high percent cover of epibionts (> 50%). In order to assess the effect of epibionts on *C. seminervis*, the epibiosis cover of each epibiont species was first assessed using two methods: computer-based image analysis (using the software ImageJ) and a conventional estimation technique using millimeter-squared paper. In order to assess the effects of epibiont cover on this seaweed, we (1) compared herbivore consumption (amphipods and sea urchins) of fouled and non-fouled specimens of *C. seminervis,* and (2) compared antifouling activity of fouled and epibiont-free algae. The more abundant epibiont on *C. seminervis* was the bryozoan *Membranipora membranacea*, with a cover as high as 90% of the thallus. The consumption of specimens fouled by *M. membranacea* was significantly higher than the consumption of surface-free ones, either by the amphipod community dominated by *Elasmopus brasiliensis* or by the sea urchin *Lytechinus variegatus* ($p < 0.01$). Epibiosis by an unidentified sponge (order Haplosclerida) also increased consumption of *C. seminervis* ($p < 0.001$), suggesting that the common epibiont cover of this seaweed may really act as a lure to herbivores, i.e., epibionts may attract consumers that otherwise would not feed significantly on the host plant. Additionally, epibiosis increased thallus weight as much as 51%. The presence of epibionts seems to have triggered the production of antifouling defenses, since the extracts of algae with epibiosis showed significantly more antifouling activity toward the common algal epibiont *Perna perna* than the extracts of their clean conspecifics.

CAPES, CNPq, and FAPERJ supported this research.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

EFFECTS OF TEMPORAL VARIABILITY OF DISTURBANCE, SEQUENCE AND AGE ON FOULING COMMUNITIES FROM A TROPICAL BAY

T F Porto[1], **S Hampl**[2], **B A P da Gama**[1], **R C Pereira**[1], **M Lenz**[3] and **M Wahl**[3]

[1] Universidade Federal Fluminense, Brazil
[2] Philipps-Universität Marburg/Lahn, Germany
[3] Leibniz-Institut für Meereswissenschaften, Germany

Causal forces in natural systems are variable in time and space. Therefore, the dynamics in disturbance regimes, which are known to be a structuring factor in communities per se, have been proposed to be an important factor structuring marine benthic communities. The aim of this study was to assess the effects of temporal variability in a physical, non-selective disturbance regime and its intrinsic sequences of disturbances, on hard-bottom communities at an early and late successional stage. Several temporally variable disturbance regimes were applied for 5 months to marine hard-bottom communities previously developed on PVC panels for 2 and 12 months in an eutrophic tropical bay (Guanabara Bay, Brazil). All regimes included the removal of biomass with the same intensity and frequency, but had different levels of temporal variability, i.e. lengths of inter-disturbance intervals, as well as different timings of disturbance events within each variability level. Undisturbed communities served as a reference to test for the exclusive effects of disturbance. Disturbance in general had a significant effect on the biomass of the younger and the composition of the older communities. Temporal variability of disturbance, as well as the sequence of disturbance events, had no effects on community structure, while, however, dominant organisms such as *Hydroides* sp., *Bugula turrita*, *Balanus eburneus* and the biofilm significantly responded to disturbance. Moreover the seaweed *Ulva fasciata* was more abundant under temporally variable disturbance regimes. Finally, the relationship between the variance and the mean of species abundances has shown a pattern opposite to the expected: variance was slightly reduced by disturbance treatments. Our results highlight the importance of the successional stage to ecological studies, and suggest that temporal variability in a disturbance regime and the specific timing of disturbance events are not key factors in the system studied.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

Antifouling mechanisms in the green sea turtle *Chelonia mydas*

Freitas GADEM[1]; da Gama BAP[1]; Pereira RC[1] & Salgado LT[2,3]

1. Departamento de Biologia Marinha, Universidade Federal Fluminense
2. Departamento de Biologia Celular e Molecular, Universidade Federal Fluminense
3. Departamento de Histologia, Universidade Federal do Rio de Janeiro

