



*International Congress on  
Marine Corrosion and Fouling*

University of San Diego  
21-26 July 2002



*International Congress on  
Marine Corrosion and Fouling*

**11<sup>th</sup> International Congress on Marine  
Corrosion and Fouling**

**PROGRAM  
AND  
BOOK OF ABSTRACTS**

**The University of San Diego**

**San Diego, California, USA**

**21 – 26 July 2002**

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<i>Dail Thomas</i>	<i>Naval Sea Systems Command, USA</i>
<i>Pat Turley</i>	<i>Arch Chemicals, Inc., USA</i>

### Sessions

<b>ANTIFOULING AND THE ENVIRONMENT</b>	<i>Mike Champ and Steve McElvany</i>
<b>ASSESSMENT OF RISK</b>	<i>Steve McElvany</i>
<b>BIODEGRADATION OF WOOD</b>	<i>Gareth Jones</i>
<b>BIOFOULING, NAVY, AND INDUSTRY PERSPECTIVE</b>	<i>Colin Anderson</i>
<b>BIOCIDES, COBIOCIDES, AND DETERRENDS</b>	<i>Pat Turley</i>
<b>COPPER FOR BIOFOULING CONTROL</b>	<i>Neal Blossom</i>
<b>CORROSION IN BALLAST AND HOLDING TANKS</b>	<i>Joanne Jones-Meehan</i>
<b>FOULING-RELEASE AND MINIMALLY ADHESIVE SURFACES</b>	<i>Bob Brady, Jim Callow and Maureen Callow</i>
<b>HYDRODYNAMICS OF SHIP HULL COATINGS</b>	<i>Mike Schultz</i>
<b>INVASIVE SPECIES</b>	<i>Eric Holm and Richard Everett</i>
<b>INVERTEBRATE MICROBIAL AND ALGAL FOULING</b>	<i>Tony Clare and Helen Dalton</i>
<b>MICROBIOLOGICALLY INFLUENCED CORROSION</b>	<i>Stephen Dexter</i>
<b>NATURAL ANTIFOULING MECHANISMS</b>	<i>Peter Steinberg and Rocky de Nys</i>
<b>NEW MATERIALS</b>	<i>Harvey Hack</i>
<b>SAN DIEGO BAY: A CASE STUDY FOR ANTIFOULING STRATEGIES</b>	<i>Pete Seligman and Leigh Taylor Johnson</i>
<b>SHIP COATINGS AND CORROSION CONTROL</b>	<i>Dail Thomas</i>

### Publications

<b>BIOFOULING</b>	<i>Maureen Callow and Len Evans</i>
<b>CD</b>	<i>Steve McElvany</i>

Time	Monday		Tuesday		Wednesday		Thursday				
	Session A	Session B	Session A	Session B	Session A	Session B	Session A	Session B			
8:00											
8:20											
8:30	Welcome		Key Note		Key Note						
8:40							Key Note				
8:50	Biofouling, Navy, & Industry Perspective										
9:00			AF ENV	MIC		NAT AF					
9:10											
9:20			AF ENV	MIC		Key Note	NAT AF	INVASIVE	BIOCIDES		
9:30											
9:40			AF ENV	MIC		FR	NAT AF	INVASIVE	BIOCIDES		
9:50											
10:00	AF ENV	MIC		FR	NAT AF	INVASIVE	BIOCIDES				
10:10											
10:20	Break		Break		FR	NAT AF	Break				
10:30											
10:40	Break		Break		Break						
10:50									INVASIVE	BIOCIDES	
11:00	Key Note	TANKS	COPPER	Key Note	FR	NAT AF					
11:10		TANKS	COPPER	HYDRO			INVASIVE	BIOCIDES			
11:20					FR	NAT AF					
11:30	IMAF	TANKS	COPPER	HYDRO			INVASIVE	BIOCIDES			
11:40					FR	NAT AF					
11:50	IMAF	TANKS	COPPER	HYDRO			INVASIVE	BIOCIDES			
12:00					FR	NAT AF					
12:10	Lunch		Lunch				INVASIVE	BIOCIDES			
12:20					FR	NAT AF					
12:30											
12:40											
12:50											
13:00											
13:10											
13:20	IMAF	TANKS									
13:30											
13:40	IMAF	TANKS	SD BAY	HYDRO	FR		INVASIVE	RISK			
13:50											
14:00	IMAF	TANKS	SD BAY	HYDRO	FR	NAT AF	INVASIVE	RISK			
14:10											
14:20	IMAF	COATING	SD BAY	HYDRO	FR	NAT AF	INVASIVE	RISK			
14:30											
14:40	IMAF	COATING	SD BAY	HYDRO	FR	NAF AF	INVASIVE	RISK			
14:50											
15:00	Break		Break		Break	NAF AF	INVASIVE				
15:10											
15:20	Break		Break								
15:30					IMAF	COATING	SD BAY	HYDRO	FR	Break	Break
15:40											
15:50	IMAF	COATING	SD BAY	HYDRO	FR	WOOD	INVASIVE				
16:00											
16:10	IMAF	COATING			FR	WOOD	INVASIVE				
16:20											
16:30	IMAF	NEW MAT	SD BAY PANEL DISCUSS	Break	FR	WOOD	INVASIVE				
16:40											
16:50	IMAF	NEW MAT			FR		INVASIVE				
17:00											
17:10	IMAF	NEW MAT			FR		INVASIVE				
17:20			Break								
17:30	IMAF	NEW MAT			FR		INVASIVE				
17:40											
17:50											
18:00											
18:10											
18:20			Poster Session				Congress Barbeque and Conclusion				
18:30											
18:40											
18:50											
19:00											

<b>TIME</b>	<b>MONDAY</b>			
<b>8:30</b>	<b>WELCOME</b> <b>Location: Auditorium</b>			
	<b>BIOFOULING, NAVY, AND INDUSTRY PERSPECTIVE</b> <b>Session Chair: Colin Anderson</b>			
<b>8:50</b>	<b>AUTHORS</b>	<b>TITLE</b>		
	Ingle, Mark Kaznoff, Alexis	Advanced, Environmentally Acceptable Antifouling Coating Development		
<b>9:20</b>	Eliasson, Johnny	Marine Corrosion and Biofouling - An owner's perspective		
<b>9:50</b>	Falwell, Pat	Corrosion Issues in the Marine Industry		
<b>10:20</b>	<b>REFRESHMENT BREAK</b>			
	<b>SESSION A</b> Location: Auditorium		<b>SESSION B</b> Location: Room 206	
<b>10:50</b>	<b>INVERTEBRATE, MICROBIAL, &amp; ALGAL FOULING</b> <b>Session Chairs: Tony Clare &amp; Helen Dalton</b>		<b>CORROSION IN BALLAST &amp; HOLDING TANKS</b> <b>Session Chair: Joann Jones-Meehan</b>	
	<b>AUTHORS</b>	<b>TITLE</b>	<b>AUTHORS</b>	<b>TITLE</b>
<b>11:10</b>	<u>Beech, Iwona</u> Paiva, Mauricio Coutinho, Claudia Zinkevich, Vitaly	The role of biofilm matrix in the fouling process	<u>Fultz, Ben</u>	Retention of Pre-Construction Primer (PCP) as an Integral Portion of Ballast Tank Lining Systems
			<u>Webb, Arthur A.</u> Bergh, Jan O. Foster, Richard L. Brinckerhoff, Beau Harris, Tyler	New Tank and Void Coating Systems for Increased Life and Reduced Maintenance in Seawater and Compensated Fuel Service
<b>11:30</b>	<u>Dalton, Helen M.</u> March, P.E. Ober, C. Wooley, K.	Selective Microbial Fouling of Coatings	<u>Kuljian, Gordon G.</u>	State of the Art Procedures for Optimum Coating Longevity in Shipboard Ballast Tanks
<b>11:50</b>	Morin, D. Vallée-Réhel, K. <u>Grasland, B.</u> Quemener, E. Le Pennec, J.P. Haras, D.	The communication network in biofilm and planctonic cultures of marine bacteria	<u>Lemieux, E.J.</u> Lucas, K.E. Thomas, E.D. Slebodnick, P. Hogan, E.A. Seelinger, A.	Integrated Condition Based Maintenance Systems for Monitoring and Evaluation of Ballast Tank Coatings Integrity and Life Prediction
<b>12:10</b>	<b>LUNCH</b>			

<b>TIME</b>	<b>SESSION A</b> <b>Location: Auditorium</b>		<b>SESSION B</b> <b>Location: Room 206</b>	
<b>13:20</b>	<b>INVERTEBRATE, MICROBIAL, &amp; ALGAL FOULING</b> <b>Session Chairs: Tony Clare &amp; Helen Dalton</b>		<b>CORROSION IN BALLAST &amp; HOLDING TANKS</b> <b>Session Chair: Joann Jones-Meehan</b>	
	Higgins, M.J. Mulvaney, P. <u>Wetherbee, R.</u>	Characterization of the adhesive mucilages secreted by live diatom cells using atomic force microscopy	<u>Ross, Angela</u>	Visible Light Cured Coatings for Corrosion Control
<b>13:40</b>	<u>Callow, Maureen</u> Callow, J. A. Finlay, J.A. Jennings, Alice R. Patel, Pratixa Brennan, A. B. Seegert, C. E. Gibson, Amy Feinberg, A. Baney, R. Ista, Linnea K. Lopez, G.P.	Cue detection and surface selection in the settlement of spores of the green alga enteromorpha	<u>Lee, Jason S.</u> Lowe, Kristine Ray, Richard I. Jones-Meehan, Joanne Little, Brenda J.	Corrosion Behavior of 316L in Glycol / Seawater Mixtures
<b>14:00</b>	Wahl, Martin <u>Lenz, Mark</u>	Biogenic Neighborhood Effects in Recruitment Dynamics	<u>Jones-Meehan,</u> <u>Joann</u> Jones, William Ewell, Michael	Microbial additives for shipboard collection, holding and transfer (CHT) tank systems
<b>14:20</b>	<u>Clare, Anthony S.</u> Matsumura, Kiyotaka Kirby, Richard R.	The proximate basis of barnacle gregariousness: the adult-associated cue to settlement of Balanus amphitrite cypris larvae is similar to the alpha 2-macroglobulin family of proteins	<b>SHIP COATINGS &amp; CORROSION CONTROL</b> <b>Session Chair: Dail Thomas</b>	
			<u>Webb, Arthur</u> Bergh, Jan O. Lucas, Keith E. Slebodnick, Paul Hogan, Elizabeth Berry, Fred	Low Solar Absorbance (LSA) Coatings Performance and Reliable Evaluation Techniques
<b>14:40</b>	<u>Martensson, Lena</u> Albertsson, Chirstian Dahlstrom, Mia Jonsson, Per J. Wallin, Margareta Elwing, Hans	New methods for neurotransmitter and receptor studies on Balanus improvisus cyprids	<u>Bohlander, G.S.</u> Thomas, W.M.	Development and Demonstration of an Automated Paint Application Containment and Treatment System
<b>15:00</b>	<b>REFRESHMENT BREAK</b>			

TIME	SESSION A Location: Auditorium		SESSION B Location: Room 206	
	15:30	<u>Hellio, Claire</u> Prescott, Mark Henry, Sheelagh Wainwright, Geoffrey Rees, Huw Clare, Anthony	Age-related settlement success by cyprids of the barnacle <i>Balanus amphitrite</i> with special reference to consumption of CMP, lipids and hormonal levels.	<u>Lynn, D.C.</u> Bohlander, G.S. Field, A.F.
15:50	Dahlstrom, Mia Martensson, Lena Jonsson, Per Lausmaa, Jukka <u>Elwing, Hans</u>	The chemical background of the surface affinity of medetomidine (catemine), a settlement-impeding compound directed against the colonization of barnacle larvae	Bohlander, G.S.	Underwater Hull Coating System Life Cycle Issues for 12-Year Extended Service
16:10	Watson, Megan Williamson, Jane <u>de Nys, Rocky</u> Steinberg, Peter	Biofilm cues for generalist herbivores? Settlement of the sea urchin <i>Heliocidaris erythrogramma</i> larvae in response to biofilms	<u>Smart, John</u> Bryant, Deborah	Dehumidification for Ballast Tank Corrosion Control in a Tension Leg Platform
16:30	<u>Rittschof, D</u> Y-X, Cai TM, Sin	Fouling on Cylindrical Surfaces: Edge and Depth Effects	<b>NEW MATERIALS</b> <b>Session Chair: Harvey Hack</b>	
			<u>Jenkins, James F.</u>	New technology stainless steels and nickel alloys for marine applications
16:50	<u>Yan, Tao</u> Yan, Wen Xiz	The study of offshore fouling in China – a review	Hogan, <u>Lucas</u> , Natichan, Martin, Grolleau, and Brinkerhoff	Performance of Nickel Alloys for Applications in Seawater Piping Systems
17:10	<u>Kavanagh, Chris</u>	Recruitment and Growth of Marine Invertebrates on Silicone Coatings	<u>Agarwal, D.C.</u>	UNS N06059, a highly alloyed ternary Ni-Cr-Mo alloy, solves crevice corrosion problems in marine environments
17:30	Fant, Camilla <u>Elwing, Hans</u> Höök, Fredrik	A surface sensitive method for investigation of cross-linking and protein-protein interaction of marine adhesives without influence of the solid surface.	<u>Webb, Arthur</u> Ingle, Mark W.	Use of Composite Technology for the Replacement of Shipboard Metallic Components
17:50	<b>SESSION CLOSE</b>			



TIME	<b>TUESDAY</b>			
<b>8:15 to 8:55</b>	<b>Location: Auditorium</b>			
	<b>AUTHOR</b>	<b>TITLE</b>		
	<u>Lewis, John A.</u>	Fouling prevention in the Royal Australian Navy: Where we are, and where we are going		
	<b>SESSION A</b> Location: Auditorium		<b>SESSION B</b> Location: Room 206	
<b>9:00</b>	<b>ANTIFOULING &amp; THE ENVIRONMENT</b> Session Chair: <b>Stephen McElvany</b>		<b>MICROBIOLOGICALLY INFLUENCED CORROSION</b> Session Chair: <b>Stephen Dexter</b>	
	<b>AUTHORS</b>	<b>TITLE</b>	<b>AUTHORS</b>	<b>TITLE</b>
	<u>Berg, Eivind A.</u>	Challenges from the IMO AFS Convention for the antifouling industry, shipping, and authorities	<u>Jones-Meehan, Joanne</u> Little, Brenda Ray, Richard Mansfield, Florian	Coated 4140 steel exposed to marine, mixed bacterial communities containing sulfate-reducing bacteria (SRB)
<b>9:20</b>	<u>Senda, Tetsuya</u> Miyata, Osamu Kihara, Takeshi Yamada, Yasujiro	Inspection Method for Identification of TBT-Containing Antifouling Paints	<u>Little, Brenda</u> Ray, Richard	Microbiologically Influenced Corrosion in Tanks, Holds and Cargo Spaces
<b>9:40</b>	<u>Cameron, Patricia</u> Otto, Sabine	Biocide-free Antifouling Paints -the Long-term Solution to Preserve the Marine Environment	Baier, Robert <u>Forsberg, Robert</u> Meyer, Anne	Corrosion Protection of Ballast Tanks by Surface-Active-Inhibitor-Based Displacement of Aquatic Nuisance Biofilms
<b>10:00</b>	Turley, Patricia Ritter, James C. <u>Fenn, Robert J.</u>	“Antifoulant Biocides - Why Laboratory Testing is not Enough (or Maybe Too Much)”	<u>Dexter, Stephen C.</u> Xu, Kunming	Mn Cycling in Marine Biofilms: Effect on Rate of Localized Corrosion
<b>10:20</b>	<b>REFRESHMENT BREAK</b>			
<b>10:50</b>	<b>COPPER FOR BIOFOULING CONTROL</b> Session Chair: <b>Neal Blossom</b>		<b>HYDRODYNAMICS OF SHIPS HULL COATINGS</b> Session Chair: <b>Mike Schultz</b>	
	<u>Blossom, Neal</u>	Copper-The Natural and Effective Antifouling Ingredient	Townsin, R.L. <u>Anderson, Colin</u>	The ship hull fouling penalty
<b>11:10</b>	<u>Tomasgaard, Lars</u>	Restrictions on the use of Biocidal Antifoulings The Scandanavian case	<u>Candries, M.</u> Pazouki, K. Atlar, M. Ehsan, M.	Hydrodynamic characteristics of Tin-free Self-Polishing Copolymers and Foul(ing) Release systems
<b>11:30</b>	<u>Haslbeck, Elizabeth</u> Seligman, Peter F Valkirs, Aldis O. Vos, Marcel	Biocide Release Rate Measurement – Lab and Field	Haslbeck, Elizabeth <u>Holm, Eric R.</u> Talbot, Walter J. Field, Andrew	Evaluation of Hydrodynamic Drag on Antifouling and Fouling Release Coatings using the Friction Disk Machine

	<b>SESSION A</b> Location: Auditorium		<b>SESSION B</b> Location: Room 206	
<b>11:50</b>	<u>Dryden, Christina</u> Donat, John R.	Biogeochemical Cycling of Copper in the Elizabeth River	<u>Kiil, Søren</u> Dam-Johansen, Kim Weinell, Claus E. Pederson, Michael S. Codolar Santiago Arias	Design and Estimation of Antifouling Paint Behaviour Using a Combination of Mathematical Models and Rotary Experiments
<b>12:10</b>	<b>LUNCH</b>			
<b>13:40</b>	<b>SAN DIEGO BAY – A CASE STUDY (PM SESSION)</b> Session Chairs: <b>Peter Seligman &amp; Leigh Taylor Johnson</b>		<b>HYDRODYNAMICS OF SHIPS HULL COATINGS (PM SESSION)</b> Session Chair: <b>Mike Schultz</b>	
	<u>Seligman, Peter F</u> Valkirs, Aldis O. Haslbeck, Elizabeth G. Johnson, H.D.	Environmental Loading of Copper From Antifouling Marine Coatings in San Diego Bay	<u>Klijnstra, Job W.</u> Overbeke, K. Sonke, H. Head, R. Ferrari, G.M.	Critical speeds for fouling removal from a silicone coating
<b>14:00</b>	<u>Rivera-Duarte, I.</u> Rosen, G. Chadwick, D.B. Lapota, D. Zirino, A.	Effects of Copper in Heavily Impacted Coastal Embayments: Chemical Speciation and Toxicity in San Diego Bay	<u>Kovach, Brett</u>	Hydrodynamic Evaluation of Ship Hull Coatings
<b>14:20</b>	<u>Chadwick, D.B.</u> Rivera-Duarte, I. Wang, P.F. Katz, C. Carlson, A. Zirino, A.	Modeling the Mass Balance and Fate of Copper in San Diego Bay	<u>Nedved, Brian T.</u> Bird, Christopher E. Parker, Kristian P. Smith, Celia M. Hadfield, Michael G.	Shear forces necessary to remove newly settled fouling organisms from test surfaces: data from a precision flow cell.
<b>14:40</b>	<u>Johnson, Leigh Taylor</u>	Involving Boat Owners and Industry in Pleasure Craft Antifouling Policies – A San Diego Bay Case Study	<u>Schultz, Michael P.</u>	Turbulent Boundary Layers on Surfaces Covered with Marine Algae
<b>15:00</b>	<b>REFRESHMENT BREAK</b>			
<b>15:30</b>	<u>Dobalian, Lesley</u> Arias, Chrisina	Shelter Island Yacht Basin Total Maximum Daily Load for Dissolved Copper	<u>Schultz, Michael P.;</u> Finlay, John A.; Callow, Maureen E.; Callow, James A.	Three Models to Relate Detachment of Low Form Fouling at Laboratory and Ship Scales
<b>15:50</b>	<u>Schiff, Kenneth</u> Diehl, Dario	Assessment of Trace Metal Emissions From Antifouling Paints During Underwater Cleaning Events and Passive Leaching	<u>Weinell, Claus E.;</u> Olsen, Kenneth; N. Christoffersen, Martin W.; Kiil, Søren	Experimental study of drag resistance on sea water immersed surfaces using a laboratory scale rotary set-up.
<b>16:10</b>	<b>SAN DIEGO BAY</b>		<b>BREAK</b>	
<b>16:30</b>	<b>PANEL DISCUSSION</b>			
<b>17:10</b>	<b>BREAK</b>			

17:30	<b>POSTER SESSION</b> <b>Location: The Foyer</b>	
<b>ANTIFOULNG AND THE ENVIRONMENT</b>		
<b>AUTHORS</b>	<b>TITLE</b>	
<b><u>Fernández Estarlich, F.</u></b> ; Lewey, Susan <b>A.</b> ; Wybrow, Peter	SEAM; Assessing Concepts Systems and Tools for a Safer, Efficient and Environmentally Aware and Friendly Maritime Transports	
<b>BIOCIDES, COBIOCIDES, &amp; DETERRENTS</b>		
<b><u>Braithwaite, Richard A.</u></b> ; Fletcher, <b>Robert L.</b>	Toxicity of the Antifouling Agents Irgarol 1051 and Sea-Nine 211 and the use of an Image Capture and Analysis System in Macroalgal Bioassays	
<b><u>Klijnstra, Job W.</u></b> ; Head, R.; Ferrari, <b>G.M.</b>	Pepticoat: Protein technology for control of fouling	
<b>Mary, Sr. Avelin; <u>Waldron, Craig;</u></b> <b>Matias, Jonathan R.</b>	Inhibition of cyprid attachment by the combination of (-) menthol and copper Omadine <sup>®</sup> biocide	
<b><u>Kjell K., Alm</u></b>	Poison free only, please.	
<b><u>Vallée-Réhel, Karine;</u></b> Thouvenin, <b>Muriel;</b> <b>Ulvé, Stéphane;</b> Grohens, Y.; Péron, <b>Jean-Jacques;</b> Haras, Dominique	Past and future of erodable polymers in antifouling paints	
<b>FOULING-RELEASE AND MINIMALLY ADHESIVE SURFACES</b>		
<b>Fant, Camilla;</b> Sott, Kristin; Nylander, <b>Tommy;</b> <b><u>Elwing, Hans</u></b>	Compression and decompression of <i>Mytilus edulis</i> foot protein – 1 (Mefp-1) at the air water interface.	
<b>Hudd, Adrian</b>	Boatscrubber – Environmental Hull Cleaning	
<b><u>Finlay, J.A.</u></b> Callow, J.A.; Callow, <b>Maureen</b>	Evaluation of Novel Foul-release Coatings using Algae	
<b><u>Quinn, Ronan;</u></b> Swain; G., Touzot, A.; <b>Kovach, B.;</b> Kavanagh, C.	Investigations into the release of epoxy from clear silicone coatings	
<b><u>Walker, Gilbert C.</u></b>	An Advanced Scanning Probe Microscopy Tool-Kit for Studying Anti-fouling Surfaces	
<b>HYDRODYNAMICS OF SHIP HULL COATINGS</b>		
<b><u>Touzot, Arthur;</u></b> Kovach, B.; Kavanagh, <b>C.;</b> <b><u>Quinn, R.;</u></b> Rochereau, C.; Swain, G.	Hull roughness experiment, Comparison with different coating type and extrapolation to ship full economy	
<b>INVASIVE SPECIES</b>		
<b><u>Farrell, Paul;</u></b> Fletcher, Robert L.	The spread of the invasive, fouling macroalga <i>Undaria pinnatifida</i> (Harvey) Suringar in the UK	
<b><u>Lantzouni, M.;</u></b> Nicolaidou, A.; Zenetos, <b>A.</b>	An account of fouling invaders in Greek waters	
<b>INVERTEBRATE, MICROBIAL, AND ALGAL FOULING</b>		
<b><u>Bers, Valeria;</u></b> Wahl, Martin	Surface structures of marine organisms and their influence on fouling	
<b><u>Faimali, Marco;</u></b> Garaventa, Francesca; <b>Chiantore, Maria Chiara;</b> Cattaneo- <b>Vietti, Riccardo</b>	Can substrata nature influence biofilm interactions during the settlement of <i>Balanus amphitrite</i> larvae?	
<b><u>Faimali, Marco;</u></b> Gallus, L.; Amaroli, A.; <b>Piazza, V.;</b> Tagliafierro, G.	Involvement of ACh in settlement process of <i>Balanus amphitrite</i>	
<b>Gallus, L.;</b> <b><u>Faimali, M.;</u></b> Piazza, V.;; <b>Tagliafierro, G.;</b> Geraci, S.	Serotonin neurotransmitter in <i>Balanus amphitrite</i> cyprids and its putative role in settlement	
<b><u>Heede, Monja;</u></b> Wahl, Martin	The Neighborhood effect: Larval settlement patterns in waters of different origin	

<b><u>Jouuchi, Tomoyuki;</u> <u>Kitamura, Hitoshi</u></b>	Inducing effect of microbial films on the larval settlement of the barnacle, <i>Balanus amphitrite</i>
<b><u>Tomoda, Keijiro;</u> <u>Taniguchi, Atsunori;</u> <u>Kitamura, Hitoshi</u></b>	Sessile organisms on the artificial reef made of coal-fly ash concrete blocks placed at depth of 80 m in the coast of Nagasaki, Japan
<b>NATURAL ANTIFOULING MECHANISMS</b>	
<b><u>Kitano, Yoshikazu;</u> <u>Nogata, Yasuyuki;</u> <u>Shinshima, Kyouji;</u> <u>Yoshimura, Erina;</u> <u>Chiba, Kazuhiro;</u> <u>Tada, Masahiro;</u> <u>Sakaguchib, Isamu</u></b>	Synthesis and Antifouling Activity of 3-Isocyanotheonellin and Its Analogues
<b><u>Nogata, Yasuyuki;</u> <u>Yoshimura, Erina;</u> <u>Shinshima, Kyouji;</u> <u>Kitano, Yoshikazu;</u> <u>Sakaguchia, Isamu;</u></b>	Antifouling compounds against Barnacle <i>Balanus amphitrite</i> Larvae from the Marine Sponge

TIME	<b>WEDNESDAY</b>			
<b>8:15</b> to <b>8:55</b>	<b>Location: Auditorium</b>			
	<b>AUTHORS</b>		<b>TITLE</b>	
	<u>Armistead, Paul</u> Chrisey, Linda McElvany, Stephen	Research and Development in Marine Biofouling Control at the Office of Naval Research		
	<b>SESSION A</b> Location: Auditorium		<b>SESSION B</b> Location: Room 206	
<b>9:00</b>	<b>FOULING RELEASE &amp; MINIMALLY ADHESIVE SURFACES</b> (AM SESSION) Session Chairs: <b>Bob Brady, Jim Callow, &amp; Maureen Callow</b>		<b>NATURAL ANTIFOULING MECHANISMS</b> (AM SESSION) Session Chairs: <b>Peter Steinberg &amp; Rocky de Nys</b>	
	<b>AUTHORS</b>	<b>TITLE</b>	<b>AUTHORS</b>	<b>TITLE</b>
	Keynote Speaker: <u>Gay, Cyprien</u>	Some fundamentals of adhesion in synthetic adhesives	<u>Ferrari, Gabriele M.</u> ; Braekman, J.C.; Plehiers, M.; Klijnstra, J.W.; Overbeke, J.C.; Vos, M.; Kramer, J.; Kugler, M.; Kretschik, O.; Silvagno, V.; Ricci, M.; Croquette, J.; Quiniou, F.; Arzul, G.	The Camellia project: from natural products to model antifouling coatings.
<b>9:20</b>			<u>Burgess, Dr. J. Grant</u>	The Development of Marine Natural Product Based Antifouling Paints
<b>9:40</b>	<u>Chaudhury, Manoj K.</u> Vorvolakos, Katherine	Roles of Interfacial Chemistry and Mechanics in Release Phenomena	<u>Matias, J</u> Mary, A.	On the Antifouling Properties of Menthol and Related Compounds. Results from Poseidon's Natural Bioproducts Screening Program
<b>10:00</b>	<u>Singer, I.L.</u> Patterson, M. Lakrou, H.	Barnacle Removal from Silicone Coatings in Shear and Pull off Tests	<u>Steinberg, Peter D</u> de Nys, Rocky	On the generality of seaweed natural antifoulants
<b>10:20</b>	<u>Callow, James A.</u> Finlay, John A. Callow, Maureen E.	Adhesive Properties of Algal Spores and Release Mechanisms	<u>Meyer, W.</u> Baum, C. Wirth, U. Bollhorn, M.	General defense mechanisms against bio-coating of the integument in non-cetacean marine mammals
<b>10:40</b>	<b>REFRESHMENT BREAK</b>			

	<b>SESSION A</b> Location: Auditorium		<b>SESSION B</b> Location: Room 206	
<b>11:00</b>	<u>Kavanagh, Christopher J.</u>	Effect of Coating Thickness on Adhesion of Marine Invertebrates to Silicone	<u>Baum, C.</u> ; Simon, F.; Meyer, W.; Fleischer, L-G.; Siebers, D.; Kacza, J.; Seeger, J.	Surface properties of the skin of delphinids
<b>11:20</b>	<u>Berglin, Mattias</u> Gatenholm, Paul	The Barnacle Adhesive Plaque: Morphological and Chemical Differences as a Response to Substrate Properties	Scardino, Andrew <u>de Nys, Rocky</u> Steinberg, Peter	Microtopography of shell surfaces as a defence against fouling in molluses
<b>11:40</b>	<u>Wiegemann, Maja</u> Watermann, Burkard	Peculiarities of barnacle adhesive cured on non-stick surfaces	Lee, On On <u>Qian, Pei-Yuan</u>	Chemical control of bacterial epibiosis in the red sponge Mylae adherence: phylogenetic analysis of benthic bacterial isolates and their susceptibility to sponge derived compounds.
<b>12:00</b>	<u>Kowalewski, Tomasz</u>	In Situ Atomic Force Microscopy Studies of Wettability of Polymer Surfaces	Harder, Tilmann Lau, Stanley C. K. Dobretsov, Sergey Fang, Tsz K. <u>Qian, Pei-Yuan</u>	Chemical control of bacterial epibiosis in the soft coral Dendronephthya sp.: phylogenetic analysis of benthic bacterial isolates and their susceptibility to coral derived compounds.
<b>12:20</b>	<u>Gardella, Jr., Joseph A.</u> ; Hawkrigde, Adam M.; Tulevski, George; Hou, Yuanxue; Mahoney, Christine M.; Nowak, Richard W.; Chen, Lu; Toselli, Maurizio; Lee, Won Ki	The Surface Structure and Reorganization of Siloxane and Fluorocarbon based Polymers: Effects of Polymer Properties on Surface Properties	Dobretsov, Sergey <u>Harder, Tilmann</u> Qian, Pei-Yuan	Deterrence of larval metamorphosis by the green macroalga Ulva reticulata: the inhibitory effect of bacterial and algal metabolites.
<b>12:40</b>	<b>LUNCH</b>		<b>LUNCH</b>	

	<b>SESSION A</b> Location: Auditorium		<b>SESSION B</b> Location: Room 206	
<b>13:40</b>	<b>FOULING RELEASE &amp; MINIMALLY ADHESIVE SURFACES</b> <b>Session Chairs: Bob Brady, Jim Callow, &amp; Maureen Callow</b>		<b>LUNCH</b>	
	<u>Brennan, A. B.</u> Estes, T.; Feinberg, A.; Gibson, A.; Seegart, C.; Wilson, L.	Bioadhesion - Topographically or Chemically Mediated?		
<b>14:00</b>	Stein, Judith <u>Darkangelo Wood, Christina</u> Truby, Kathryn Holm, Eric Weibe, Deborah Smith, Celia Swain, Geoff Kavanagh, Chris Kovach, Brett Meyer, Anne Vorvolakos, Katherine Ortiz, Christine Montemarano, Jean	Why Don't Barnacles Stick to Silicones?	<b>NATURAL ANTIFOULING MECHANISMS</b> <b>Session Chairs: Peter Steinberg &amp; Rocky de Nys</b>	
			<u>Faimali, Marco</u> Geraci, Sebastiano <u>Secpic, Kristina</u> Turk, Tom	Antifouling activity of polymeric 3-alkylpyridinium salts isolated from the marine sponge Reniera sarai (Pulitzer Finali)
<b>14:20</b>	<u>Afsar, Anisul</u> de Nys, Rocky Steinberg, Peter	The effects of low surface energy coatings on behaviour, settlement, adhesion strength and morphology of invertebrate larvae and algal spores	<u>Hellio, Claire</u> Andriamialisoa, Zo Giraud, Michel Bremer, Graham Beupoil, Claude Pons, Anne-Marie Bourgougnon, Nathalie Le Gal, Yves	Macroalgae of the Brittany shores: antifouling activities and potential use for paints.
<b>14:40</b>	<u>Yu, Jian</u>	Biodegradation-based Polymer Surface Erosion and Surface Renewal for Foul Release at Low Ship Speeds	<u>Rittschof, Dan</u> Lai C. H. Kok L. M. Teo, S.L.M.	Pharmaceuticals as Antifoulants for Barnacles
<b>15:00</b>	<b>REFRESHMENT BREAK</b>		<u>da Gama, Bernardo;</u> Pereira, Renato C.; Soares, Angelica R.; Teixeira, Valeria L.; Yoneshigue-Valentin Y.	Is the mussel test a good indicator of antifouling activity? A comparison between laboratory and field assays
<b>15:20</b>			<b>REFRESHMENT BREAK</b>	

	<b>SESSION A</b> Location: Auditorium		<b>SESSION B</b> Location: Room 206	
<b>15:30</b>	<u>Webb, Arthur A.</u> Foster, Richard L. Ingle, Mark W. Kaznoff, Dr. Alexis I.	Development in Easy Release Antifouling Coatings Technology	<b>REFRESHMENT BREAK</b>	
<b>15:50</b>	<u>Ober, Christopher K.</u> ; Kang, Seok Ho; Andruzzi, Luisa; Younglood, Jeffrey P.; Li, Xuefa; Senaratne, Wageesha; Hexemer, Alexander; Kramer, Edward J.; Callow, Jim A.; Finlay, John A.; Callow, Maureen E.	Poly(ethylene glycol) and Fluorocarbon Containing Polymers for Biofouling Resistance and Biofouling Release	<b>BIODEGRADATION OF WOOD (PM SESSION) Session Chair: Gareth Jones</b>	
			<u>Jones, E.B. Gareth</u> Wen, Luo Vrijmoed, L.L.P.	Ligno-cellulose degradation by marine fungi
<b>16:10</b>	<u>Fernández Estarlich, F.</u> Eaton, P. J. Ewen, R. J. Fletcher, R. L. Lewey, S Nevell, T. G.	The effects of incorporated silicone oils and calcium carbonate on the surface properties and antifouling performance of a silicone elastomer	Oevering, P. Pitman, P.J.	<i>Pselactus spadix</i> – a weevil attacking marine timber structures
<b>16:30</b>	<u>Brady, Jr., R. F.</u>	Elastomeric Fluorinated Polyurethane Coatings for Nontoxic Fouling Control	Pitman, P.J. Jones, E.B.G. Jones, M.A.	The biology of the wharf borer <i>Narcedes melanura</i>
<b>16:50</b>	<u>Schmidt, Daniel</u> Giannelis, Emmanuel P.	Silicone Nanocomposites as Minimally Adhesive Polymer Coatings	<b>SESSION CLOSE</b>	
<b>17:10</b>	<u>Youngblood, Jeffrey P.</u> ; Andruzzi, Luisa; Senaratne, Wageesha; Ober, Christopher K.; Callow, Jim A.; Finlay, John A.; Callow, Maureen E.	Ether linked, Side Chain Poly (ethylene glycol) and Fluorocarbon Containing Polymers With Controlled Architecture for Biofouling Resistance and Release		
<b>17:30</b>	<u>Wynne, Kenneth J.</u>	Nontoxic Fouling Release Coatings: Prospects for Improvements		
<b>17:50</b>	<b>SESSION CLOSE</b>			



TIME	<b>THURSDAY</b>			
<b>8:40 to 9:15</b>	<b>Location: Auditorium</b>			
	<b>AUTHOR</b>	<b>TITLE</b>		
	<u>Whitlatch, Robert B.</u>	On the Ecology and Natural History of Macrofaunal Organisms Fouling Vessel Surfaces		
	<b>SESSION A</b> Location: Auditorium		<b>SESSION B</b> Location: Room 206	
<b>9:20</b>	<b>INVASIVE SPECIES</b> Session Chairs: <b>Eric Holm &amp; Richard Everett</b>		<b>BIOCIDES, COBIOCIDES, &amp; DETERRENTS</b> Session Chair: <b>Pat Turley</b>	
	<b>AUTHORS</b>	<b>TITLE</b>	<b>AUTHORS</b>	<b>TITLE</b>
	<b>OPENING REMARKS</b>		<u>Seabrook, Guy</u> Lindburg, Bob	Nontoxic phytochemical fouling control for the marine industry
<b>9:40</b>	<u>Ruiz, Gregory</u>	Ships as Vectors: Assessing the Role of Hull Fouling in Biological Invasions	<u>Nys, Jan</u> Van Der Flass, Mark Goodwine, Bill	New metal free biocides for anti-fouling paints. ECONEA™ 028 a safe alternatives for the future
<b>10:00</b>			<u>Willemsen, P. R.</u>	A bioassay system for the semi-high throughput screening of novel antifouling compounds
<b>10:20</b>	<b>REFRESHMENT BREAK</b>			
<b>10:50</b>	<u>Bohlander, Gerard</u> Montemarano, Jean	Marine Fouling Characteristics and Performance Effects on U.S. Navy Hulls	<u>Schneider, Ib</u> Allermann, Knud	Enzymes as antifouling agents in marine coatings for ships and offshore constructions
<b>11:10</b>	<u>Forsberg, R.</u> Baier, R. Meyer, A. Dobbs, F. Doblin, Martina Drake, lisa Jenkins, P.	Internal Hull Biofouling: Effects of Surface Properties and Resuspension of NO-BOB Sediments	<u>Guo, Ipin</u> <u>Jacobson, Andy</u>	The Environmental Fate of the Marine Antifoulant 4,5-Dichloro-2-(n-octyl)-4-isothiazolin-3-one (DCOI).
<b>11:30</b>	<u>Drake, Lisa A.</u> Baier, Robert E. Doblin, Martina A. Dobbs, Fred C. Johnson, William Meyer, Anne E. Ruble, Parke A.	Global Dispersal of Microorganisms and Pathogens: Biofilms Inside Ballast-Water Tanks	<u>Satpathy, K.K.</u> Jebakumar, K.E. Kannan, S.E.	Biofouling & its control strategy in the cooling water of Prototype Fast Breeder Reactor
<b>11:50</b>	<u>Lewis, John A.</u>	Hull fouling as a vector for the introduction of exotic marine species to Australia	Faimali, Marco Garaventa, Francesca Magillo, Francesca Cozzolino, Davide <u>Geraci, Sebastiano</u>	Efficacy and toxicity of Zinc pyrithione as antifouling biocide: a multi-bioassays approach.

	<b>SESSION A</b> Location: Auditorium		<b>SESSION B</b> Location: Room 206	
<b>12:10</b>	<u>Godwin, L. Scott</u>	Hull Fouling of Maritime Vessels as a Pathway for Marine Species Invasions to the Hawaiian Islands	<u>Brizzolara, Robert A.</u> Walch, Marianne Nordham, David J. Lennen, Rebecca Hoover, Scott Mazzola, Michael Burnett, Evan Simmons, Ron	Non-Chemical Biofouling Control in Heat Exchangers and Seawater Piping Systems Using Acoustic Pulses Generated by an Electrical Discharge
<b>12:30</b>	<b>LUNCH</b>			
<b>13:40</b>	<b>INVASIVE SPECIES</b> <b>Session Chairs: Eric Holm &amp; Richard Everett</b>		<b>ASSESSMENT OF RISK</b> <b>Session Chair: tba</b>	
	<u>Coutts, Ashley D. M.</u> Taylor, Michael D.	Managing biosecurity risks from hull fouling: a perspective from down under	<u>Paquin, P.R.</u> Mathew, R. Santore, R. Di Toro, D.M.	Consideration of Bioavailability in Assessing Exposure and Effects of Antifouling Agents
<b>14:00</b>	<u>Zabin, Chela J.</u> Wasson, Kerstin	Intraregional transport of marine biological invaders: a case study from California	<u>Poremski, Heinz-Jochen</u> Beulshausen, Tessa	OSPAR and EC – Methodology for the Selection and Prioritization and the Risk Assessment of Hazardous Substances and Antifoulings in the Marine Environment
<b>14:20</b>	<u>Hayden, Barbara J.</u> Inglis, Graeme J. James, Philip	Vessel hulls: a variable vector of nonindigenous species	<u>Mackie, Carol</u>	Incorporation of Bioavailability of Copper in Risk Assessments and Setting Water Quality Standards
<b>14:40</b>	<u>Floerl, Oliver</u> Inglis, Graeme J.	Enhanced settlement of fouling organisms on boat hulls following in-water hull cleaning: implications for the spread of marine fouling species	<u>Jacobson, A.</u>	The Fate of the Marine Antifoulant DCOI applied to a Vessel.