Sea turtles have hard carapaces that are prone to be covered by epibionts. However, very few individuals are found to be fouled, and, with some exceptions like specialized barnacles, few epibiont species occur on sea turtle carapaces. Turtle carapaces are constituted by bony plates, which are covered by a horny top layer formed from skin tissue plates called scutes. The understanding of the mechanisms by which marine organisms remain devoid of fouling may be very important to the development of new, environmentally friendly antifouling technologies. In order to investigate the existence of some possible antifouling mechanism on the carapace of the common green turtle *Chelonia mydas*, scutes from a dead specimen were carefully removed and their antifouling properties examined. Laboratory assays using brown mussels (*Perna perna*) were performed, comparing mussel attachment in scutes with a control of roughened PVC. Scutes were also glued to PVC plates and exposed to the natural fouling community in the field. Surprisingly, mussels significantly preferred to attach to sea turtle scutes when compared to PVC controls ($p < 0.05$, *t*-test for dependent samples), and there was no difference in the total fouling cover between scutes and controls in field assays. The analysis of MEV images of scutes revealed the existence of several layers of queratinous microplates, with an apparent sloughing of the outer layer. Our results strongly suggest the existence of a fouling-release mechanism in this sea turtle, allying structural features to a behavioral mechanism of fouling removal, perhaps through carapace scraping in marine sediments or rocks. However, more studies including intensive field observations should be made to further elucidate this question.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

ANTIFOULING ACTIVITY OF SYNTHETIC ANALOGUES OF KUANONIAMINE

LCS Pinheiro[1], BAP da Gama[2], AMR Bernardino[1] & RC Pereira[2]

1. Programa de Pós-Graduação em Química Orgânica, Instituto de Química, Universidade Federal Fluminense
2. Departamento de Biologia Marinha, Universidade Federal Fluminense

Marine biofouling is today perhaps one of the major contraints to human activities at the sea. With the ban of TBT-based compounds in antifouling paints, researchers worldwide are looking at marine natural products in the search for new antifouling agents. Kuanoniamines are alkaloids isolated from marine sponges and ascidians that exhibit potent anticancer and antivirus activities. Based on the structure-activity relationship, this project was aimed at synthesizing the novel system benzo[*b*]thieno[3,2-*h*]-1,6-naphthyridine (5). The new compounds 4-(3-chlorophenylamino)-5-cyanothieno[2,3-*b*]pyridine (1), 4-(4-chlorophenylamino)-5-cyanothieno[2,3-*b*]pyridine (2), 4-(4-chlorophenylamino)thieno[2,3-*b*]pyridine-5-carboxylic acid (3), 4-(3-chlorophenylamino)thieno[2,3-*b*]pyridine-5-carboxylic acid (4), are key intermediates to the synthesis of compounds in this system. Compounds 1 and 2, were synthesized from 5-cyano-4-chlorothieno[2,3-*b*]pyridine with their respective anilines. These were hydrolyzed into their acids 3 and 4. The cyclization of the acids yielded the new system 5. All 5 compounds were tested against the common fouling mussel, *Perna perna*, in laboratory assays at the concentration of 1 mg per Petri dish (n = 10 replicates per treatment). The number of byssal threads produced was assessed as the response variable and compared to byssal attachment in controls. Among the compounds assayed, only compound 1 exhibited significant antifouling activity ($p < 0.01$, ANOVA followed by Tukey test). A single change in chlorine position (from *meta* to *para*) led to a complete reversal of activity, significantly stimulating mussel attachment (compound 2, $p < 0.001$). Compound 1 has shown an extremely strong antifouling activity, as well as low toxicity to mussels, thus being a good candidate to the development of new antifouling paints that are both effective and environmentally friendly. Next steps include testing this substance in more ecologically realistic field assays and more thorough ecotoxicological studies.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

TEST STRATEGY AND HAZARD ASSESSMENT FOR MEDETOMIDINE – A NEW ANTIFOULING CANDIDATE

H Blanck, Å Granmo, L Förlin, G Birgersson, A Hilvarsson, A Lennqvist, C Petersson, J Bellas, R Ekelund, M Haraldsson, L Norrgren, T Backhaus

Göteborg University, Sweden

Medetomidine is an α_2-adrenoceptor agonist used as sedative in veterinary medicine. It has been shown to prevent settling of barnacle larvae at nanomolar concentrations with lethal effects only at 100 000-fold higher levels. The Marine Paint programme was started to evaluate the potential of medetomidine as an active ingredient in commercial antifouling coatings, and to assess the risk for marine and coastal environments. A broad test strategy was developed focussing on growth, reproduction and behaviour of marine species, since such effects were known to occur in mammals. Microcosms were used to investigate effects on structure and function of algal and bacterial communities. Medetomidine was also tested in a battery of fish biomarkers, with the aim to develop tools to monitor the environment for potential effects once medetomidine is in use. Based on its physico-chemical properties, as well as leaching and degradation rates, the predicted environmental concentrations of medetomidine in sediment and water were estimated for a set of harbour, marina and shipping lane scenarios using the MAMPEC model. Our strategy sets out to make a selection of test systems and endpoints of particular relevance for the marine use of medetomidine under consideration of its mode of action, but still allowing for detection of unexpected responses. We also wanted to address the question of species dependent sensitivity, and use a realistic environmental setting to avoid oversimplification of ecological processes. Fish lethality was observed only at high concentrations (195 µM medetomidine) and in general the base set toxicity tests responded in the µM-concentration range (2.2-195 µM). A full life-cycle test with zebrafish indicated impairment of reproduction only at relatively high concentrations (0.5 µM). However, with our focussed test strategy, several sublethal effects on marine biota were found at < 1 nM. To our surprise barnacle larvae maintained their position as a highly sensitive organism, and only the EROD response of one fish species (the turbot) was more sensitive with a NOEC of 0.05 nM. More than 22 endpoint/species with significant NOEC values were included in the data set, making a species-sensitivity-distribution approach highly relevant. The predicted medetomidine concentrations in water within harbours and marinas were in the range of 0.0001-0.001 nM. Thus, for the worst-case scenario with a medetomidine concentration of 0.001 nM, a 50-fold increase would be required to reach the No-Effect-Concentration of the most sensitive response in the most sensitive species.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

BIOMIMETIC INSPIRED DESIGNS FOR PREVENTION OF BIOFOULING

Rocky de Nys

Biofouling Research Group, School of Marine Biology & Aquaculture,
James Cook University, Australia

Biofouling occurs on all surfaces in a fluid environment ranging from microbial biofilms on medical implants and contact lenses, through to complex invertebrate communities on the hulls of boats. In the marine environment some organisms stand out by having little or no fouling on their surfaces. Elucidating the mechanisms that marine plants and animals use to prevent fouling gives us a range of tools to develop new biomimetic technologies to control fouling. These mechanisms range from novel chemicals exuded onto the surface of algae that prevent colonisation by bacteria, plants and invertebrates, through to unique micro-textured surfaces at the scale of microns that prevent the settlement and growth of invertebrate larvae.

Our research has focused on characterising and understanding the mechanism of action of natural surfaces, in particular the shells of marine bivalves and gastropods, in preventing fouling. Fouling resistance is correlated to parameters of shell surfaces providing promising new guidelines for surface-dependent antifouling coatings. These parameters also correlate with the attachment strength of fouling communities. The micro-topography discovered on the surface of fouling resistant molluscs has been reproduced onto polymer surfaces (biomimics) and tested against common fouling organisms in laboratory and field bioassays to investigate the mechanisms that underpin fouling resistance. Understanding how the attachment of fouling organisms is affected by the scale and fractal dimension of micro-topography has also led to the development of new micro- and nano-scale surfaces inspired by natural architectures. Furthermore, comparing natural surfaces and biomimics has demonstrated the importance of multiple defensive strategies, where in nature surface-bound natural products and surface architecture combine to prevent both micro- and macro-fouling. This combined strategy uses chemical defences to restrict the development of biofilms and protect the effective micro-topography of natural surfaces. We are targeting this approach of combining surface-bound natural products and surface micro-topography to develop and improve surface- based designs for the prevention of fouling. Nature has developed a diversity of strategies to prevent fouling and in many cases our own powers of observation limit our understanding of natural defences. Further research into the diversity of natural defensive mechanisms, and an approach of looking beyond the obvious, will provide novel models for the development of antifouling technologies.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