	<b>SESSION A</b> Location: Auditorium		<b>SESSION B</b> Location: Room 206	
<b>15:00</b>	<u>Lieberman, Stephen H.</u> He, Li-Ming Timothy, Adam	Use of automated image processing coupled with an artificial neural network based classifier for identifying fouling organisms on ship hulls.	<b>SESSION CLOSE</b>	
<b>15:20</b>	<b>REFRESHMENT BREAK</b>			
<b>15:50</b>	<u>Cassidy, Maria</u> Jones, Liz	Hull fouling and Cleaning in New Zealand		
<b>16:10</b>	<u>O'Brien, Chris</u>	Management of a biofouling threat		
<b>16:30</b>	<u>Hayes, Keith R.</u>	Identifying hazards in complex ecological systems - Part 2: Infection Modes and Effects Analysis for biological invasions		
<b>16:50</b>	<u>Minchin, Dan</u> Gollasch, Stephan	Fouling and ships' hulls: how spawning events may result in exotic species spread.		
<b>17:20</b>	<b>CLOSING REMARKS FOR INVASIVE SPECIES</b>			
<b>18:00</b>	<p><b>CONGRESS DINNER</b></p> <p><b>Location: University</b></p>			

**ABSTRACTS  
IN ALPHABETICAL ORDER OF  
AUTHOR**

### **The effects of low surface energy coatings on behaviour, settlement, adhesion strength and morphology of invertebrate larvae and algal spores**

Afsar Anisul<sup>1,2</sup>, de Nys Rocky<sup>3</sup> and Steinberg Peter<sup>1,2</sup>. <sup>1</sup>Centre for Marine Biofouling and Bio-Innovation, The University of New South Wales, Sydney, NSW 2052, Australia. <sup>2</sup>School of Biological, Earth and Environmental Sciences, The University of New South Wales, Sydney, NSW 2052, Australia. <sup>3</sup>School of Marine Biology & Aquaculture, James Cook University, Townsville, Queensland 4811, Australia.

In this study the effects of low surface energy coatings containing wax and silicone oil were tested on the behaviour, settlement, adhesion strength or growth of the barnacle *Balanus amphitrite amphitrite* Darwin, bryozoan *Bugula neritina*, the green alga *Ulva lactuca* Linnaeus, the red alga *Polysiphonia* sp. and the brown alga *Ectocarpus* sp. Settlement of barnacle cyprid larvae and *Ulva* gametes were strongly inhibited on coatings containing silicone oil at concentration of 5% or above. However, the settlement of bryozoan larvae and *Polysiphonia* & *Ectocarpus* spores were not inhibited. The behaviour of barnacle cyprid larvae was altered on coatings containing 5% and above silicone oil with cyprids assuming an inverted position, preventing adhesion. Adhesion strengths of settled barnacles were also reduced on coatings containing silicone oil. The growth of *Ulva* gametes and *Ectocarpus* spores were reduced on coatings containing silicone oil. Though suitable for some applications, these coatings indicate a wide variance in response by different fouling organisms.

### **UNS N06059, a highly alloyed ternary Ni-Cr-Mo alloy, solves crevice corrosion problems in marine environments**

Agarwal D.C., Krupp VDM Technologies, 11210 Steeplecrest,#120, Houston, Texas 77065-4939, USA

Materials used in the marine industry, such as the U.S. Navy and offshore platforms, encounter numerous corrosion problems. The corrosion problems of primary concern are uniform corrosion, localized corrosion (pitting and crevice), stress corrosion cracking, galvanic corrosion, corrosion fatigue, and erosion corrosion. The major concern and mode of failure in marine environments has been pitting corrosion but more so crevice corrosion. A large amount of corrosion data has been generated over the last few decades and is well publicized in the technical literature. Even though the precise determination of all corrosion variables as related to site specific marine corrosion is not fully categorized, there is ample laboratory, field, and case history experience available to make cost effective and functionally reliable maintenance-free selection. Even though several stainless steels and a few nickel based alloys have shown promise and are used in marine environments, under very severe crevice corrosion conditions, most of these have suffered from localized crevice attack. The search for alloys that are essentially immune to crevice corrosion attack in marine environment led the industry to increase the alloy content of nickel based alloys primarily in chromium and molybdenum. One such alloy, UNS N06059 having a typical chemical composition of 59% nickel, 23% chromium, 16% molybdenum and iron levels of less than 1%, appears to have fulfilled this need. Extensive laboratory and field tests by various companies and corrosion laboratories in USA, U.K., Norway, France and the U.S. Navy have shown this alloy to be essentially immune to crevice corrosion attack. Based on the excellent crevice corrosion resistance of this alloy, the U.S. Navy has tested this alloy for a prototype component in a butterfly valve and is conducting further tests for overlay welding application as a superior alternative to alloy 625 and C-276. This alloy is also being tested for fastener applications in cold reduced conditions (bar product) to yield strength levels of 110-130 KSI and 150KSI minimum. Alloy UNS N06059 filler metal has been successfully used in North Sea offshore platforms to combat localized corrosion on flanges and other equipment.

This paper presents a brief description of this alloy's development, its physical and metallurgical characteristics and its localized corrosion resistance data from various test programs.

### **Poison free only, please.....**

Kjell K. Alm President, SealCoat Group. Shanghai.

Since 1992 we have been developing the use of micro fibres as a mechanical method to combat macro fouling. Whilst much of the scientific and industrial community have been looking to find solutions to replace tributyltin (TBT) based antifouling paints with either longer performing copper solutions or more environmentally acceptable biocides we have focused our research and development solely towards a completely poison free solution. With the International Marine Organisations (IMO) ruling on the ban of TBT now effectively in place, considerable pressure from NGO's, Governments and elements of the shipping community is now being applied to the copper based alternatives that the manufacturers are bringing to market. The pressure is being applied from two key fronts. Firstly the environment. Despite claims that these new alternatives are not poisonous and that copper is a natural material, it is quite clear that whilst this may be so, in limited quantities, where it is introduced in concentrations and released without full control of dispersion, copper is detrimental to the environment. Secondly cost. New solutions are proving expensive and there is a fear from within the shipping community that by the time paint manufacturers can offer an efficient price level that such solutions will certainly be banned and once again the shipping community will be forced to pay for new products that may still not meet their efficiency needs. At SealCoat we have proven that a complete poison free solution is possible and efficient. In April of 2002, perhaps one of the most eminent groups from the shipping community recognized the work, we have done, the success we have had at both scientific and commercial level and the enormous positive impact that SealCoat AF, our poison free coating will have on the environment. As such we were awarded the Seatrades Award 2002 for the category 'Countering Marine & Atmospheric Pollution.' Amongst the Judges is The Chairman of the IMO and many of the leaders of the worlds largest and most influential shipping institutions. The award was presented to our team at a Gala Dinner in London, by the Guest Of Honour, HRH The Princess Royal. It is clear that whichever path the scientific community and manufacturers pursue it must be one that leads to a poison free solution. Anything less may be of great scientific interest but will have little commercial future.

### **Research and Development in Mairne Biofouling Control at the Office of Naval Research**

Armistead,Paul, Chrisey Linda, McElvany Stephen.

The US Navy's Office of Naval Research is supporting the research and development of environmentally friendly marine hull coatings. The Navy is seeking new ship coatings capable of meeting current and anticipated performance specifications (e.g., 12-year repainting cycle, compatibility with existing spray systems) and global regulatory standards, which will enable the Navy to train and operate worldwide, in an unrestricted fashion.

Specific objectives of the ONR program include basic and applied research on the development of novel foul-release polymeric coatings (elastomers, nanostructured coatings, polymers with patterned surface chemistries, fluoropolymers, coatings with tethered biocides); surface characterization; fracture mechanics/tribological studies of organism adhesion and debonding processes; and interactions of biofouling organisms with surfaces and with each other. A variety of laboratory and field exposure-based tests are used to characterize the performance of these coatings, and will be described in the presentation. The ONR program is unique in that it tightly couples the study of biofouling biology/ecology with the development and characterization of novel surfaces, in an iterative fashion, to maximize the potential for developing a non-toxic coating that exhibits desired fouling-control and durability qualities. The ONR coatings program is addressing the Navy's intermediate through long-term coating needs for environmentally protective yet operationally acceptable marine hull coatings.

## **Corrosion Protection of Ballast Tanks by Surface-Active-Inhibitor-Based Displacement of Aquatic Nuisance Biofilms**

Baier Robert, Forsberg Robert, Meyer Anne, University at Buffalo, 110 Parker Hall, Buffalo, NY 14214-3007

Internal corrosion is a problem for ballast compartments, and control of ballast water or biofilm-transported bioinvasive organisms requires proof that applied control measures do not exacerbate corrosion processes. Classification societies will not issue assurances of safe operation without such proof. Personal inspections of actual ballast tank compartment walls, struts and other structures, and analyses of test coupons suspended in ballast tanks during trans-oceanic voyages lasting from weeks to months, with and without re-ballasting, document the concurrent presence of biofilm (slime/sediment) formation and active corrosion on all steel surfaces not protected with compliant, biofouling-resistant coatings. Infective microorganisms, and other pathogenic vectors, can require more than 1000X concentrations for their disinfection than these same organisms in the volume phase. We are exploring the application and benefits of periodic displacement of biofilms into the planktonic bulk for routine treatment and discharge. The biofilm-displacement process employs a surface-active concentrate, with a corrosion inhibitor, for addition to any available service water that can be sprayed onto the ballast compartment walls. The surface-active formulation spontaneously penetrates and spreads into cracks, crevices, and prior-corroded regions. Chlorine minimization goals for the Great Lakes region prompt our current studies of the application of SADS (Surface-Active Displacement Solutions) to ballast tank simulating steel coupons and panels, bare, painted, and biofouled, prior to exposure to high concentrations (~1000ppm) of NaOCl as a corrosion challenge. The best-performing coatings are those based on silicone-modified epoxy chemistries, that provide both compliance and easy-release (~50psi spray force required for biofilm displacement). A disadvantage is that a component of the best-performing SADS formulation (employing n-butanol and an amphipathic betaine) swells the paints during very long (>24 hours) contact times --an unlikely event in the field-- and can cause delamination. The preliminary observation is that the SADS residues continue to protect steel coupons from NaOCl-accelerated corrosion even in the regions of coating delamination. A major challenge to the testing program is to adequately simulate the ballast tank environment, where there is long-term quiescence interrupted by short periods of turbulent influx/efflux of seawater contaminated with biological and harbor pollutants, and the products of biofouling and corrosion processes are not frequently removed.

### **Surface properties of the skin of delphinids**

Baum Christof<sup>1,2</sup>, Simon Frank<sup>3</sup>, Meyer<sup>2</sup> Wilfried, Fleischer<sup>4</sup> Lutz-Günther, Siebers<sup>1</sup>, Dietrich, Kacza<sup>5</sup> Johannes, Seeger<sup>5</sup> Johannes, Alfred Wegener Institute Foundation for Polar and Marine Research, Bremerhaven, Germany<sup>1</sup>, Anatomical Institute, Department of Histology and Embryology, School of Veterinary Medicine, Bischofsholer Damm 15, 30173 Hannover, Germany<sup>2</sup>, Institute of Polymer Research Dresden, Hohe Straße 6, D-01069 Dresden, Germany, Institute of Food Technology and Center of Biotechnology, Technical University of Berlin, Amrumer Str. 32, D-13353 Berlin, Germany<sup>4</sup>, Institute of Veterinary Anatomy, University of Leipzig, An den Tierkliniken 43, D-04103 Leipzig, Germany<sup>5</sup>

In delphinids small biofoulers are potentially challenged to high shear water flow and liquid-vapor interfaces of air bubbles during jumping. In the present study we investigated the skin of the pilot whale, *Globicephala melas*, with emphasis on topological, biochemical and rheological properties of the skin surface enhancing the efficiency of self-cleaning based on the common behaviour of dolphins.

The surface properties were characterized combining rheological measurements with cryo-scanning electron microscopy (C-SEM), transmission electron microscopy (TEM), photoelectron spectroscopy (XPS), and enzyme histochemistry.

The results obtained show that the skin of the pilot whale exhibited only marginal loads of biofoulers. The skin surface was even and smoothed by a hydrated jelly material alternating with embedded lipidic droplets. The surface topology demonstrated displayed no particular microniches in the size of biofoulers. The jelly material derived from deeper intercellular space between stratum corneum lamellae and was enriched by various hydrolytic enzymes. Unlike the mucoid-based properties of marine fouling polymers, the rheological measurements revealed the high elasticity in combination with high energy dissipation rates of the jelly material of the dolphin skin assembled from covalently cross-linked aggregates. XPS measurements carried out on deep-frozen skin samples and the bare jelly material showed the presence of free amino groups and lipidic ester groups, which were dominant chemical features of the skin surface.

Since cetaceans lack skin glands the protective power of the skin was considered to be based on the biochemical adaptation of the corneocytes. In regard to the higher shear resistance of the jelly material collected from the stratum corneum contrasting to the biophysical properties of mucoid-based biopolymers, we concluded that the gel is not a substitute of mucus, can withstand higher shear regimes and evens the skin surface. The retention of hydrolytic enzymes incorporated within the gel to some extent broadens the self-cleaning abilities of the dolphin integument by degrading non-dolphin biopolymers. Moreover, the hydrolytic enzymes initiate the desquamation process and probably remove contaminations as large as the desquamating cells (50x80 µm). Since the skin surface exhibits less contact area and microniches biofoulers may adhere to or hide within, we argue that biofoulers challenged to air bubbles or high shear water flow during jumping are easily removed from the skin surface. In this connection, the implications to the self-cleaning abilities are discussed, as based on chemical heterogeneity of the amphiphilic skin surface of the pilot whale and the fouling polymers of conditioning films in relation to the hydrophobic liquid-vapor interfaces of air-bubbles and hydrophilic water flow.

We thank Dr. D. Bloch and Dr. H.-P. Joensen, University of the Faroe Islands, for their help in specimen collection from legal harvest. This study was supported by a grant of the Deutsche Forschungsgemeinschaft (ME 1755/1-1 and 1-2).



### **The role of biofilm matrix in the fouling process**

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The growth of bacterial biofilms, which frequently leads to fouling, is considered to be a result of complex processes involving attachment of cells facilitated by the production of extracellular polymeric substances (EPS). Bacterial EPS are a mixture of macromolecules varying with microbial species and environmental conditions. These macromolecules include polysaccharides, proteins, lipids and nucleic acids and are key constituents of the biofilm matrix. EPS material is also released into the bulk phase of surrounding liquid as planktonic or “free” EPS. Bacterial exopolymers, including LPS which are associated with cells of Gram negative bacteria and which can be a part of the EPS material, are able to form a conditioning layer on metallic surfaces. The presence of such a layer influences the irreversible bacterial attachment, either promoting or hindering a subsequent biofouling of the surface. The presence of physiologically diverse microbial species within biofilms facilitates diverse chemical-physical reactions which govern processes within fouling matrix. These include the consumption of oxygen, production of acids, sulfides and enzymes that promote the establishment of localized chemical gradients. It is documented that bacteria produce a wide range of enzymes *e.g.* hydrolytic and proteolytic enzymes, as well as lyases, able to interact with substrates beyond the cell wall. The chemical properties of biofilm matrix, *i.e.* the presence of different types of binding sites within exopolymers forming the matrix, promote association between EPS, extracellular enzymes and exogenous molecules. The majority of reports on monitoring enzyme expression in biofilms focuses on activities associated with sessile cells. Relatively few investigations attempt to elucidate activity within cell-free EPS material. Since the latter forms significant part of the fouling layer it is of interest to understand what type of enzyme-regulated processes could take place to render such a layer damaging or protective to the underlying substratum. This communication will present an overview on the effect of EPS conditioning layers on the adhesion of marine bacteria to metallic substrata under aerobic and anoxic conditions and will discuss the activity of enzymes within biofilm matrix. Emphasis will be placed on demonstrating the aspect of species specificity in both above phenomena using as an example marine strains of sulphate-reducing bacteria.

### **Microbial “footprints” of *Pseudomonas aeruginosa* – analysis with FITC-labeled lectins.**

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Understanding the mechanisms of microbial adhesion at molecular level requires the identification and characterization of the nonspecific adhesive biopolymers responsible for the attachment of microbes to inanimate surfaces. Microbial footprints, the bacterial structures left on a substratum after removal of attached microbes (Neu & Marshall, Biofouling 3, 101-112, 1991), present an efficient mean for obtaining the full complement of adhesive biopolymers of microorganisms. The plane of shear that separates the compounds present in footprints from the rest of the cell is located somewhere in the outer region of the cell surface. Footprint components are therefore compounds whose adhesive contact with the substratum is stronger than the cohesive interlocking with the cell surface. This work presents the results obtained in the analysis of footprints of *Pseudomonas aeruginosa* formed on hydrophilic (glass) and hydrophobic (silanized glass) substrata with FITC-labeled lectins. Lectins are proteins which bind specifically to particular carbohydrates. Lectins from *Grifonia simplicifolia* did not bind to either cell surfaces or footprints. The binding pattern obtained with the lectins Concanavalin A and *Ulex europeus* UEA I was similar. Both lectins bound to clusters of biopolymers on cell surfaces and in footprints. The lectins from *Triticum vulgare* produced weak labelling of footprints on hydrophilic surfaces, but strong labeling of the same structures on hydrophobic surfaces suggesting that the oligosaccharides detected by these lectins were present in larger quantity in footprints formed on hydrophobic surfaces. *Triticum vulgare* lectins also revealed the presence of fibrous materials not visible in phase contrast microscopy on hydrophilic surfaces. The fibers were not detected on hydrophobic surfaces. Lectins from *Phaseolus vulgaris* labeled clusters of materials in footprints that originated from cells attached sideways on hydrophilic surfaces. The same footprints were, however, labeled in uniform fashion on hydrophobic surfaces. Cells attached vertically via an endpoint contact had the contact area labeled very strongly with this lectin. The results obtained in the lectin-labelling experiments suggest that the composition of the carbohydrate components in footprints varies greatly depending on whether the footprints were formed on hydrophilic or hydrophobic surfaces.

### **Challenges from the IMO AFS Convention**

Berg, Eivind A. The IMO AFS Convention has made 2002 a transitional year for the antifouling paint industry. More than 70% of the marine antifouling paint volume is currently TBT containing. Also for the shipping industry and authorities, adapting to the convention represent challenges.

Industry has contributed extensively during the long process of establishing the convention text. Expert's input will greatly benefit development of outstanding guidelines on surveys, certification, inspection and port state control. More than 10 environmental and industry NGOs have taken part in antifouling working and drafting groups at IMO meetings. The paint, shipping and classification industries have also been represented in national delegations.

Authorities are now challenged with adopting national (or EU) legislation to make ratification possible. Prior to entry into force and the introduction of the International Anti-fouling System Certificate, flag states also need systems to facilitate ship owners' to documentation their vessel's compliance.

The shipping industry, classification societies and dockyards must now understand, plan and prepare for the effects and opportunities created by last year's adoption of the convention. The paint industry needs to show to the market that the best TBT free systems provide the same degree of fouling protection as TBT paints. Customers must also be made confident that a compliant paint system is accepted as such by all authorities when enforcement of the convention begins. Paint suppliers are finally challenged with avoiding carrying a surplus of TBT paint becoming toxic waste needing expensive disposal.

### **Surface structures of marine organisms and their influence on fouling**

Bers Valeria and Wahl Martin, Institute of Marine Science, Research Division 3, Experimental Ecology II, Duesternbrooker Weg 20, 24105 Kiel, Germany

Marine organisms often combine physical, mechanical or chemical mechanisms to prevent fouling by other organisms.

Recent studies (Lenz 1997; Andersson *et al.* 1999, Berntsson *et al.* 2000) have shown that microtextured surfaces (1-100  $\mu\text{m}$ ) – either living or non-living – may reduce fouling.

In this study we investigate the role of surface microtopography (< 500 $\mu\text{m}$ ) of different marine invertebrate species, such as crustaceans, echinoderms and bivalves, as a possible contribution to their multiple antifouling strategies.

In our field experiments, we are going to expose high resolution epoxy resin replicates of invertebrate surfaces to natural fouling. Abundances of recruits will be determined and compared to those on untextured control surfaces in order to detect the influence of the microtopography on fouling rates.

### **The Barnacle Adhesive Plaque: Morphological and Chemical Differences as a Response to Substrate Properties**

Berglin Mattias and Gatenholm Paul, Biopolymer Technology, Department of Polymer Technology, Chalmers University of Technology, SE-412 96 Sweden

This paper reports the differences in structure and composition of the adhesive plaque biosynthesized by the barnacle, *Balanus Improvisus*, growing on poly(methylmethacrylate) (PMMA) and polydimethylsiloxane (PDMS). Barnacles growing on the elastic PDMS synthesized a rubbery cement matrix with granular morphology, as determined with atomic force microscopy (TM-AFM). Three distinct proteins and some minor polypeptides were found with SDS-PAGE analysis when the cement plaque was dissolved in a buffer containing 0.5 M dithiothreitol and 7 M guanidine hydrochloride. No calcium could be detected in the cement matrix with X-ray photoelectron spectroscopy (ESCA), X-ray mapping with the EPMA/EDS technique or infrared spectroscopy (FT/IR). This should be compared with the hard, continuous cement plaque produced by barnacles growing on the glassy PMMA polymer. Single granules could be detected with TM-AFM but most of them had merged together forming a continuous film. No proteins could be dissolved when cement plaque from PMMA was treated in the same buffer used for PDMS plaque. Calcium was detected with EPMA/EDS and FT/IR analysis showed that calcium was incorporated as calcite, one of the crystal polymorphs of  $\text{CaCO}_3$ . This adaptation of the adhesive plaque to substrate surface properties affects adhesion and fracture mechanics during release and thus affect the design of new innovative fouling-release coatings.

## **Copper – The Natural and Effective Antifouling Active Ingredient**

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Copper is the 29<sup>th</sup> element in the periodic table. It is ubiquitous in the natural world. It is a necessary micronutrient for the normal growth and life of organisms. Yet, when used correctly, it is an effective antifouling agent for marine vessels. Organisms have mechanisms to bioregulate copper as part of their normal metabolic processes. Copper concentration within organisms can vary significantly during natural biological cycles. Copper has been used for nearly 250 years as an antifouling agent, yet its presence in the marine environment due to antifouling coatings is extremely small compared to its natural occurrence and additions. After repelling organisms at the vessel surface, the cupric ion from copper containing antifouling coatings becomes significantly bioavailable within the surrounding marine environment. Relevant recent literature regarding the use of copper in antifouling as well as other use scenarios where copper is present will be discussed.

## **Marine Fouling Characteristics and Performance Effects on U.S. Navy Hulls**

Bohlander G.S. and Montemarano J.A., Naval Surface Warfare Center Carderock Division, 9500 MacArthur Blvd., West Bethesda, MD 20817

The U.S. Navy has 318 ships and submarines, all of which depend on the use of antifouling paints to retard the attachment and growth of marine fouling. The Navy has long-term service requirements from 5 to 12 years between dry-docking and painting, and experiences extended pier side time, where the majority of marine fouling occurs. There can be a significant propulsive fuel penalty and possible compromise of the ship's mission if the hull is allowed to foul. Perhaps the most well known benefit from the use of an effective AF paint is in the area of propulsive fuel savings. The accumulation of marine fouling on the hulls of ships increases the hydrodynamic drag, requiring the expenditure of more horsepower to move ships through the water. This increases propulsive fuel consumption. Ship trials have documented reductions of from 10 to 60% in propulsive fuel consumption as a result of removing marine fouling from a ship hull. The U.S. Navy propulsive fuel bill is approximately \$500M/year, of which about \$75M to \$100M is expended to overcome the increased drag to marine fouling. Underwater hull cleaning to remove marine fouling has been a standard process since 1978. A new hull cleaning system that also provides maintenance data and effluent capture during the cleaning process is being developed. A prototype system is being evaluated. Over the past 15 years, environmental regulations have driven new marine industrial coating developments and will continue to do so until EPA goals are achieved. Currently, mitigating levels of toxic constituents that are harmful to the environment (non-target organisms) are the primary regulatory emphasis for antifouling coating technologies.

## **Development and Demonstration of an Automated Paint Application Containment and Treatment System**

G.S. Bohlander and W. M. Thomas; Naval Surface Warfare Center, Carderock Division, West Bethesda, Md. 20817.

The Naval Surface Warfare Center (NSWC), Carderock Division is developing an automated paint application, containment, and treatment system (APACTS) for dry-docks painting operations. The system is designed to apply marine coatings to the hull and freeboard of US Navy ships, while collecting and treating paint over spray including hazardous air pollutants (HAPs), particulate materials (PM) and volatile organic compounds (VOCs). The development of technology for this program is sponsored by the U.S. Navy Office of Naval Research (ONR).

The project goal is to demonstrate that a semi-automated painting system can apply uniform layers of marine coatings on Navy ships' hulls at a production rate of up to 2500 ft<sup>2</sup>/hr, collecting and treating more than 95 percent of the over spray. This will provide environmental compliance and more uniform coatings application. Early demonstrations of key subsystems followed by incremental integration of the subsystems will ensure that the end product meets the Navy's ship painting needs and mitigate the technical risks involved.

The system, based on the use of a computer-modified man lift vehicle and a 6-degree of freedom robotic arm, has been designed and constructed. It was evaluated both at a contractor facility and at BMI shipyard in Baltimore, Md. The system was able to apply both epoxy and antifouling paints to a simulated ship hull structure. The paint transfer efficiency was over 95% and the capture efficiency of the particulate materials was 98%. Further shipyard trials are planned for 2002 with prototype deployment in Navy and commercial shipyards in 2003.

## **Marine Fouling Characteristics and Performance Effects on U.S. Navy Hulls**

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## **Underwater Hull Coating System Life Cycle Issues for 12-Year Extended Service**

Gerard S. Bohlander Naval Surface Warfare Center, Carderock Division, 9500 MacArthur Blvd., W. Bethesda, Md.  
20817

The U.S. Navy coats underwater ship hulls with commercial epoxy anticorrosive (AC) paints for corrosion protection, and commercial ablative antifouling (AF) cuprous oxide-based paints to repel marine fouling. These materials have been evaluated for Naval service in accordance with military specifications. These materials play a critical role in the life cycle management of Navy ships. There can be a significant propulsive fuel penalty and possible compromise of the ship's mission if the hull is allowed to corrode and foul. Until recently, the typical time between removal and replacement of these paints has been about 5 years. Improvements in marine coatings combined with the development of dry-dock and in-situ evaluation processes has enabled the Navy to extend the time between dry-docking for selected ships, including the aircraft carrier fleet, to 12 years. This work was sponsored by the Chief of Naval Operations (OP 42). The decision to retain the underwater hull coating system must be based on solid technical information including the thickness of the antifouling coating system during service and the condition of the anticorrosive coating. This process starts with comprehensive evaluation of the coating application, including surface preparation parameters and paint thickness surveys to assure the application process meets all requirements. The ship is then periodically evaluated afloat during the operating cycle to make certain the paint system is performing properly. NSWC Carderock has developed a remotely operated vehicle (ROV) to perform underwater hull evaluations on Navy ships. The advantages of using an ROV to deploy underwater sensors are the automated acquisition of data and information on the location of the data over the underwater hull. In addition the use of the ROV permits the observation of underwater hull conditions with minimum impact on ship routine. Over 35 ship evaluations have been conducted in support of extending the mission cycle of carriers and other surface ships. In addition, underwater cleaning for fouling removal, and in-water application of specialized AC paints to touch-up corrosion areas, provides the support necessary to achieve this extraordinary operating cycle. Ship mechanical systems, including shaft and rudder bearings, and valves and waster sleeves associated with cooling water suction and discharge are also evaluated for extended service.

### **Elastomeric fluorinated polyurethane coatings for nontoxic fouling control**

Brady, Robert F. Jr., 706 Hope Lane, Gaithersburg, MD 20878-1883 [Work performed in the Chemistry Division, Naval Research Laboratory, Washington, DC 20375-5342]

Nontoxic coatings intended to supplant toxic coatings have been investigated for many years. However, because every nontoxic coating put into sea water fouls, these coatings must be designed so that only a weak, easily-broken bond to fouling organisms can be formed. Two types of coatings are preeminent. Fluorinated coatings are tough, have low surface energy and resist fouling, but ultimately form a tight bond to fouling. This bond fails in shear, a relatively high-energy process. Silicone coatings are soft, relatively weak, and easily damaged or torn by marine debris. Because their surface energy is higher than that of fluoropolymers, they form a somewhat stronger bond with fouling. This bond fails by peeling, a process which is slower but requires less energy than shear. This paper describes a coating which combines the best features of fluorinated and silicone adhesion-resistant coatings. We have prepared a tough fluorinated elastomeric coating which tolerates no more than a weak or imperfect joint between fouling and itself, a joint which is predisposed to early and easy failure. The elastomer has low surface energy and resists the attachment of fouling, also has a low elastic modulus which permits the joint between fouling and coating to fail in peel, and also has the ability to be applied in a thickness which favors failure of the fouling-coating joint by peel. The surface energy, elastic modulus, and thickness may be varied as desired over wide ranges. The coating was tested for one season in the Chesapeake Bay, and successfully resisted fouling for this period.

### **Toxicity of the Antifouling Agents Irgarol 1051 and Sea-Nine 211 and the use of an Image Capture and Analysis System in Macroalgal Bioassays**

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A programme of research was initiated to provide information on the efficacy of the antifouling agents Irgarol 1051 and Sea-Nine 211 to a range of both target and non-target macroalgae. Faster, more sensitive and more accurate bioassays are continually being sought to allow the generation of toxicological data for today's novel biocides where data are lacking. Information on Irgarol 1051 is particularly required in view of reports of significant and persistent high levels of this biocide in some coastal waters.

Algal spores/zygotes were exposed to a range of biocidal concentrations in seawater solution, prepared using modified von Stosch culture medium. These were incubated under controlled environmental conditions and with the aid of a PC based image capture and analysis (ICA) system, rapid measurements of a range of parameters were recorded daily. ICA allowed the determination of effects which would otherwise have been missed, e.g. through the measurement of compactness. This process was automated through the development of macros and toxicological data, based on quantitative measurements, were statistically analysed using Probit analysis and ANOVA.

Preliminary results suggest that Sea-Nine 211 is relatively more toxic than Irgarol 1051 and their toxicities with respect to time vary in relation to their degradative properties. There is also evidence to show the toxicity of Irgarol 1051 is much greater to green algae as opposed to brown.

The significance of these toxicological data with respect to environmental concentrations will be given and the usefulness of the methodology considered.

### **Bioadhesion – Topographically or Chemically Mediated?**

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The understanding of contact guidance has developed rapidly in the last decade. A large body of basic research has been accumulated in that time, but application of this technology has been limited. A focus of our lab is designing topographically patterned materials for specific applications and then reducing these designs to practice. Polymer samples were patterned with micron scale features that varied by separation distances and lengths. In addition to topography, however, we have added chemical and mechanical aspects to our designs, creating hierarchical systems. These topographical, chemical and mechanical factors are significant for all biofouling studies. To elucidate the influence of the polymer's mechanical behavior on bioadhesion we used PDMS samples of different moduli, but constant surface tension.

Minimization of cell adhesion via manipulation of these properties is possible, as we have seen in a model system using porcine vascular endothelial cells (ECs). ECs were grown on PDMS substrates with different textures and surface treatments. Optical microscopy reveals few cells adhered to the texture, and of the adherent cells, most exhibited an altered morphology. On surfaces without texture, the ECs formed a confluent layer after 3 days. Some 5 $\mu$ m high pillars were most effective at discouraging cell growth. In some instances, cells appear to congregate on the texture. At the molecular level, atomic force microscopy has been used to characterize the specific and nonspecific forces of adhesion in receptor-ligand systems on the ECs. In summary, the surface features have been shown to direct both the growth pattern and morphology of cells. The effectiveness of this model will be compared to marine soft fouling experiments.

### **Non-Chemical Biofouling Control in Heat Exchangers and Seawater Piping Systems Using Acoustic Pulses Generated by an Electrical Discharge**

Brizzolara Robert A., Walch Marianne, Nordham Dave, Lennen Rebecca, Hoover Scott, Naval Surface Warfare Center, Carderock Division; Burnett Evan and Mazzola Michael, Mississippi State University; Simmons Ron, SBB Technologies.

Acoustic pulses generated by an electrical discharge (pulsed acoustics) were investigated as a non-chemical means of biofouling control in two test formats: on straight 5/8" diameter titanium tubes and on a mockup heat exchanger. The pulsed acoustic device, when operated at 17 kV, demonstrated 95% biofouling inhibition over a 20' length of 5/8" diameter titanium tube, comparable to that of chlorination in combination with a high-velocity flush. The pulsed acoustic device inhibited biofouling over a one-way distance of 15'; therefore, a single pulsed acoustic device is theoretically capable of protecting at least a 30' of tube length from biofouling (15' on either side of the device). Acoustic measurements were performed on the titanium tube: a correlation between the acoustic intensity in the frequency range 0.01-1 MHz and the level of biofouling inhibition was observed. There was no correlation between the acoustic intensities in the 1-9 kHz and 1-25 MHz frequency ranges and biofouling inhibition. The threshold acoustic intensity for biofouling inhibition was determined for the 0.01-1 MHz range. The pulsed acoustic device was also tested on a mockup heat exchanger that consisted of two titanium tubes attached to a 26" x 26" x 3/4" thick titanium plate. One side of the titanium plate was immersed in flowing seawater. The pulsed acoustic device was mounted on the dry side of the titanium plate. These tests demonstrated that the acoustic energy produced by the pulsed acoustic device is highly directional; therefore, the orientation of the device will be critical to obtaining good biofouling inhibition on a heat exchanger. In summary, the pulsed acoustic technology has good promise as a non-chemical means of biofouling control, and has a demonstrated biofouling inhibition comparable to that of chlorination over a 20' length of 5/8' diameter titanium tube. This work was funded by the Office of Naval Research Environmental Quality Program.

### **The Development of Marine Natural Product Based Antifouling Paints**

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Ecological problems associated with current antifouling technologies, which rely on tin and copper compounds, have highlighted the need to develop new antifouling paints. We have shown that marine bacteria and fungi isolated from living surfaces in the sea are a promising source of natural products with antifouling properties, which are also biodegradable. Using novel isolation media and scale up methods including “niche mimic bioreactors”, 650 isolates of epiphytic marine bacteria from a range of algae and invertebrates were obtained in pure culture and screened for active compounds. Forty two (6.5 %) strains exhibited antimicrobial activity against a test panel of fouling bacteria. Four of these strains were used to formulate ten water based paints and all but one of the paints showed activity against the test panel of fouling bacteria. Five of the paints were further tested for their ability to inhibit the settlement of barnacle larvae, *Balanus amphitrite*, and algal spores of *Ulva lactuca*, and to inhibit the growth of *Ulva lactuca*. Two of the five showed a significant decrease in the number of settled barnacles in comparison with the control. One of the paints based on the extract of a *Pseudomonas* sp. isolated from the surface of the nudibranch, *Archidoris pseudoargus*, showed excellent activity in all laboratory assays. The antifouling chemicals responsible for the activity of the extract were isolated, using bioassay guided fractionation, and characterised. In addition parallel studies with marine fungi demonstrated their potential as a source of effective antifouling compounds.

### **Adhesive properties of algal spores and release mechanisms**

Callow James A, Finlay John A. and Callow Maureen E., School of Biosciences, University of Birmingham, Birmingham B15 2TT, UK

Fouling by *Enteromorpha*, the most important macroalga that fouls ships and submarines, is initiated through motile spores that secrete a physically strong glycoprotein adhesive. Our objective is to understand the mechanical properties of this adhesive, its relationship with different substrata, including foul-release polymers, and the processes associated with adhesive curing. AFM and Environmental Scanning Electron Microscopy (ESEM) have been used to examine the topographical structure and materials properties of settled spores and their adhesive without fixation and dehydration artefacts. In contrast to previous imaging methods the *Enteromorpha* adhesive is revealed to be a swollen gel-like pad, approximately 1  $\mu$ m thick, surrounding the spore body. Freshly released adhesive exerts an average adhesion force of 200 nN on the AFM tip. Within minutes of release the adhesive undergoes progressive ‘curing’ with a 65% reduction in mean adhesive strength and a 10-fold increase in Young’s modulus. Further studies are now in progress to explore how adhesive properties and topographies are influenced by the surface energy characteristics of the substratum. The tenacity of spore adhesion on a range of different surfaces including foul-release materials is being assessed by hydrodynamic methods. Adhesion strength is strongly influenced by the time the cells are in contact with the surface, surface energy and whether or not the spores settle in groups. The mode of release of adhered spores from a surface is currently being studied by ESEM. Current interpretations of foul-release mechanisms favour the ‘JKR’ model in which coating modulus and thickness play an important role. However, this model was primarily developed for rigid, macroscopic adherands. While this is appropriate for macrofoulers such as barnacles, it may be less appropriate for microscopic, compliant ‘soft-fouling’ organisms. The paper will describe investigations towards developing an alternative model for the release of soft-foulers.

### **Cue detection and surface selection in the settlement of spores of the green alga *Enteromorpha*.**

Callow Maureen E<sup>1</sup>, Callow J A<sup>1</sup>, Finlay J A<sup>1</sup>, Jennings A R<sup>1</sup>, Patel P<sup>1</sup>, Brennan A B<sup>2,3</sup>, Seegert C E<sup>3</sup>, Gibson A<sup>2</sup>, Feinberg A<sup>3</sup>, Baney R<sup>2</sup>, Ista L K<sup>4</sup> and P López G P<sup>4</sup>

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*Enteromorpha* is the most important alga that fouls ships and submarines. Its success is partly due to its response to settlement cues that promote rapid recruitment to, and exploitation of a surface in a competitive, turbulent environment. Our main objective is to understand the role of diffusible chemical, physico-chemical, biological and topographical signals in stimulating and inhibiting attachment of the motile spores of *Enteromorpha* to surfaces.

Spores respond to a number of external chemical cues such as fatty acids. In the natural environment, settlement is moderated by microbial biofilms that develop on all submerged surfaces and which may provide a range of both stimulatory and inhibitory cues. Observations of gregarious settlement and kinetic analysis of spore attachment data led us to speculate that chemical cues released by settled spores could influence the colonisation of surfaces. Recent data provide evidence for compounds produced by vegetative tissue and spores that are able to promote and inhibit spore settlement. Spores also settle preferentially on microtopographic features. Features fabricated in PDMS included valleys and ridges, pillars and pits. The results suggest that spores are able to 'select' the most energetically favourable place to settle. Spore settlement on self-assembled monolayers (SAMs) has revealed a differential response to surface chemistry and wettability. In general, spore settlement increases as wettability decreases, although the strength of attachment to hydrophobic surfaces is less than to hydrophilic surfaces. Thus, in common with invertebrate larvae, an array of cues appears to be involved in the settlement of motile algal spores.

### **Biocide-free Anti-fouling Paints -the Long-term Solution to Preserve the Marine Environment**

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As a result of the world-wide ban of organotin compounds in anti-fouling paints by the International Maritime Organization (IMO), a lot of alternatives are now available on the market and the development of new, environmentally sound systems is of utmost importance. Especially, as the new anti-fouling convention includes the possibility to restrict other biocides used in anti-fouling systems, if there are indications of impacts on non-target species in the marine environment. In the European Union the Biocidal Product Directive will have a serious impact on the market of anti-fouling paints as it is expected that the number of biocides will be reduced dramatically. Additionally, as a result of the decision to phase out emission, discharges and losses of hazardous substances into the marine environment taken in 1998 by the Oslo-Paris-Convention for the North-East-Atlantic and the Helsinki-Convention for the Baltic, systems which release biocides into the water have to be considered only as temporary solutions. The long-term perspective of anti fouling research and development should be the avoidance of leaching biocides and any toxic, bioaccumulative and persistent substance.

In October 1999, a multi-stakeholder project was initiated by WWF Germany to prove the efficiency of biocide-free systems for sea going vessels. The project involves a wide range of interest groups, including Ministries, shipping companies (both federal and private) and paint manufacturers. Trials with non-biocidal anti-fouling paints on deep-sea going vessels are performed. About 80 test patches have been applied on 19 different vessels operating in the North Sea, North- and South-Atlantic, Caribbean as well as in polar regions. Cruise liners, container ships, bulk carriers, a frigate, research vessels, patrol boats, a fish trawler and coastal passenger ferries will be inspected during the project. Some coastal vessels were taken over from a previous projects and the coatings remained. As the project will last until mid 2003, it will be possible to collect information over a period of 5 years in total. A broad scale of coatings from 15 paint manufacturers are under investigation: fouling-release systems, biocide-free self polishing coatings and microfibre coatings. Promising first results could prove the efficiency of: 1. biocide-free SPC for fast sailing vessels; 2. microfibre coating against barnacles and 3. fouling release systems over a period of 36 month even for slow moving vessels. The project design, experiences and results will be shown in the presentation as well future requirements for anti-fouling paints due to political developments. Additionally the "Group 2003", a WWF initiative for ship owners, paint manufacturers and others to push the phase-out of TBT-paints, will be presented.



### **Hydrodynamic characteristics of Tin-free Self-Polishing Co-polymers and Foul(ing) Release systems.**

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An experimental study has been carried out to compare the hydrodynamic characteristics of a Tin-free Self-Polishing Co-polymer (SPC) and a Foul Release system. Rotor measurements have been carried out using different cylinders coated with both paint types. An indirect method was used to relate the measured torque differences to the roughness function. The experiments showed that the frictional resistance for the Foul Release test cylinders was lower than for the Tin-free SPC cylinders.

The hydrodynamic characteristics were related to the roughness measurements of surfaces coated with either paint type. The roughness parameters were measured with an optical measurement system. Roughness profile parameters such as the mean absolute slope angle (Sa) and the density of zero-crossings (Dz) indicate that the texture of the Foul Release surface is significantly different from SPC systems.