MECHANICAL AND MOLECULAR PROPERTIES OF THE ULVA SPORE ADHESIVE SYSTEM

J.A. Callow

School of Biosciences, University of Birmingham, Birmingham, B15 2TT, UK

The main subject of this talk will be the physico-chemical and molecular properties of the adhesive glycoprotein used by the green alga *Ulva* (formerly *Enteromorpha*) and the relevance of this biofouling. Microscopic (5 μm diam.) spores of *Ulva* release the adhesive glycoprotein on settlement. We have shown that the spore 'glue' is a space-filling, hydrophilic material, which undergoes cross-linking (curing) processes within minutes of release from the spore. Adhesive and viscoelastic properties during adhesive curing have been characterized by AFM. Partial peptide sequence data and other evidence shows that the adhesive has homology to specific types of extracellular matrix proteins in other algae. The tenacity of spore adhesion on a range of different surfaces, including foul-release materials, has been assessed by hydrodynamic methods. Adhesion strength is strongly influenced by the time the cells are in contact with the surface, the properties of the surface and whether or not the spores settle gregariously. Recent use of self-assembled and grafted monolayers, together with ESEM, has shown a strong influence of surface energy on the degree of wetting of the surface by the adhesive. Resultant differences in surface area of contact are likely to be critical to the ease of detachment.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

BARNACLE CEMENT FROM THE MOLECULAR ASPECT

Kei Kamino

Marine Biotechnology Institute, Japan

Sessile organisms attach to foreign substrata in water. This underwater attachment is an essential physiological process in the organisms, and is achieved by a specialized molecular system. Underwater attachment is multi-functional, and the underwater adhesive used has to cooperatively fulfill all these functions. This solution to overcoming the problems associated with joining two different materials in water is thought to be completely different from the approach used in the development of man-made adhesives in air. Studies of the biological adhesive systems used by diverse aquatic sessile organisms could benefit the design of new biomaterials and biomimetics that may lead to significant advances in nanobiotechnology.

The underwater adhesive produced by the barnacle is historically called cement. This cement joins two different materials, *i.e.*, the organism's own calcareous base and several foreign substrata including both naturally occurring and man-made types. Recent progress has shown the cement to be a multi-protein complex whose subunits are distinct from each other and have no similarity to the mussel holdfast proteins. An analysis of the functions of each cement protein enabled a molecular model for barnacle underwater attachment to be produced. This presentation summarizes the characteristics of the cement proteins and the molecular model. Recent progress is also presented on identifying what contributes to the adhesive strength, adaptation of the cement to different surfaces and peptide-based material design.

Some of this work was performed as part of the industrial science and technology project entitled "Technological Development for Biomaterials Design Based on Self-organizing Proteins" supported by New Energy and Industrial Technology Development Organization (NEDO).