In contrast to Tin-free SPCs and other toxic antifouling, the findings show that roughness profiles representative of a newly applied Foul Release system will not correlate with its measured hydrodynamic drag when characterised solely by a height parameter, such as the parameter (Rt50). Instead, the correlation requires the use of a characteristic roughness measure (h), which takes both the amplitude and texture of the surface into account, calculated at bandwidth parameters which depend on the degree of roughness.

### **Hull fouling and Cleaning in New Zealand**

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As New Zealand is an isolated island nation located in the South Pacific Ocean shipping is an important potential vector of exotic marine organisms. New Zealand has put in place ballast water controls to reflect International Maritime Organisation (IMO) guidelines and continues to support IMO's direction in developing international controls for ballast water. We are now turning our attention to the issue of hull fouling to determine the threat fouling poses to the marine environment.

Research has shown hull fouling to be a major source of introductions of exotic species to New Zealand historically and suggests that exotic species are likely to continue to arrive via this vector pathway. Changing patterns in the types of vessels traveling to New Zealand could be why fouling species continue to arrive in New Zealand. Preliminary research indicates that some vessel types eg yachts tend to be more heavily fouled than others eg larger cargo vessels. The Ministry of Fisheries is undertaking further research to determine whether the hull fouling species reaching New Zealand are a threat to its marine environment and how the hull fouling threat ranks against other marine biosecurity threats.

While there is limited information on the threat hull fouling poses to the marine environment, New Zealand is taking a precautionary approach to this issue and is in the process of considering the development of hull cleaning controls. If accepted by the Government, these controls will require the collection and containment of fouling material removed from hulls; control the disposal of material from vessel hulls that are cleaned in or near the coastal marine area and will also require the treatment of any discharge resulting from hosing, water blasting or in-water cleaning of hulls. Comment and information gathered from stakeholders through a consultation process will help determine the advice to Government on the exact nature of the final controls.

It is important that we all continue to collect and share information in relation to the threat posed by hull fouling. This will allow the international community to be in a better position to determine the need for any future hull fouling controls.

### **Modeling the Mass Balance and Fate of Copper in San Diego Bay**

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Because of its broad use in antifouling coatings, copper is one of the most ubiquitous and problematic contaminants in harbor, estuarine and coastal marine environments. Other general sources of copper include municipal discharges, industrial discharges, stormwater and non-point source runoff, and mining and ore handling. Previous studies in San Diego Bay suggest that the combination of these loadings has led to chronic elevations of copper in ambient water at levels that approach or exceed the water quality criteria in some areas. Subsequent transport of this copper to the sediments also presents the potential for ecological impairment. While there is still considerable debate as to the site-specific toxicity of copper in marine waters and sediments, there is clearly a need to understand the overall loading, distribution, and fate of copper in urbanized coastal harbors and bays such as San Diego Bay.

In general, the distribution of copper in the water column of a bay is controlled by a balance among sources, transport to the sediments (sinks), and exchange with the ocean (flushing). Thus our ability to understand the balance of copper in a prototype system such as San Diego Bay depends on the effectiveness with which we can either measure or model these processes on a prototype scale. San Diego Bay is ideally suited for this purpose because the sources of copper are relatively well characterized, the sources are chronic in nature resulting in near steady-state conditions, and the salinity balance provides an independent means of verifying the flushing properties of the bay. In this study, we combine a calibrated, one-dimensional exchange model of San Diego Bay with a scale-matched set of field measurements to evaluate the overall mass balance of copper, which is further quantified for the interactions, including transformation and other fate processes, among different species components. The study includes a description the field measurements and distributions that are used as a basis for evaluation and tuning of the models, the calibration of the one-dimensional model based on salt balance, an evaluation of the total copper budget based on a balance between estimated copper sources, bay flushing, and loss to the sediments and a comparison of the importance of various processes and an identification of the key processes governing the fate of copper in San Diego Bay. The results from the one-dimensional model are then extended to a two-dimensional model that provides better insight into spatial and temporal variability of copper in the Bay. Results from the full-scale copper fate and transport models can then be used to address regulatory issues, including TMDLs, discharge permits, mixing zone studies, and general water quality compliance.

### **Roles of Interfacial Chemistry and Mechanics in Release Phenomena**

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Adhesion between solid materials results from intermolecular interactions. The fracture resistance of the interface is however determined jointly by the mechanical deformation and the chemical interactions at the interfacial region. Because of the complex interaction between interfacial chemistry and mechanics, adhesive release properties of polymer surfaces cannot always be predicted on the basis of their surface free energies - the role of interfacial dynamics must also be considered. These concepts are illustrated in the release behavior of silicones and other well-defined model systems with which we have carried out extensive adhesive and tribological measurements. While no clear correlation can be found between the release properties of these coatings and their surface energies, some significant correlation is discovered with their tribological properties. These studies have also been extended to oil-added silicone networks. The adhesive and the tribological properties of these materials as a function of the molecular weight of the oil will be addressed.

**The proximate basis of barnacle gregariousness: the adult-associated cue to settlement of *Balanus amphitrite* cypris larvae is similar to the  $\alpha_2$ -macroglobulin family of proteins.**

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Many factors potentially modulate settlement behaviour of barnacles, but for those species that are gregarious, physical factors appear secondary in significance to chemical cues of biological origin. As a fouling species of major economic importance, *Balanus amphitrite* has attracted considerable attention in recent years. This species lends itself to laboratory studies of settlement. Recently these have included: biofilm-cypris larval interactions, physiological energetics of cypris larvae, the signal transduction pathways operating at settlement, bioadhesives employed for fixation to substrata and the chemical basis of gregarious settlement. The latter, and particularly the nature of the adult stimulus to cyprid settlement, will be the focus of this presentation. The adult cue, which has long been known to be a glycoprotein, was isolated by a previously reported bioassay-directed procedure. The 3 major subunits, 76, 88 and 98 kDa, of the glycoprotein, termed the settlement-inducing protein complex (SIPC), were isolated by SDS-PAGE and subjected to N-terminal sequencing. Partial sequence obtained for the 88 and 98 kDa subunits suggested that they are related. The 76 kDa subunit was, however, N-terminally blocked. Microsequencing of the 76 kDa subunit was successful and 20-base pair degenerate primers were designed for nested PCR to obtain a partial nucleotide sequence. Additional sequence was obtained by 3' and 5' RACE reactions. Comparison of the putative amino acid sequence of SIPC with sequences in the GenBank and EMBL databases revealed a significant alignment with a consensus sequence of the  $\alpha_2$ -macroglobulin family of glycoproteins. These results will be discussed in relation to new research that is attempting to understand the ability of cyprids to discriminate between barnacle species at settlement.

**Managing biosecurity risks from hull fouling: a perspective from down under**  
Coutts, Ashley D. M., Taylor, Michael D., Cawthron Institute, Nelson, New Zealand.

Translocation via hull fouling on slow moving sailing ships is probably responsible for the widespread global distributions of many coastal organisms. Since the early 20<sup>th</sup> century, however, the significance of ship's hulls as a vector for dispersing fouling organisms appears to have been reduced owing to factors such as faster vessels speeds and improved anti-fouling paints. Fouling on active merchant vessels, for example, is largely confined to hydrodynamically protected areas and areas lacking antifouling paint (Coutts 1999; James and Hayden 2000). Nevertheless, these areas of the hull, and inactive merchant vessels that suddenly become active again, may remain responsible for the transfer of unwanted marine species to new locations (Coutts and Taylor, in prep).

Biosecurity risks from hull fouling may be even greater on towed vessels, which are relatively slow moving and are often moved to new locations after being stationary for long periods of time. Foster and Willan (1979), for example, documented the survival of 12 barnacle species on the hull of an oil platform after it was towed from Japan to New Zealand in 1975. More recently, Apte *et. al.* (2000) documented the successful translocation of the smooth shelled blue mussel *Mytilus galloprovincialis*, from the hull of the *USS Missouri* to a submarine ballast tank in Pearl Harbour, after it was towed from Bremerton, Puget Sound.

In October 2001, a compound ascidian was found to be abundant on wharf piles in Whangamata and Tauranga Harbours in the North Island, New Zealand. It was later identified as a *Didemnum* sp. that may be indigenous to New Zealand,. In mid-December 2001, Cawthron divers discovered the same ascidian on the bottom of a barge moored in the Marlborough Sounds in the South Island, and it was later discovered that the barge had been relocated from Tauranga Harbour. An estimated 24,182 kg of total wet fouling on the hull of the barge including an estimated 2,845 kg of *Didemnum* sp..

Even though the ascidian may be indigenous to New Zealand, a level of concern remains regarding the potential biosecurity risks, especially to the Greenshell™ mussel (*Perna canaliculus*) industry in the Marlborough Sounds. The industry is susceptible to impacts from smothering of mussels by fouling organisms, and management options are being considered.

Several towed vessels visiting New Zealand also visit Victoria and Tasmania, Australia, where several unwanted marine pests have been introduced but are not yet recorded in New Zealand, e.g. the northern Pacific seastar *Asterias amurensis* and the European green crab *Carcinus maenas*. Hence, evidence to date suggests that the biosecurity risks to New Zealand from towed vessels may be high. Research at Cawthron is investigating these risks in greater detail.

**Is the mussel test a good indicator of antifouling activity? A comparison between laboratory and field assays**  
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Current antifouling technologies rely on metal-based paints, but due to the significant environmental damages caused by their toxicity, there is an expected worldwide ban of organotin-containing paints prompting the quest for safe and effective alternatives. One of the most promising alternatives is the development of antifouling coatings whose active components are naturally occurring compounds from marine organisms. A number of laboratory bioassays has been designed to search for antifouling compounds. However, there is no convincing evidence to date that these assays really provide results reproducible through ecologically realistic field experiments. Natural concentrations of the extracts from the Brazilian seaweeds *Laurencia obtusa* (Rhodophyta) and *Stypopodium zonale* (Phaeophyta) were tested in the lab through the 'mussel test' and in the field through the 'phytagel method' in order to compare the efficiency of these methods in assessing antifouling activity. *L. obtusa* extract significantly inhibited fouling in both laboratory and field assays, while *S. zonale* stimulated fouling in both assays. Major compounds from both extracts were identified. Our findings suggest that the 'mussel test' is a reliable time and cost-saving screening method for antifouling substances, although field assays are more sensitive to detect their activity spectrum.

## **The chemical background of the surface affinity of medetomidine (catemine), a settlement-impeding compound directed against the colonization of barnacle larvae**

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**Introduction.** Two different surfaces (polystyrene and hydrophilised, negatively charged, polystyrene) incubated with the alpha-2 agonist medetomidine ((±)-4-[1-(2,3-dimethylphenyl)-ethyl]-1-H-imidazole-hydrochloride) have a significant ability to impede settlement of cyprid larvae of the barnacle *Balanus improvisus* for an extended period of time. The association of medetomidine to the polymer surface appears stable, however the association forces are sufficiently weak to allow medetomidine to be released from the surface and enter the larvae. A series of experiments have been conducted to examine the chemical forces involved in the surface association of medetomidine. **Methods.** The two different polystyrene surfaces were incubated with medetomidine using three different pH conditions (3.6, 5.6 and 7.9 (the pH of seawater)) after which the dishes were rinsed thoroughly and cyprid larvae were added. Also, Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS), were used to enable the detection of the surface-associated medetomidine molecules. Furthermore, we examined the surfactant properties of medetomidine by studying the influence on the critical micelle concentration (CMC) on ionic and non-ionic surfactants. **Results.** The adsorption of medetomidine to hydrophobic surfaces, but not hydrophilic surfaces, was inhibited by low pH (3.6), which suggests that when the slightly basic medetomidine molecules become protonized in the incubation solution, the increased electrostatic repulsion between the charged molecules prevent adsorption to the hydrophobic surface. However, in experiments where the medetomidine molecules were allowed to adsorb to the surface at neutral pH, rinsing of the surfaces with a solution with low or high pH did not remove the inhibitory effect of medetomidine on any of the surfaces. This indicates that the electrostatic effects are of minor importance for the already adsorbed molecules. The addition of medetomidine to a solution of an anionic surfactant (Berol 496) and to a non-ionic surfactant (Berol 535) significantly lowered the CMC indicating that medetomidine itself acts as a weak cationic surfactant with the possibility for hydrophobic interactions. **Conclusion.** Medetomidine associate with the polystyrene surfaces mainly through elements of hydrophobic interactions. Electrostatic association effects are of less importance, once the molecule has adsorbed.

## **Selective Microbial Fouling of Coatings**

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The immersion of a clean surface into an aqueous environment leads to rapid and efficient colonisation by microorganisms. The lifestyles and metabolic capacity of microorganisms, especially bacteria, must be considered when designing novel coatings for application in the marine environment. Bacteria are extraordinarily diverse and it is essential that the coating provide neither a physical nor a nutritional niche. In view of these considerations we have developed a program for testing the performance of coatings upon exposure to marine microorganisms. Exposures to pure cultures of marine bacteria and also exposures to naturally occurring communities of marine microorganisms were employed to test coatings. An important component of our experimental design is to test surfaces following aging in sterile seawater. We have previously shown that bacteria are sensitive to micro-scale changes in coatings following exposure to seawater. As a consequence performance, as measured by bacterial surface colonisation is dramatically affected. Evaluation of a diverse array of coatings has been undertaken. Testing has shown that in some cases these coating are extremely resistant to colonisation by microorganisms. Analysis of colonisation by naturally occurring microorganisms for one series of related coatings provided an unexpected result. The coatings appeared to attract specific species of protozoan that graze on bacteria. Each coating in the series attracted a different protozoan. This finding highlights the diverse and unpredictable nature of the response of microorganisms to a surface. It may be of great benefit to develop coatings that attract efficient grazers to a surface.

### **Mn Cycling in Marine Biofilms: Effect on Rate of Localized Corrosion**

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It is well known that the action of microorganisms in biofilms can influence both the initiation and propagation of various forms of marine corrosion. The rates of pitting, crevice and galvanic corrosion in seawater are increased by up to one order of magnitude when microbial biofilms are present on the cathode surface. Manganese cycling within the biofilm has been shown to be capable of accounting for the observed rate increases. Microelectrodes of the Au-Hg Amalgam type have been used together with square wave voltammetry to measure profiles of oxygen, peroxide, Fe, Mn and Sulfur chemical species through the thickness of natural assemblage marine biofilms grown on stainless steel alloy N08367. These data show  $Mn^{+2}$  and peroxide together at locations where the dissolved oxygen concentration was low. Oxidized species of iron were also found at some locations. Sulfur species (predominantly  $S^{2-}$ ) was often found at locations where the dissolved oxygen concentration was below the detectable limit. Scanning laser confocal microscopy was used to image the microbial assemblage at the locations of the chemical profile data. Organisms with a filamentous morphology were found in consortia with rod and coccoidal shaped microbes at locations where dissolved Mn and peroxide were measured. The filamentous forms were usually absent at locations where manganese was not detected. It is suggested that the filamentous organisms may be manganese metabolizers, and that peroxidatic manganese oxidation may be taking place within the biofilm.

### **Shelter Island Yacht Basin Total Maximum Daily Load for Dissolved Copper**

Dobalian, Lesley and Arias, Christina, California Regional Water Quality Control Board, San Diego Region, 9174 Sky Park Court, Suite 100, San Diego, CA 92117

A TMDL represents a strategy for meeting water quality objectives by allocating quantitative limits for point and non-point pollution sources. The California Regional Water Quality Control Board, San Diego Region (Regional Board) is developing a Total Maximum Daily Load (TMDL) for the Shelter Island yacht basin (SIYB) for dissolved copper. SIYB is a semi-enclosed recreational marina located in the north end of San Diego Bay. The Regional Board, a state regulatory agency, placed SIYB on the 1998 Clean Water Act Section 303(d) list as an impaired waterbody due to elevated levels of dissolved copper. The SIYB TMDL is being established to meet water quality criteria for dissolved copper as set forth by US EPA in the California Toxics Rule.

In the draft TMDL analysis, it was determined that the vast majority of dissolved copper loading to SIYB originates from copper-based antifouling paints. Copper-based antifouling paints are commonly applied to the hulls of recreational vessels to prevent marine fouling. Dissolved copper enters SIYB through the combined effects of passive leaching (53%) and in-water hull cleaning (40%) from copper antifouling paints, as well as through wet and dry weather flow (7%), to a lesser extent. In order to comply with the TMDL, significant reductions in source loading will need to be achieved.

Effective implementation of the TMDL requires a coordinated approach by governmental agencies, responsible parties, and stakeholders. The draft TMDL identifies parties responsible for implementation of the TMDL, including the San Diego Unified Port District (Port), port tenants, boat owners, in-water hull cleaners, and the City of San Diego. In order to achieve the TMDL, management plans should be developed to reduce copper loading from identified sources over time. Management plans should focus on implementation of Management Measures (MMs) and Best Management Practices (BMPs) designed to reduce dissolved copper source loading. For example, MMs and BMPs may include switching to low-toxicity or nontoxic antifouling paints, using nonabrasive techniques during in-water hull cleaning, and increasing public education and outreach. An important component of the implementation process also includes evaluating the effectiveness of the load allocations and management plans in meeting water quality objectives, and making revisions to the TMDL as necessary.

**Deterrence of larval metamorphosis by the green macroalga *Ulva reticulata*: the inhibitory effect of bacterial and algal metabolites.**

Sergey Dobretsov, Tilmann Harder, Pei-Yuan Qian, Department of Biology, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR

In Hong Kong waters, the marine macroalga *Ulva reticulata* Forsskal (Chlorophyta) is often free of macro-fouling organisms. Previously, a waterborne glycoproteinacious algal compound of high molecular weight (> 100 kDa) isolated from this alga was highly inhibitive to larval metamorphosis of the polychaete *Hydroides elegans*, the barnacle *Balanus amphitrit*, and the bryozoan *Bugula neritina*. In this study, we investigated the role of *U. reticulata*-associated bacteria in the antifouling effect of *U. reticulata*. Seven bacterial strains were isolated from *Ulva* blades, taxonomically characterized and assayed for their effect on larval settlement of the fouling organisms mentioned above. The waterborne bacterial metabolites of one isolate, a *Vibrio* sp., significantly inhibited larval metamorphosis of *H. elegans*. Gel-filtration and SDS-PAGE revealed similar chromatographic properties of the bacterial metabolites and the waterborne compounds from the alga. The purification and partial characterization of the biologically active components in the metabolite fraction are discussed.

**Global Dispersal of Microorganisms and Pathogens: Biofilms Inside Ballast-Water Tanks**

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The economic and ecological threats posed by nonindigenous invertebrate species transported by ships' ballast water are much better understood and documented than the corresponding epidemiological threats posed by the potential introduction of microorganisms pathogenic to humans, plants, and animals. While a limited number of studies has focused on microorganisms in ballast water, even less information exists concerning the organic biofilms that cover internal tank and hold surfaces. Surfaces submerged in an aquatic milieu are covered to some degree with biofilms, organic matrices that can contain bacteria, microalgae, and associated protozoans, sometimes including pathogenic (disease-causing) forms. Biofilms may accumulate in ballast-water tanks and holds to create "interior hull fouling". Although biofilms in ballast-water tanks—particularly pathogens in biofilms—remain little investigated, we can pose several hypotheses based on our general knowledge of biofilms and microorganisms, as well as our specific knowledge of microorganisms in ballast water. Sampling and experiments are underway to assess the potential for biofilms in ballast-water tanks to globally transport microorganisms and pathogens. Specifically, this work is testing the following hypotheses:

Biofilms in ballast-water tanks and holds contain viral, bacterial, and protozoan pathogens.

Biofilms in ballast-water tanks and holds contain elevated numbers of microorganisms relative to concentrations of microorganisms in ballast water.

Pathogens in ballast-tank biofilms can be released and survive, even grow, in aqueous environments.

This research is supported by Virginia Sea Grant.

### **Biogeochemical Cycling of Copper in the Elizabeth River**

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The Elizabeth River (ER) is a sub-estuary of the Chesapeake Bay, the largest and historically most productive estuary in the United States. Two major regional centers of commercial shipping and the world's largest naval base are located on the ER, and the ER supports a diverse mix of heavy industry and chemical and fertilizer companies. Metal contamination is a significant issue in the ER.

We are part of a team of investigators that performed an integrated study of the biogeochemical cycling of Cu, Cd, and Zn in the ER. We studied the interrelationships among: (1) metal concentrations, complexation and speciation (Donat, Consolvo, Carrasco); (2) *in situ* microbial production of Cu chelators (Gordon, Donat, Dryden); (3) phytoplankton metal uptake (Sunda, Huntsman, Donat); and (4) fluxes of metals and chelators from sediments (Donat, Burdige, Carrasco). This talk will highlight water column Cu results and the *in situ* production of Cu chelators by the ER natural resident microbiota.