12th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

THE BYSSUS OF THE BLUE MUSSEL: FORM AND FUNCTION

Nick Aldred[1], **James A. Callow**[2] and **Anthony S. Clare**[1]

[1]The University of Newcastle upon Tyne, UK
[2]The University of Birmingham, UK

Of all bioadhesive systems used by marine organisms, that of the blue mussel (*Mytilus edulis*) is the most comprehensively studied. It is now well established that mussels use a variety of dedicated "foot proteins" and modified collagen-like materials to enable the rapid formation of a byssus of elastic threads which facilitates their attachment to surfaces. Interest in this system has stemmed primarily from two fields: first, the anti-biofouling sector, that aims to prevent the attachment of these organisms to marine structures and, secondly, interest in the development of synthetic materials that can mimic the combined strength and elasticity of mussel byssus. Presented here are the results of two recent studies with relevance to both of these fields. Mechanical studies of mussel byssus demonstrate that it is a highly effective attachment mechanism and that its success is likely to be derived from the interaction of several factors within the bulk of the material, facilitating its yielding character. Further, the morphology of the byssal plaque, which mediates attachment to the surface, is shown to respond predictably to changes in surface wettability. This is promising for the development of non-toxic fouling-resistant coatings. Results, however, suggest that contrary to conventional wetting theory, exploiting this characteristic alone would not be sufficient to interfere with the fundamental adhesion of this organism and prevent its successful attachment.

13th International Congress on Marine Corrosion and Fouling
23th July to 28th July 2006 - Rio de Janeiro - Brazil

GENETIC VARIATION IN ADHESIVE TENACITY AND ADHESIVE PLAQUE CHARACTERISTICS IN THE BARNACLE *BALANUS AMPHITRITE*

Holm, Eric R.[1], **Beatriz Orihuela**[2], **Christopher J. Kavanagh**[3], and **Daniel Rittschof**[2].

[1]Naval Surface Warfare Center, 9500 MacArthur Blvd., West Bethesda, MD USA. [2]Duke University Marine Laboratory, Beaufort, NC USA. [3]Department of Marine & Environmental Systems, Florida Institute of Technology, Melbourne, FL USA.

Silicone fouling-release coatings represent a reputedly non-toxic alternative to current toxic antifouling coatings, for controlling hull fouling. In contrast to antifouling coatings, fouling-release coatings allow organisms to adhere to the coated surface, but prevent their firm attachment. Ideally, fouling is sloughed from the hull while the ship is underway. Thus, effectiveness of a particular fouling-release coating is not necessarily determined by the rate or extent to which it fouls, but by the ease with which that fouling may be removed. Typically, adhesion strength or tenacity (in shear) observed for attached organisms varies both inter- and intraspecifically. This variation may be a consequence of differences among individual foulers in their adhesives, or in the adhesive-adherend interaction. In an effort to understand potential biological causes of intraspecific variation, we carried out a quantitative genetic analysis of adhesive tenacity of barnacles *Balanus amphitrite*, attached to a commercially available fouling-release coating (International Veridian) and a silicone rubber used for mold-making (Dow Corning Silastic T-2). Mean tenacity (removal stress) for barnacles set on Veridian was 0.092 MPa (SE=0.001), and measured values of removal stress spanned an order of magnitude, from 0.018 to 0.189 MPa. For barnacles set on T-2, mean tenacity was 0.137 MPa (SE=0.002), and ranged from 0.018 to 0.276 MPa. Variation in tenacity for the Veridian material was weakly influenced by family. The family effects suggested a broad sense heritability (h^2) for adhesion strength of approximately 0.12. In contrast, variation in tenacity on the T-2 material was not heritable. For Veridian, the genetic component to the phenotypic variation in tenacity was associated with characteristics of the adhesive plaque. The condition of the adhesive plaque affected removal stress, and was significantly heritable (h^2=0.46). Adhesive plaque structure was also heritable for barnacles attached to the T-2 material (h^2=0.59), although plaque condition did not affect tenacity. Genetic variants for tenacity or adhesive plaque characteristics may provide another avenue by which to explore biological adhesives and their interactions with potential adherends.
Funded by the US Office of Naval Research.

META 20 anos
MARKETING E EVENTOS

13th ICMCF Secretariat
Av. Nilo Peçanha, 50 grupo 1610
20044-900 - Rio de Janeiro - RJ - Brazil
Phone: 55 21 2220-2097
Fax. 55 21 2220-2305
E-mail: meta@wb.com.br