Water column results from our two field studies in July 1999 and May 2000 indicate that concentrations of total dissolved Cu increased upriver. In all surface water samples, Cu was more than 99.9% complexed by one strong organic ligand class, L (average  $\log K' = 12.2$ ). The concentrations of free  $\text{Cu}^{2+}$  (the toxic/bioavailable form of copper) increased upriver by 10-fold ( $\text{Cu}^{2+}$ ). While free  $\text{Cu}^{2+}$  was generally below literature-reported estuarine phytoplankton toxic response levels.

May and November 2000 *in situ* results indicated that Cu additions to cultures incubated *in situ* increased the concentration of Cu-complexing ligands, with a corresponding decrease in the bioavailable free  $\text{Cu}^{2+}$  ion. *In situ* incubation results appear to confirm the hypothesis that microorganisms are capable of buffering their environment against toxic levels of  $\text{Cu}^{2+}$  by producing Cu-complexing ligands.



### **Marine corrosion and Biofouling – An owner’s perspective**

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The ship owning and ship operating industry has come under increasing pressure from many corners and interested parties that force changes to how ships are operated and maintained. The tools we can use to assure a safe and cost effective transport of good between continents are constantly being modified to fit new regulatory changes, the eminent “TBT-ban” is only one example of many changes imposed upon us.

There are undisputedly good intentions and reasoning behind most if not all of these changes, even if a better over all coordination of these efforts would benefit not only the environment but also the shipping industry. As an example I can mention the intention to reduce green house gas and nitrous oxide emissions into the air, which I think is commendable, is in conflict with the eminent TBT-Ban. Another example is the layers of ship inspections taking place presently; Classification Societies are inspection more thoroughly and often, the customers have their own inspections, and the customers trade organizations have their inspections, US and other Coast Guards have their inspections, etc.; many inspection points being duplicated or even triplicated, causing unnecessary burden on the ship’s staff, possibly distracting them from maintenance work, etc. The port states in Europe are creating a new ship inspection regime as we speak, and the classification societies are working on tightening up further the rules governing cargo tanks, bulk ships, etc. With customer mergers, fewer and larger buyers, the income side is depressed from intense competition reducing the economical “space” to absorb more burdens.

Other looming black clouds are age discrimination on ships – The attempt to use an age restriction to address a quality problem. This solution naturally is doomed to fail, but that might not be a strong enough argument to prevent it from becoming law. Many of these new rules and regulations are politically rather than technically driven, which complicates the issues greatly.

Ships carry 98% of all goods traded between countries and continents. Needless to say, the world economy is very much dependent on good safe and cost effective sea transport. Disruptions in sea transport would have severe economical consequences, and that would not be in anyone’s interest.

The ship owners only want to have the tools available that are necessary to be able to cost effectively serve our customers, and earn a sustainable return on the investment they make. Whatever new future rules, regulations, legislations, and other laws and burdens are forced upon the shipping industry we will face and deal with. There comes, however, a point when the cost of running ships prevents the owner from earning a sustainable return on the investment and that will without doubt reduce desire to make the necessary investments to assure undisturbed flow of goods between markets in the future.

The ship owner must have the tools and the ability to operate cost effectively and safely and only then can undisturbed good, cheap, transport of goods on ships be assured. There is no cheaper way to transport goods between countries and continents than by ship, let us keep it that way.

### **Antifouling activity of polymeric 3-alkylpyridinium salts isolated from the marine sponge *Reniera sarai* (Pulitzer Finali)**

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Water-soluble polymeric 3-alkylpyridinium salts (poly-APS), isolated from the Mediterranean sponge *Reniera sarai*, were found to be responsible for antifouling activity previously observed with the crude extract of the sponge. Antimicrofouling activity of poly-APS was monitored and compared to that of copper pyrithione, a non-persistent booster biocide. Settlement inhibition was estimated on cyprids of *Balanus amphitrite*, and toxicity tests were performed on microalgae *Tetraselmis suecica*, larvae of *Mytilus galloprovincialis*, and nauplii of *B. amphitrite*. Compared to the booster biocide, poly-APS caused lower inhibition of cyprids settlement with an EC<sub>50</sub> of 0.27  $\mu\text{g ml}^{-1}$ , but showed significantly lower toxicity towards the organisms used in the toxicity bioassays. Moreover, they exerted a totally reversible mechanism of antifouling activity towards *B. amphitrite* cyprids. At least for these organisms, this mechanism can be considered as a non-toxic. We have also assessed the antimicrofouling efficiency of poly-APS. The formation of biofilm in presence of poly-APS was detected by means of scanning electron microscopy. The obtained results showed a dose-depending reduction of the total number of settled microorganisms. Moreover, changes in the microfouling community, closely correlated to poly-APS concentration, have been observed.

Most commercially available toxic biocides will soon be banned from the European market. The observed antifouling activity and the low toxicity of poly-APS make these molecules a good candidates for potential applicative use. They moreover justify our current efforts to chemically synthesize poly-APS and their analogues for further tests.

### **Can substrata nature influence biofilm interactions during the settlement of *Balanus amphitrite* larvae?**

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Larval settlement of the barnacle *Balanus amphitrite* is influenced by natural multi-species biofilms. This aspect had been discussed under different aspects by many authors. The aim of this work is to understand whether (I) the nature of substrata can influence cypris settlement; (II) the nature of substrata can influence the formation and the structure of biofilm; (III) different biofilms formed in this way influence larval settlement; (IV) the age of biofilm could modify the substrate-larval interactions.

Therefore, different kind of natural and artificial substrata (marble, quartz, glass and cemonit) were biofilmed under laboratory conditions for periods of 5, 10 and 20 days at the temperature of 28°C. Settlement response was investigated with 5-day-old cyprids. The obtained biofilms were quantitatively and qualitatively analysed by scanning electron microscopy. The results show that *B. amphitrite* larvae change their settlement behaviour in relation to the kind of substrata; the biofilm formation is influenced by substrata typology both in term of number of settled microorganisms than in biodiversity of the microbial community; moreover, when substrata are biofilmed, the age of biofilm tend to hide the effect caused by the different attractiveness of substrata.

### **Efficacy and toxicity of Zinc pyrithione as antifouling biocide: a multi-bioassays approach.**

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The increased use of antifouling coatings based on booster biocides will be one of the first consequences of the TBT ban. The zinc complex of pyrithione is a metal-based biocide successfully used as TBT alternative; yet, few and insufficient data are available in respect to antifouling efficacy and toxicity of this compound toward marine organisms. Recently, some environmental fate studies have shown that booster biocides in the water column rapidly degrade to less toxic chemical forms.

This paper discusses the results of a broad spectrum of laboratory bioassays (settlement test, acute and sub-lethal toxicity tests, degradation test), carried out both on the biocide and on the leaching products of experimental antifouling paints exposed in a Mediterranean harbour (raft static immersion test). Larvae of *Balanus amphitrite* (cyprids and nauplii), *Mytilus galloprovincialis* (trochophora and veliger), and the microalga *Tetraselmis suecica* were used as bioassay organisms, and showed different responses to the biocide. The antifouling efficacy of zinc pyrithione is based on a toxic mechanism of action with both lethal and sub-lethal effects. Compared with other antifouling biocides, zinc pyrithione has a lasting efficacy inside the tested antifouling paints, and it soon degrades in seawater. In this way, the toxic action could be limited near the painted surface, resulting in a relatively low environmental impact.

The evaluation of antifouling efficacy and environmental impact of zinc pyrithione, provided by this multi-bioassay approach, gives new data to the knowledge of its ecotoxicological profile in the antifouling field.

### **Involvement of ACh in settlement process of *Balanus amphitrite***

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Normally, the competent stage of barnacles (cypris) settle and moult according to the water temperature, as well as by chemiotaxis and phototaxis. The presence of molecules belonging to the cholinergic system was shown in the larvae. Nevertheless, no data are yet available about the presence of cholinergic molecules in the cyprids' nervous system, even if different signal molecules (cAMP, adrenaline, dopamine, etc.) seem to be involved in the settlement process. The aim of the present work is to investigate the localisation and possible role of cholinergic molecules in the settlement process. Cyprids used were obtained from a laboratory culture of *B. amphitrite* collected in the Gulf of Genova (Italy). Cyprids, samples and control, were fixed in Bouin or 4% paraformaldehyde and either embedded in Paraplast, or used as whole mount specimens. Dewaxed sections were immunostained using an anti-cholineacetyltransferase (ChAT) polyclonal antiserum. Whole mount specimens were exposed to FITC-conjugate  $\alpha$ -bungarotoxin or were treated by cholinesterase (both acetyl- and pseudocholinesterases), Karnovsky-Root method. To test the effect of neurotransmitters on settlement, laboratory culture of *B. amphitrite* cyprids were exposed to cholinergic antagonists and agonists at different logarithmic concentrations: eserine, isoOMPA, BW284c51 (classical anti-ChE agents), nicotin (acetylcholine receptor agonist), diazinon, methomil, mercaptodimetur (ChE inhibiting pesticides) and atropine. The acetylcholine (ACh)-biosynthetic enzyme, ChAT, was immunodetected on dewaxed sections of *B. amphitrite* cyprids, using an UV equipped microscope. These indirect data about the presence of ACh were further supported by positive results obtained from FITC-conjugate  $\alpha$ -bungarotoxin and AChE, BChE, and PrChE activity revelation method on whole mount cypris. By biochemical spectrophotometric measure of AChE activity by a modified version of the Ellmann method we have obtained good results for the AChE and PrChE activity. Laboratory settlement experiments showed that all the drugs used, except isoOMPA, are able to alter the settlement process in. The activation or the inhibition is related to the drug and the concentration used. The results suggest involvement of the cholinergic signal system in the regulation of the settlement.

## Corrosion Issues in the Marine Industry

Falwell, Pat

No abstract submitted

### **A surface sensitive method for investigation of cross-linking and protein-protein interaction of marine adhesives without influence of the solid surface.**

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Introduction. The proteins in the byssus threads of blue mussel, contains highly reactive dihydroxyphenylalanin (DOPA) that take part in both adhesion and cohesion of the byssus thread proteins. In an earlier study we investigated adhesion and cross-linking of monolayers of *Mytilus edulis* foot protein-1 (Mefp-1) with the use of quartz crystal microbalance–dissipation (QCM-D). We found that adsorption behaviour of Mefp-1 was very different on hydrophilic and hydrophobic solid surfaces, which make studies of protein-protein interaction very difficult. The aim of this study was to develop a surface sensitive method for investigation of binding Mefp-1 to other mefp proteins without ”disturbing” effects of the solid surface. Method: Biotin doped phospholipid bilayers was formed on flat silicon dioxide QCM-D sensor surfaces. Mefp-1 was biotinylated (Mefp-1b) and was allowed to bind to the phospholipid bilayer via streptavidine. Binding of Mefp-2 on top of the b-Mefp-1 layer was then investigated. Results and discussion: Binding of Mefp-1b to Mefp-2 did not occur without enzymatic oxidation of DOPA in the presence of the enzyme tyrosinase which, also seems to be copolymerised with b-Mefp-1 and Mefp-2. Conclusion: The described method may be very useful in studies cohesion and assembly of the Mefp proteins and may be also suitable for investigation of adhesive/cohesive proteins from other biofouling organisms.

### **Compression and decompression of *Mytilus edulis* foot protein –1 (Mefp-1) at the air water interface.**

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Introduction. Mefp-1 contains highly reactive dihydroxyphenylalanin (DOPA) involved in cross-linking of the byssus proteins. With the use of surface sensitive methods such as ellipsometry and quartz-crystal microbalance–dissipation (QCM-D) we have demonstrated that an adsorbed monolayer of Mefp-1 is rapidly collapsed at a hydrophobic surface from about 20 nm to about 5 nm when DOPA is enzymatically oxidised or oxidised with NaIO<sub>4</sub>. We were interested if we could demonstrate a lateral component of the collapse of Mefp-1 and therefore surface pressure area isotherms were recorded at air/water interface under different conditions. Method Mefp-1 was spread at the air/water (0.1 M acetate buffer) interface of a surface balance apparatus (KSV 500 LB high performance film balance system) The surface pressure was monitored by the Wilhelmy plate method. Results The protein film was compressed until an area of 900 Å<sup>2</sup>/molecule was reached followed by decompression to the original value. The obtained isotherms showed a continuous increased of surface pressure with area per molecule until 18 mN/m was reached at 900 Å<sup>2</sup>/molecule, when the surface film was expanded. Surprisingly little hysteresis effect was found between compression and decompression isotherms indicating absence of desorption and irreversible changes during compression. When similar experiments was performed on spread monolayers of Mefp-1 on acetate buffer also containing NaIO<sub>4</sub>, we found that isotherm on compression show irregularities and a large hysteresis between compression and decompression isotherms. The area per molecule obtained from the decompression isotherm had decreased dramatically to about 370 Å<sup>2</sup>/molecule. Conclusion Mefp-1 layers at the air/water interface undergoes a considerable lateral shrinking when the DOPA molecules are oxidised and cross-linked. If cross-linking of the mefp proteins can be inhibited we may find a way of preventing colonisation of blue mussel at marine surfaces.

### **The spread of the invasive, fouling macroalga *Undaria pinnatifida* (Harvey) Suringar in the UK.**

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The large, adventive Japanese kelp *Undaria pinnatifida* has considerably extended its distribution around the world. Originally native to Japan Korea and China, this invasive alga has been identified as being of worldwide concern as a potential pest species. Reports of its introduction have come from regions as far apart as the UK, the Mediterranean coast of France, the Adriatic, the Atlantic coast of France and Spain, New Zealand, Tasmania, Australia and more recently, Southern California. The authors have carried out a study of the spread of *Undaria* in the UK and it has been shown that leisure boat traffic is the major method of spread around the UK. The study also reports on the invasive and fouling properties of *Undaria*, recording rates of spread within locations, and its ecology and biology in the UK.

### **SEAM; Assessing Concepts Systems and Tools for a Safer, Efficient and environmentally aware and friendly Maritime Transports**

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The volume of maritime transport in European waters is increasing and many European short sea-shipping initiatives will aim to move freight from the roads to the sea. This increased European and non-European traffic creates a need to improve the environmental acceptability maritime operations. SEAM will move towards these societal needs.

SEAM focuses on formulating safety and environmental measures and procedures to mitigate the impact of three key elements of shipping operations on the marine environment: Ballast water Management, Antifouling paints and Quality of air and fuel emissions.

SEAM will utilise Formal Safety and Environmental Assessment (FSEA) methodology as a rational structure for achieving its objectives. It will assess risks associated with shipping activities and evaluate the costs and benefits of measures to prevent or reduce such risks. SEAM will assess current regulation and policies, and suggest alternative rules and policies. A cost-effectiveness analysis will then systematically and quantitatively assess the expected outcomes and resource costs of alternative interventions in a way that facilitates decision-making by the different stakeholders.

This methodology follows the following steps: Identification of hazards, Hazards Risk assessment, Risk control measures, cost benefit assessment, and finally recommendation for decision making.

SEAM (Assessment and development of mitigation measures and procedures for environmentally friendly shipping operations) is a Research Project partly funded by the European Commission (DG Energy and Transport).

## **The effects of incorporated silicone oils and calcium carbonate on the surface properties and antifouling performance of a silicone elastomer**

Francis Fernández Estarlich<sup>1,2</sup>, Peter J Eaton<sup>1‡</sup>, Richard J Ewen<sup>3</sup>, Robert L Fletcher<sup>4</sup>, Susan Lewey<sup>2</sup>, Thomas G Nevell<sup>\*1</sup> and John Tsibouklis<sup>1</sup>

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The surface properties of some filled silicone elastomers have been compared with their resistance to marine biofouling. Elastomers, based on General Electric RTV11, containing 0 - 57 %w/w CaCO<sub>3</sub> and 0 or 5 %w/w PDMS oils (viscosities 50 - 10000 cp) have been studied using atomic force microscopy, contact angle goniometry and X-ray photoelectron spectroscopy. In laboratory experiments using selected organisms (eyed larvae of the oyster *Crassostrea gigas*, cyprids of the barnacle *Balanus amphitrite* and embryos of the brown alga *Sargassum muticum*) settlement and strength of adhesion have been investigated using a linear stress flow chamber. Exposure trials have also been carried out, including measurements of the ease of removal of attached organisms.

The surface studies showed that filler particles, protruding from the surface of the elastomer, gave rise to increased roughness but also formed softer local surface regions, apparently associated with less-cross-linked material immediately surrounding each particle. Surface energy (20.2 mJ m<sup>-2</sup>) was slightly increased (21.3 mJ m<sup>-2</sup>) by addition of low-viscosity silicone oils but was reduced (19.0 mJ m<sup>-2</sup>) by added high-viscosity oil, which formed surface droplets. For all coatings, contact with water gave reversible increases in surface energy, *ca.* 6 mJ m<sup>-2</sup> over 5 h; surface roughness also increased.

Of the experiments in which the displacement of settled organisms was measured as a function of the water-flow stress, those using barnacle cyprids were inconclusive (small numbers attached) but both the oyster larvae and the *Sargassum* embryos showed large differences between the silicones and the control surfaces. For oyster larvae, the results were similar for all the silicones, but the *Sargassum* embryos were more easily displaced from the oil-bloomed coating and from the smooth unfilled elastomer, than from the silicones containing added low-viscosity oil. Organisms were displaced no less easily for coatings containing greater proportions of the CaCO<sub>3</sub> filler, even though separate tests showed that glued pseudo-barnacles were more strongly adhered to these materials. In exposure trials (6 months, both protected and unprotected from 'grazing'), all the silicone coatings attracted similar surface densities of barnacles; these were more easily removed from the oil-bloomed surfaces.

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### **The Camellia project: from natural products to model antifouling coatings.**

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Secondary metabolites coming from a large number of sponges have been screened for their anti-fouling properties. In an iterative process compounds have been isolated because of their antifouling properties and identified. From a limited number of leads obtained by this initial work, more than 120 compounds have been synthesised. Systematic variation in structure of the basis molecules was meant to obtain structure-activity relationships. These novel synthetic compounds have been widely tested for their anti-fouling and anti-microbial properties. Moreover a number of environmental tests, specially dedicated to the marine environment have been performed on the most promising products. The results of all these tests combined with suitable physical and chemical properties for incorporation into paints and the economic potential (costs of production), resulted in three new antifouling compounds. These three novel compounds have been scaled up for testing in model and company related paints at different locations around the world. One of them has been applied as testpatches on three ships. Results are promising, however at the moment further development and commercialisation is hindered by the high costs required for registration in Europe.

### **Evaluation of Novel Foul-release Coatings using Algae**

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Biofouling still causes great problems for both naval and commercial vessels. With progressively tighter environmental legislation, endeavours to produce effective but environmentally benign coatings are being made. The limitations of silicone elastomers as foul-release coatings have prompted the search for alternative chemistries based on low-adhesion systems. Laboratory scale evaluation allows a relatively rapid assessment of the performance of a range of experimental polymers under identical conditions. Coatings evaluations using algae can be divided principally into three categories; (1) settlement *i.e.* the attractiveness of a surface for cell attachment, (2) the strength of attachment of cells to the surface, and (3) the strength of attachment after a period of growth. However, in addition to these evaluations, detailed biological examination and the controlled conditions of laboratory tests can help identify other interactions such as toxicity, chemoattraction and the modification of growth forms. Assessments have been made using zoospores of the green alga *Enteromorpha* and cells of the diatom *Amphora*. The flow of water around the hull of a ship is turbulent, and ideally test conditions for measuring strength of attachment of organisms need to reflect this. A water-channel, specially designed for this purpose (Schultz *et al.*, 2000) provides suitable turbulent flow and associated wall shear stresses. Another method, based on the design of Swain & Schultz (1996), uses a high-pressure water jet to create greater shear stresses to remove more tightly adhered cells. Silicone-elastomer coatings have been shown to possess characteristics desirable in foul-release coatings. A number of properties are thought to contribute to their success including smoothness, low surface energy (hydrophobicity), low glass transition temperature and low elastic modulus. As part of the ONR Coatings Programme we are investigating the effects of altering some of these parameters in simple PDMS matrices. In addition, a range of ultrahydrophobic and hydrophilic materials, structured amphiphilic, nanocomposite and microtextured surfaces are being studied. A process of successive testing followed by modification is aimed at optimising materials for use as foul-release or minimally adhesive coatings. A general background to laboratory assessments and results demonstrating the effects



## **Enhanced settlement of fouling organisms on boat hulls following in-water hull cleaning: implications for the spread of marine fouling species**

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Transport of fouling organisms on the hulls of vessels is one of the most important means of spread of nonindigenous aquatic species. Because of the costs involved in dry-docking and antifouling a vessel, 53 % of the owners of yachts and other recreational craft surveyed in six marinas in Queensland, Australia, often manually remove fouling communities by scraping or brushing the hull while the boat is careened or still in the water. This procedure may increase the risk of transmission of exotic species in several ways: (1) by depositing the scraped organisms on the seafloor, (2) by causing release of competent gametes from damaged adults, or (3) by increasing the susceptibility of visiting vessels to colonization by local fouling assemblages. We tested the last of these risk factors experimentally by monitoring the development of fouling assemblages on fiberglass tiles coated with an aged commercial antifouling paint. Colonization patterns of fouling organisms were compared among tiles on which both local and non-local fouling assemblages had initially been allowed to develop, and from which the existing biota was then either (i) removed by scraping, (ii) removed by surface sterilization, or (iii) left intact. The tiles were incubated in a recreational vessel marina for periods of 2 and 6.5 weeks to simulate vessels residing for relatively short and moderately long periods. Despite considerable spatial variability in the data, between 1.8 and 5.8 times more individuals and colonies recruited to tiles from which fouling had been manually removed, and these tiles consistently had the largest number of recruiting taxa. Elevated recruitment rates to these surfaces compared to others were observed for the majority of taxonomic groups in the dataset, and maximal levels were often reached after a period of only two weeks. In contrast, recruitment to surfaces bearing established fouling assemblages was low for all taxonomic groups except for erect bryozoans and the amphipod *Corophium*. In all treatments, there were no clear or consistent differences in recruitment rates of the various taxa to surfaces that carried locally or non-locally developed fouling assemblages. Our results suggest that in-water hull cleaning of recreational vessels considerably elevates the potential of recreational vessels to act as transmission vectors for locally established, potentially nonindigenous fouling species, as such vessels become significantly more susceptible to fouling, and are likely to attract a larger quantity of recruiting organisms and taxa than prior to manual hull cleaning. Causes for these elevated levels of recruitment are twofold: (1) when a hull is cleared of fouling, small quantities of soft tissues and hard structures remain on the hull and might attract taxa exhibiting gregarious and/or associative settlement, and (2) the presence of especially the hard calcareous remains might protect the underlying antifouling paint from abrasion by the manual scraping action and prevent the release of residual toxins from deeper layers of the paint.

### **Internal Hull Biofouling: Effects of Surface Properties and Resuspension of NO-BOB Sediments**

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Control of bioinvasion pathways on an international basis requires attention to ship-surface biofilms and sediments, as well as source ballast waters. We have developed hardy, inexpensive, in-tank suspended devices called Ballast Organic Biofilm samplers (BOBs) and successfully deployed them in transAtlantic, Mediterranean-Atlantic-Panama Canal-Pacific Rim return commercial cruises. Most recently, they have been deployed in shipping entering the North American Great Lakes. Circumstances surrounding shipping to the upper Great Lakes introduce a new issue of re-suspension of biota-rich ballast tank sediments that must be understood with regard to subsequent influences on seeding exotic species into Great Lakes ports. About 75% of the ships entering the St. Lawrence Seaway are self-defined as being in the No Ballast On Board (NO-BOB) condition, not requiring ballast tank water exchanges before entering the Great Lakes system. The inevitable inch or so of bottom water and sediments, impossible to remove with current ballast water pumping systems, amounts to about 50 tonnes for typical vessels bringing world commerce to the Great Lakes region. These vessels, arriving in Lake Ontario, take on ballast water to transit the Welland Canal into Lake Erie and thence to the other Lakes. The Lake Ontario re-ballasting is a dramatically energetic process as water pours into the ballast holds and resuspends the bottom materials for delivery to later ports, when cargo is put on and water is released. Here, we report the results of a Sea Grant-funded investigation of ballast tank conditions in an international NO-BOB vessel re-ballasted in Hamilton harbor (ONT, Canada), and transiting through the Great Lakes to Chicago (IL, U.S.). The sampler, containing 50 sets of duplicate test coupons of different surface energies—half facing up and half facing down—was suspended in the vessel's forepeak tank prior to re-ballasting in Lake Ontario. The test plates effectively integrated the biofilm-forming and sediment settling events during the remainder of the voyage. A significant up vs. down asymmetry was noted with regard to the biofilm inclusion of particulate matter, upper faces being surprisingly rich in diatoms for dark ballast spaces. Examinations of biofilms from prior power-plant studies and from Sea Grant-funded projects addressing the introduction of zebra mussels to the Great Lakes, also showed high abundances of diatomaceous remnants in dark flow paths, with surrogate "ballast" biofilms having an apparent association of diatoms and settled Dreissenid veligers. The association of potential pathogens with particulate matter in ballast systems has been cited by others. Ongoing studies of ballast biofilms and sediments as "seed beds" for invasive exotic species are in progress.

### **Retention of Pre-Construction Primer (PCP) as an Integral Portion of Ballast Tank Lining Systems**

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The retention of PCP as an integral part of the ballast tank corrosion control system offers the potential for significant savings in the cost of lining ships ballast tanks during new ship construction. Historical perspectives will be presented along with some survey results from both European and Asian shipyards. Four-year test results of an actual mock-up ballast tank test program will also be presented. The US National Shipbuilding Research Program, Surface Preparation and Coatings Subcommittee sponsored the work carried out by this project.

### **Serotonin neurotransmitter in *Balanus amphitrite* cyprids and its putative role in settlement**

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The thoracican barnacle *Balanus amphitrite amphitrite* Darwin is a cyrriped crustacean, with a sessile adult stage and seven larval stages. Embryos brooded within the mantle cavity of the adult are liberated when mature at the nonfeeding, first stage, nauplius. Development then proceeds through five, planktotrophic, nauplius stages before metamorphosis to the lecithotrophic cypris larva. The final stage of barnacle life cycle, is specialized for the processes of settlement, attachment and metamorphosis. Serotonin had been previously detected in the nervous system of adult barnacles, and recently it has been demonstrated that this neurotransmitter seems to regulate larval settlement. The aim of the present research is to study the presence of serotonin by immunohistochemical methods, and its effect on larval settlement by experimental tests. Cyprids were obtained from a laboratory culture of *B. amphitrite* collected in the Gulf of Genova (Italy). Paraformaldehyde or Bouin fixed paraffin sections of different aged cyprids were used for immunofluorescent and immunoperoxidase reactions with a polyclonal anti-serotonin antiserum. Serotonin immunoreactive neurons were localised in different regions of the central nervous system both in the brain and posterior ganglion. Numerous serotonin immunoreactive nerves were observed at the periphery. Serotonin was detected also in the cement gland apical portion. To test the role of the neurotransmitter during the settlement, cyprids were treated with different logarithmic concentrations of several substances, including serotonin, fluoxetine (serotonin re-uptake inhibitor), and dopamine. Settlement tests were performed according to Rittschof et al. Serotonin did not show significative effects, (Dunnett test vs. control), while both fluoxetine and dopamine seem to affect the settlement. Our results were discussed in the light of the data reported in literature. The data obtained suggest the involvement of serotonin in the complex mechanism of settlement by the release of the adhesive cement

### **The Surface Structure and Reorganization of Siloxane and Fluorocarbon based Polymers: Effects of Polymer Properties on Surface Properties**

Gardella, Joseph A Jr.; Hawkrige, Adam M.; Tulevski, George; Hou, Yuanxue; Mahoney, Christine M.; Nowak, Richard W.; Chen, Lu; Toselli, Maurizio; and Lee, Won Ki; Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY USA 14260-

For fouling release marine applications, the study of the surface structure of soft siloxane and fluorocarbon polymers with low glass transition temperatures requires a full understanding of water induced reorganization. The use of angle dependent XPS (aka ESCA) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) methods with a low temperature sample handling probe has provided a means to answer quantitative questions about the structure and dynamics of polymer materials with appropriate physical and mechanical characteristics in the hope that defined surface chemistry will promote fouling release. This paper will report results from a range of exemplar materials systems, such as PDMS based polyimides and polyurethanes, perfluoropolyether systems and a new model system based on amphiphilic hydrogel materials. The latter materials were synthesized using narrow molecular weight dimethyl siloxane (DMS) graft structures (from anionic polymerization methods)

These graft PDMS-polyhydroxy ethyl methacrylate (PHEMA) hydrogel copolymers have been synthesized using narrow molecular weight PDMS macromers which were prepared using anionic polymerization. The XPS results show that well-defined PDMS chain lengths yield less overall PDMS surface segregation than broader molecular weight PDMS. The interpretation for this effect comes from the nature of the segregation of lower molecular weight PDMS rich oligomers. The segregation of these materials may skew the measured surface properties and yield unstable surfaces. Water induced reorganization is most dramatic for radical polymerized PDMS-PHEMA graft copolymers with broad molecular weight distributions (PDI >2.0). Similar polymers with narrow molecular weight distributions (PDI , 1.2) show very little reorganization. We propose that the lack of stability in the broad molecular weight materials is due to shorter surface segregated oligomers with low molecular weight.

We also will report on the latest synthetic efforts to utilize PDMS structures in copolymers with defined surfaces. Finally, the development of new methods, including low temperature sample handling for Time of Flight SIMS will be reported.

### **Some fundamentals of adhesion in synthetic adhesives**

Gay Cyprien, CRPP - CNRS, Av. Schweitzer, 33600 Pessac, FRANCE.

We will review some adhesion mechanisms that have been understood in the field of synthetic adhesives and attempt to link them with situations encountered in fouling issues.

Adhesives are used in the form of thin films. The discussion will include the following points. Molecular scale interactions at the surface of the adhesive, such as chemical and physical bonding with the substrates, can be tuned by suitable surface treatment and surface chemistry. They affect the quality of the contact between the adhesive and the substrate on the micron scale, depending on its surface roughness and on the adhesive and substrate viscoelastic properties. Upon traction, high negative pressures appear. Due to the incompressibility of the adhesive, this results in inhomogeneous deformations in the film : bubbles may grow in the bulk or from the interface of the adhesive film (cavitation). Alternatively, narrow regions of air may develop from the edge of the sample, whether inside the adhesive or at the interface with the substrate, so as to relieve the stress in the film (fingering). The behaviour of the adhesive is strongly affected by the substrate flexibility : peeling a tape with a flexible backing is easier than detaching a rigid body. In a structure made of several layers of different materials, a fracture will in principle migrate towards the interface that dissipates the least amount of energy, but this may be hindered by contrasted viscoelastic properties between the layers. We will also discuss experiments on rolling objects in the presence of adhesion.

### **Hull Fouling of Maritime Vessels as a Pathway for Marine Species Invasions to the Hawaiian Islands**

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The native species of the marine and terrestrial environments of Hawaii arrived as natural biological invasions through historical time, and through evolution and adaptation became the present communities associated with the archipelago. The advent of modern history has created new human – mediated, or anthropogenic, biological invasions through non-natural mechanisms. In terms of natural dispersal mechanisms, species invasions to new regions are rare in time scales measured from the human perspective because of the barriers that must be overcome. In Hawaii's marine environment, examples of these natural barriers are ocean currents and distance from continental land masses. These natural species invasion events are rare and measured on the scale of geological time. The natural barriers that exist in isolated marine environments such as Hawaii are overcome by anthropogenic influences on dispersal patterns. This creates a situation where the isolated marine environments of the Hawaiian Archipelago are more readily exposed to nonindigenous species. A case study of a particular anthropogenic dispersal mode, maritime vessel hull fouling, is reviewed. This mode has effects on altered habitats such as Honolulu Harbor and Pearl Harbor, and also pristine marine reserve habitats located in the main Hawaiian Islands.

### **The Environmental Fate of the Marine Antifoulant 4,5-Dichloro-2-(n-octyl)-4-isothiazolin-3-one (DCOI)**

Guo, Ipin and Jacobson, Andrew, Rohm and Haas Company, PO Box 904, Spring House, PA 19477, USA

DCOI is the active ingredient in the formulated marine antifoulant Sea-Nine<sup>®</sup> 211 Antifouling Agent. Previous studies have demonstrated that DCOI biodegrades very rapidly in aerobic and anaerobic marine microcosms. The fate of DCOI in fresh water aerobic and anaerobic microcosms (water/sediment systems) as well as in estuarine water have been examined. Similar to marine microcosms, DCOI biodegrades very rapidly in fresh water microcosms. Biodegradation involves cleavage of the isothiazolone ring yielding alkyl compounds with no observable biocidal activity. Similar results, rapid biodegradation and cleavage of the isothiazolone ring, are observed for DCOI in estuarine water. These results demonstrate that DCOI will not persist in the aqueous or sediment environments.

## **Chemical control of bacterial epibiosis in the soft coral *Dendronephthya* sp.: phylogenetic analysis of benthic bacterial isolates and their susceptibility to coral derived compounds.**

Tilmann Harder, Stanley C. K. Lau, Sergey Dobretsov, Tsz K. Fang, Pei-Yuan Qian, Department of Biology, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, SAR Hong Kong, China

To investigate a potential defense mechanism against bacterial epibiosis in the soft coral *Dendronephthya* sp., the diversity of culturable bacteria on the coral was compared with indigenous benthic bacteria isolated from an inanimate reference site in the close vicinity. Unlike the predominance of *g-Proteobacteria* among the culturable bacteria obtained from the reference site, a significant portion of culturable bacteria on the coral surface belonged to *a-Proteobacteria* and *Cytophaga-Flexibacter-Bacteriodes* branches. Organic extracts of coral tissue and waterborne products of coral-associated bacteria distinctly inhibited the growth and attachment of indigenous benthic bacteria. These results suggest an endogenous chemical and an exogenous biological mechanism against bacterial epibiosis in *Dendronephthya* sp., respectively. The combined antibacterial effects may explain the observed difference in bacterial species composition on the coral and the inanimate reference site.

### **Biocide Release Rate Measurement – Lab and Field**

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The rate of biocide release from antifouling (AF) coatings used to control marine fouling has been studied for decades, and has been found to be influenced by physical factors such as hydrodynamics, temperature, pH, and salinity, as well as biological factors such as the presence and nature of biofilms at the paint surface. Further complicating this phenomenon, release rates tend to change over time and are affected by the nature of the biocide and the nature of the coating system itself. This makes determining release rate quite challenging. Because knowledge of coating release rate helps us to understand many aspects of coating performance, it is an important hurdle to overcome. Accurate release rate measurements may provide useful insight into potential environmental impact by providing an estimate of biocide loading. They also serve to determine whether or not one coating system releases more biocide than another. Such information is potentially beneficial to both the formulator, the regulator, and the end user.

Both laboratory and field approaches to measuring biocide release rates have evolved over time. The rotating cylinder methods developed by the American Society for Testing Materials (ASTM) and the International Organization for Standardization (ISO) are very similar, have emerged as the “accepted” methods for measuring release rate of copper and tin (ASTM only) from antifouling paints in the laboratory. These methods involve the application of test coatings to the outer curved surface of cylinders that are then exposed in a fixed volume of artificial seawater for known lengths of time under controlled conditions of hydrodynamic regime, temperature, pH, and salinity. For in-service release rates, other methods have been developed including, but not limited to, an in-situ dome method that was developed by the Space and Naval Warfare Systems Center, San Diego (SSCSD). It has been determined, for TBT, that the release rates measured using the earlier rotating cylinder approach (ASTM) are 5 to 39 times higher than those measured by the in-situ dome method developed by the US Navy (Schatzberg, 1996). The in-situ measurements have yet to be normalized for hull conditions such as coating age and environmental conditions at the time of sampling. Others have reported this tendency toward higher ASTM values as well (Thomas et al., 1999).

SigmaKalon began development of a new method determining release rate of an organic co-biocide, Diuron, that would give more reliable and reproducible results. The research had been part of the Camellia project that had been co-sponsored by the EC. The study led to a practical lab-method that showed a good reproducibility and could be combined with long term dynamic or static ageing. In addition it has been found that the release rate in the by ISO and ASTM defined steady state release rate period (day 21-45) over-exaggerates the release rate for the period there after. The method will now be applied for other co-biocides. The analytical part will become more complex in case of fast in sea-water degrading co-biocides.

The need for research and basic understanding of release rate has never been greater. Recent studies to validate standard laboratory release rate methods have shown mixed results. In general, inter-laboratory agreement is poor. In addition, the relationship between standard laboratory and in-situ/in-service release rate methods is poorly understood. This paper outlines efforts to explore the complex nature of release rate measurement, and the possibilities for data interpretation.

## **Evaluation of Hydrodynamic Drag on Antifouling and Fouling Release Coatings using the Friction Disk Machine**

Haslbeck, Elizabeth G., Eric R. Holm, Walter J. Talbott, and Andrew Field

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Accumulation of even microbial biofilms on ship hulls results in increased roughness and, therefore, hydrodynamic drag. Increased drag results in greater fuel consumption, and for the military can interfere with mission. The Navy's current antifouling coatings experience up to an 18% drag penalty due to the build-up of microbial fouling alone. Improved coating technology could reduce fouling and improve ship performance. The consequences of fouling and subsequent drag penalties for these technologies should be evaluated before the coating systems are widely applied. We have developed a simple laboratory method employing coated rotating disks to evaluate, for experimental coatings, the drag consequences of accumulated microbial fouling. The method makes use of a friction disk machine (FDM) consisting of a variable speed motor that drives a shaft onto which coated disks are mounted. A precision dynamometer installed on the shaft measures the torque produced when the shaft rotates. Drag is calculated from the torque experienced when disks are rotated. Experiments conducted with the FDM indicate that there are significant differences among antifouling and fouling release coatings in their ability to minimize drag penalties due to microbial fouling. The method is sufficiently sensitive to detect effects due to the presence of additives in otherwise similar paint formulations. Results of previous tests with foul release coatings give results comparable to full-scale ship trials.

### **Vessel hulls: a variable vector of nonindigenous species**

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The relative risks of ships introducing nonindigenous species (NIS), whether by via hull-fouling or ballast water discharge, vary among vessel types and among ports that cater to different types of vessels. Surveys of the hulls of cargo ships and recreational yachts in New Zealand have shown that, although private pleasure craft and chartered fishing vessels do not discharge large volumes of ballast, they tend to have more variable and diverse hull-fouling assemblages than merchant vessels. They also remain in NZ waters for much longer than do merchant vessels. Thus, the risk profiles and range of NIS likely to establish in ports that cater for international yachts are likely to differ from commercial ports that handle large numbers of merchant vessels with a high volume of ballast water. Protective management strategies need to take account of these differences.

### **Identifying hazards in complex ecological systems – Part 2: Infection Modes and Effects Analysis for biological invasions**

Keith R. Hayes, Centre for Research on Introduced Marine Pests, CSIRO Division of Marine Research, GPO Box 1538, Hobart, Tasmania, 7001, Australia

This paper describes a rigorous and systematic hazard analysis, called Infection Modes and Effects Analysis (named after its industrial counterpart Failure Modes and Effect Analysis), which was used to investigate the potential spread of marine organisms by human vectors. The analysis was conducted using small craft as a model system and implemented through nine workshops targeted at owners and operators of fishing vessels, motor cruisers, yachts and trailerable boats, operating out of local ports in southeastern Australia. It identified 7 vessel components, divided into various sub-components, and 8 infection modes. Each sub-component/infection mode combination represents a possible vector for the spread of marine organisms. The analysis identified a total of 215 sub-component/infection mode combinations for displacement vessels and a further 71 combinations for trailerable vessels, which were then prioritised. Water retention and internal fouling of seawater and grey water inlets, internal fouling of sonar tubes and water (and sediment) retention in sewage holding tanks were identified as the main vectors of a displacement vessel. The burley bucket and water (and sediment) retention in the anchor well and bilge pump were identified as the main vectors of a trailerable vessel. This is the first time that Failure Modes and Effects Analysis, or a variant of it, has been applied to biological invasions. The analysis demonstrates that rigorous hazard identification techniques, originally designed for complex industrial systems, can be modified for use in ecological systems.

### **The Neighborhood effect: Larval settlement patterns in waters of different origin**

Heede, Monja and Wahl, Martin Prof. Dr. ; Zoological Institute Department of Marine Ecology and Systematics , Christian-Albrechts University , 24098 Kiel, Germany

A previous field experiment has shown that different communities establish in different biogenic neighborhoods (e.g. musslebeds, seagrass,...).

To test the hypothesis that the effect is caused by water compounds (e.g. exudates), seawater samples are taken from within monospecific habitats (e.g. blue musslebeds) and incubate with natural planctonic communities. Settlement rates are measured and compared to the ones of control samples from outside the habitat. Larval settlement patterns presumably caused by microhabitat exudates will be presented.

### **Age-related settlement success by cyprids of the barnacle *Balanus amphitrite* with special reference to consumption of CMP, lipids and hormonal levels.**

<sup>1</sup>Claire Hellio\*, <sup>2</sup>Mark Prescott, <sup>1</sup>Sheelagh Henry, <sup>2</sup>Geoffrey Wainwright, <sup>2</sup>Huw Rees and <sup>1</sup>Anthony Clare

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Sessile marine organisms, such as algae, hydroids, mussels and barnacles, often cause serious problems by settling on ship hulls, cooling systems of power plants and aquaculture cages. The control of biofouling is of particular concern in modern marine engineering and shipping operations and is one of the most important problems currently facing marine technology. Here we report the findings of a baseline study that aimed to clarify concepts of competence and discrimination during settlement of *Balanus amphitrite* cypris larvae. The effects of temperature and duration of swimming on depletion of cyprid energy reserves and hormonal status in relation to competence to settle and ability to discriminate between potential settlement sites were studied. New moulted (0-day-old) cyprids of the barnacle *Balanus amphitrite* were prevented from settling for 0 to 14 days at two different temperatures (22°C and 6°C). The effect on settlement success of prolonging the lifetime of the cyprid stage was evaluated using a nitrocellulose membrane assay. In addition, extracts of these cyprids were prepared so that physiological parameters that might be expected to influence settlement, vis-à-vis energy reserve levels (lipid and protein) and hormone titres, could be measured. The study revealed that temperature had a major influence on settlement; maximal rates of settlement (24h assay) – 91.15% and 33.63% were observed for 9-day-old cyprids at 22°C and 6°C respectively, after which settlement declined significantly. Image analysis of Western blots of cyprid major protein (CMP - a putative energy reserve) revealed a decline in levels with increasing age at 22°C, while levels remained constant at 6°C. A similar pattern pertained to lipid levels. Arthropod moulting hormone - 20-hydroxyecdysone (20E) - levels were lower in cyprids aged at 6°C compared to 22°C, as determined by radioimmunoassay. The drop in settlement rate after day 10 reflects a depletion in energy reserve levels (CMP & lipid). Moreover, differences in settlement between 6°C and 22°C aged larval can be explained in part by differences in energy reserve and ecdysteroids levels. Assays of methyl farnesoate levels are in progress and are predicted to decline with age. The feasibility of determining the physiological age of cyprids in the field will be discussed.

### **Macroalgae of the Brittany shores: antifouling activities and potential use for paints.**

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One of the most promising alternatives to heavy metal based paints is afforded by the development of antifouling coatings in which the active gradients are compounds from marine organisms operating naturally as anti-settlement agents. The surface of sessile benthic marine algae are particularly susceptible to fouling as they are restricted to the photic zone where optimal conditions exist for the growth of fouling organisms are. However, while some marine algae are heavily fouled, other species living in the same ecological niche are rarely ephytized, suggesting the possible presence of antifouling mechanisms. To assess the occurrence of biologically active substances from marine algae inhibiting the growth of fouling organisms, extracts (aqueous, ethanolic and dichloromethane) of 30 algae for the North East Atlantic Coast of France were tested for their antifouling activities. The target organisms were: bacteria (45 strains), fungi (5), microalgae (12), macroalgae (4) and *Semibalanus balanoides* and *Mytilus edulis*. Moreover, toxicity tests were conducted on larvae of *Echinus esculentus* & *Crassostrea gigas* and by assessing the mitotic & lysosomal activities of fibroblastic mouse cells. The results of the screening programme presented showed very promising results which confirm that marine algae are a rich source of bioactive compounds against colonising organisms. Some extracts exhibited activities against only 1 or 2 organisms although some others exhibit broad-spectrum activities. Two of the most active extracts, namely *Sargassum muticum* and *Ascophyllum nodosum*, were partially purified and appear very active at 250 ng/ml against marine bacteria and fungi (*A. nodosum*) and against algae (micro & macro) and mussels (*S. muticum*). These two algae have the advantage of being present in huge quantity of the Brittany's shores and so could be potentially used for an industrial application.



## **Characterization of the Adhesive Mucilages Secreted by Live Diatom Cells using Atomic Force Microscopy**

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Atomic Force Microscopy (AFM) resolved the topography and mechanical properties of the adhesive mucilages secreted by living cells of several fouling diatoms. Tapping mode images of live cells revealed a soft, cohesive mucilage layer that encased most of the diatom silica cell wall. Force curves revealed that this type of mucilage had a small adhesion strength but demonstrated considerable compressibility. High force contact mode imaging (i.e., increased set-point voltage) resulted in the 'raking' of the cohesive mucilage to reveal the underlying, silicified wall structures. Further imaging of cantilever 'cleaned' cell walls of live cells in stationary growth phase revealed the active secretion of soft mucilage via pore openings in the girdle bands. A second adhesive mucilage in the form of distinct strands was found to project through the silica valve walls at the raphes, and to be involved in cell adhesion and motility. An adhesive strand (or strands) could only be detached from the standard AFM cantilever probe using mechanical retraction of the piezo. However, we have now developed AFM cantilever 'fishing' as a technique, utilizing the Asylum 1D AFM (Santa Barbara). The cantilever tip does not contact the cell surface, but is positioned just above it, and adheres to a free, single polymer chain, or whatever molecule extends out from the complex surface mucilage into the surrounding environment. As the cantilever does not come directly in contact with the substratum, 'fishing' prevents multiple, non-specific interactions that often cloud results from force measurement. Fishing therefore enables us to control the interaction under investigation. We have successfully utilized this technique to measure single molecules (polymers) without the cantilever interacting directly with the substratum. The parameters measured are elasticity, adhesion, (binding forces of single molecules, conformational changes in molecules as they stretch). The values obtained thus far imply that the strands are very adhesive and strong compared to other single biological polymers, and could account for the complex interactions between diatom cells and their substratum. The use of the AFM in studies of bioadhesives and the processes of bioadhesion, including the interaction of diatom adhesives with different substrata, will be discussed.

### **Performance of Nickel Alloys for Applications in Seawater Piping Systems**

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An established performance record for Ni-Cr-Mo alloys in seawater piping applications is discussed. This class of alloys is generally chosen for seawater service due to favorable characteristics of strength, temperature and SCC resistance, and excellent corrosion resistance. However, a particular consideration for using Ni-Cr-Mo alloys in seawater piping that these alloys are susceptible to crevice corrosion. Corrosion potential ennoblement due to environmental influences has been linked to crevice corrosion initiation for these alloys. The relative resistances to crevice corrosion for several different Ni-Cr-Mo alloys are highlighted, demonstrating that although there can be appreciable differences in crevice corrosion resistance between different alloys none of the Ni-Cr-Mo alloys tested were immune to crevice corrosion in seawater. Some practical considerations for minimizing crevice corrosion susceptibility are also discussed.

## **Boatscrubber Environmental Hull Cleaning Closing the Loop**

Hudd, Adrian. Boat Scrubber

The proposed banning of TBT and Copper and the increasing environmental pressure to reduce the use of all biocides in antifouling paints has led to extensive research into easily cleaned non-biocide hull coatings. Experience has shown that performance deteriorates with all hull coatings and that for biocides to be reduced, there is a need for a simple cleaning device that offers the same ease of use and fast service that the Car Wash offers the motorist.

Boatscrubber International Ltd have produced device to clean the hulls of leisure craft whilst still in the water which will facilitate the reduction and eventually eliminate the use of biocides within hull coatings.

The design encompasses four main areas.

- Environmentally friendly, - steering the way for the future.

- Low cost cleaning (scrubbing) - allowing regular use by the boat owner.

- Low capital cost allowing an operator a good ROI.

- Good cleaning performance and fast throughput for the vast range of mono and multi hull profiles.

In the case of the environmental impact, two areas were considered.

- Pollution caused by the unit.

- Pollution caused by existing hull coatings.

The unit cleans a boat without the use of chemicals and relies purely on a fresh water hydraulic system, developed for the food industry.

The elimination of oil (even vegetable oil) will prevent pollution from leakage as well as accidental spillage.

To reduce pollution from existing coatings, the unit was designed to lightly wipe the boat, as opposed to scrubbing, to remove the slime. Wiping is far less abrasive than using a pressure washer.

Whilst current antifouling paints are obviously harmful to human and marine life, they are currently allowed on the hulls of boats. In some areas legislation is being introduced preventing an owner easily maintaining his boat. This leads to a different pollution and a lack of safety. In areas where legislation has been introduced preventing the use of some paints or scrubbing in the water, the laws are not being policed and are being flouted.

The obvious solution is the reduction and possible elimination of biocides especially for leisure craft.

The use of non-biocide coatings together with the Boatscrubber provides a practical solution for the vast number of leisure craft and marinas.

### **Advanced, Environmentally Acceptable Antifouling Coating Development**

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The Naval Sea Systems Command (NAVSEA) initiated a program to identify and develop advanced, environmentally acceptable, antifouling coatings in 2000. The program goal is to identify, and approve for use in the U.S. Navy, advanced antifouling coatings that are either free of copper and other persistent biocides, or that release far less copper into the environment than current Navy underwater hull coatings. The program is based on cooperative approach in which the Navy works with commercial vendors to identify underwater-hull coating systems that use non-persistent, non-metallic biocides to reduce or eliminate copper emission while still effectively preventing fouling for up to twelve years. Results from screening tests and small-scale shipboard evaluations indicate that copper-free antifouling coatings can offer performance comparable to standard Navy copper-ablative antifouling coatings.

### **The Fate of the Marine Antifoulant DCOI applied to a Vessel**

Jacobson Andrew, Rohm and Haas Company, PO Box 904, Spring House, PA. 19477, USA

Numerous laboratory studies have been performed demonstrating that the marine antifoulant 4,5-dichloro-2-(n-octyl)-4-isothiazolin-3-one (DCOI, the active ingredient in Sea-Nine<sup>®</sup> 211 Antifouling Agent) biodegrades very rapidly in marine microcosms. To assess the fate of DCOI in the environment, the concentration of DCOI in harbor water and sediment and its fate in a shipyard treatment facility were examined. Water samples were concentrated using C-18 solid phase extraction and subsequently quantitated by gas chromatography-mass spectroscopy. A strong decline in DCOI water concentration as a function of the distance from the painted vessels was observed ranging from 283 ng/L in the immediate vicinity of the vessels to less than 5 ng/L at 400 meters from the vessels' surfaces. The measured decline curve was compared to that calculated using a 1 dimensional model and it was concluded that the primary mechanism of dissipation of DCOI was degradation and not dilution. One of the DCOI painted vessels in the harbor was brought into dry-dock and the hull water washed. The wash water was collected, quantitated, and transferred into the shipyards treatment facility. After complete treatment, the concentration of DCOI in the water was less than the level of detection (5 ng/L) and significantly lower than the Predicted No Effect Level (PNEC). This indicates that there is minimal environmental risk to a harbor from the leaching of Sea-Nine 211 from painted vessels and from properly treated wash water.

### **New technology stainless steels and nickel alloys for marine applications.**

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Stainless steels production methods have changed dramatically in the last 20 years. These methods have allowed the development of alloys with improved properties and many potential marine applications. Some of these alloys have corrosion resistance equal or better than the traditional austenitic stainless steels with about twice their strength. New stainless steels and nickel alloys have been developed that have substantially better corrosion resistance than the traditional austenitic stainless steels. The metallurgy, mechanical properties and corrosion resistance of these alloys are discussed.

### **Involving Boat Owners and Industry in Pleasure Craft Antifouling Policies - A San Diego Bay Case Study**

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Effective coastal policy making must consider multiple factors and stakeholders. It will be important to consider environmental and economic factors in developing policies on copper contamination from antifouling paints in Shelter Island yacht basin of northern San Diego Bay. A Total Maximum Daily Load study by the Regional Water Quality Control Board found the average level of total dissolved copper in the basin was 6.7 ppb vs. the state and federal standard of 3.1 ppb. In nearby Orange County, Newport Bay and Dana Point Harbor have been proposed for the 303(d) list of impaired water bodies, due to copper. California's 2000 Plan for Nonpoint Source Pollution Control mandates action on pleasure craft antifouling paints. The boating industry contributed over \$11 billion to the Gross State Product in 1995.

In 1999, boaters and boating businesses knew little about changing policies and how policies would affect them. The California Sea Grant Extension Program (CSGEP) involved them in developing policies and best management practices by a "public policy research and education" approach long used by Cooperative Extension for agricultural policy issues. The goal to improve boaters' and boating businesses' ability to reduce pollution from antifouling paints while maintaining a vibrant boating industry.

CSGEP identified environmental, technical and economic factors related to antifouling paints and disseminated findings to stakeholders. In September 2000 CSGEP convened 110 international representatives of coating and boating businesses, boaters, regulatory agencies, environmentalists, scientists & policy makers to learn about these factors, exchange perspectives and recommend policy, research and education. Policy makers responded with action. In October 2001 a new state law mandated research on incentives for boat owners to use nontoxic alternatives to antifouling paints. The CSGEP is participating in this research and conducting an educational program on nontoxic antifouling paint properties, performance and economic factors with funding from California State Water Resources Control Board, Renewable Resources Extension Act, UC Davis Center for Pesticide Management, Research & Education, California Department of Boating & Waterways and California Sea Grant College Program.

### **Ligno-cellulose degradation by marine fungi**

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Many organisms are active in the decomposition of wood in the marine environment, including fungi. Some 450 higher marine fungi have been described over the past 50 years. A number have been screened for their cellulase and lignin degrading ability. Results from using agar assay methods suggest marine fungi do produce a range of enzymes: cellulases, xylanases, laccases, and probably peroxidases. Of the cellulases, most marine fungi exhibit exo- and endoglucanase activities. Xylanase is very common amongst these fungi, and those growing well in agar in-cooperated with xylan usually showing equally good CMCase (endoglucanase) activity and growth on filter paper (exo-glucanase). Of the three ligninolytic enzymes, laccase is more prevalent amongst the marine fungi tested in different laboratories. Most of the sand-inhabiting fungi were however, laccase negative (e.g. *Corollospora* species), whereas with the exception of a few (e.g. *Kallichroma tethys*, *Zalerion maritimum*), the majority of the wood-inhabiting strains were laccase positive. Peroxidase activity, as tested with the use of Poly-R dye in-cooperated in agar, have not been detected in marine fungi so far, but other tests have shown peroxidases are common in these taxa.

### **Coated 4140 steel exposed to marine, mixed bacterial communities containing sulfate-reducing bacteria (SRB)**

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Epoxy and polyurethane coatings are widely used as heavy-duty moisture- and chemical-resistant coatings and linings in immersion and atmospheric marine environments to protect underlying metals against corrosion. Nylon coatings are used because of their strength, low coefficient of friction and wear resistance. For protective coatings to be effective, they must be resistant to microbial attack. Corrosion is often extremely rapid at small discontinuities in coatings, and breaks or blisters in coatings may allow access of corrosion-inducing microbes, such as sulfate-reducing bacteria (SRB), to the metal beneath. Many biofilms accelerate corrosion of metals and alloys, but there may be situations where a biofilm provides (at least for a limited time) a protective effect/decreased corrosion rates. In accelerated corrosion testing of 4140 steel coupons, controls (sterile growth medium with 2.5% wt/vol NaCl) had similar corrosion rate values while three marine, mixed communities containing SRB had different effects on the corrosion rate of 4140 steel. One microbial community isolated from an iron phosphate primed coupon had a 7-fold lower corrosion rate than the control, while another microbial community isolated from an epoxy-coated coupon had a corrosion rate 2-fold higher than the control. Recently, other investigators have reported data on "protective" biofilms. The mechanism(s) could include the elimination of corrosive chemical agents such as oxygen, the production of antimicrobial agents, the production of corrosion inhibiting compounds that modify the localized environment in the biofilm, etc.

EDS analyses detected breaching of epoxy, nylon and polyurethane coatings applied to 4140 steel when coupons were exposed to mixed communities of marine microbes that included SRB. SEM and ESEM studies showed all coated surfaces were heavily colonized with a diverse assemblage of bacteria. Some epoxy coatings showed visible signs of coating deterioration (i.e., pinpoint holes, blistering and peeling) after a one-month exposure to the marine, mixed communities. EIS was used in laboratory testing to assess the properties of the coated 4140 steel coupons exposed to the microbial communities. Field experiments were done to evaluate the relationship between marine bacteria and localized corrosion on coated mild steel. In all cases, the distribution of microbes was strongly influenced by the presence of iron corrosion products independent of coating combinations

### **Microbial additives for shipboard collection, holding and transfer (CHT) tank systems**

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U.S. Navy ships generate substantial quantities of non-oily wastewater (sewage and graywater from laundry, sinks, showers, galley facilities and deck drains). For example, an aircraft carrier generates about 400,000 gallons of non-oily wastewater per day. CHT tanks are used to hold the non-oily wastewater during transits through restricted waters or when pierside. Health and safety issues require CHT systems to be zero leakage systems. CHT piping and tanks are subject to scaling and corrosion; pumps are subject to clogging, leakage and corrosion; and tank level sensors (pump control sensors) are subject to fouling and degradation. These problems make it difficult to achieve the desired reliability and ease of maintenance for these systems.

Microbial degreasing products were tested to determine the effectiveness of the biological products in preventing and removing the accumulation of grease and sludge in CHT tanks. Microbial degreasing products must: (1) consume cooking grease from galley waste, (2) work in freshwater and saltwater conditions at temperatures from 16°C to 25°C, (3) work in the presence of sewage and laundry detergent, and (4) reduce odor by consuming wastes without generating hydrogen sulfide and methane. Fifty-three commercially available microbial degreasing products were tested in the laboratory for solubilization of animal fat (Flair shortening from Kraft General Foods, White Plains, NY). The top 10 products were tested for fat solubilization at various temperatures in freshwater and up to 30 ppt NaCl, for bacterial numbers per gram or per ml of the product, for lipase and esterase activity, for biosurfactant production, and for grease consumption in the presence of sewage and metals (Cu, Ni and Zn). An administrative toxicity assessment was done by the Naval Environmental Health Center (NEHC/ Norfolk, VA) on 5 microbial degreasing products for use by ship's force on surface ships. Four microbial degreasing products were tested for 3 months aboard the USS Kitty Hawk (CV 63) and USS Enterprise (CVN 65) while the CHT tanks were in routine service and in the "in-port" mode. Input was provided for the Uniform Industrial Process Instruction (UIPI 0593-901A) for using microbial cleaners in sewage system sanitary tanks on surface ships and submarines.

### **Effect of Coating Thickness on Adhesion of Marine Invertebrates to Silicone**

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The hypothesis that increasing silicone coating thickness decreases adhesion strength of marine invertebrates was investigated. Test panels coated with silicones of known thickness were immersed in the Indian River Lagoon on the central east coast of Florida, USA, to accumulate barnacle and tubeworm growth. Adhesion strength was measured using a force gage to dislodge the organisms and a scanner to measure the base area of attachment (ASTM-5618). Parameters in the experimental design included silicone type, coating thickness, coating additive, invertebrate species, and age of the individual. Observations of the fracture conditions of individual measurements were made to better understand the mechanism of release.

### **Recruitment and Growth of Marine Invertebrates on Silicone Coatings**

Kavanagh Christopher J, Kovach B., Quinn R, Swain, G.W., Touzot A., Florida Institute of Technology, Department of Marine and Environmental Systems, 150 West University Boulevard, Melbourne, Florida 32901, USA

Glass panels [10 cm x 20 cm] coated with transparent silicone coatings were immersed in the Indian River Lagoon on the central east coast of Florida, USA, to monitor the invertebrate colonization of the surface and growth of individuals. A digital camera, flatbed scanner, and laptop computer were used to acquire images of organism development on varying treatments of silicone coatings. Data collection was performed on-site, on a weekly basis, at three locations over a period of months. Time series data analysis provided insight into community interactions and individual growth of barnacles and tubeworms. Growth rates, determined from the increase in basal area of contact between organism and substratum, were compared among coating treatments.

## **Design and Estimation of Antifouling Paint Behaviour Using a Combination of mathematical Models and Rotary Experiments**

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The invention and development of chemical active antifouling paints have, traditionally, been based on an almost empirical approach. This means that optimisation and evaluation of novel and existing products are conducted by means of systematic rotary paint tests in the laboratory or at sea sites. In this work, we will illustrate the usefulness of combining rotary experiments with the development of detailed mathematical models of the paint behaviour. Such models can be used in the design of suitable release systems for various active components (e.g. enzymes, peptides, hormones, or biocides) as well as estimation of release rates, for environmental and optimisation purposes, at various conditions of seawater and paint composition. As a case study, model paints based on the well-known TBT-technology have been selected. Though this paint type is facing a world-wide ban in 2003, due to its harmful effects on the environment, it is useful for illustrative purposes, being known to most paint researchers and industrialists.

Simulations from our recent works (Kiil et al., 2001, 2002a,b,c) showing, amongst others, the effects of dynamic changes in seawater conditions and ship speed on the paint behaviour will be presented. Examples of possible future uses of paint models for accelerated polishing and leaching tests and screening of novel paint components will be provided.

The modelling approach can be applied to any type of chemical active antifouling paint provided that kinetic, solubility, and diffusivity data are available (or can be acquired) for the pertinent rate-influencing steps.

## **Synthesis and Antifouling Activity of 3-Isocyantheonellin and Its Analogues**

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We discuss the structure-activity relationship in terms of antifouling activity by synthesizing an antifouling active natural compound, 3-isocyantheonellin, and its analogues. 3-Isocyantheonellin, isolated from a nudibranch, is a marine sesquiterpene of the bisabolene class with the characteristic nitrogen substituent at the C-3 position. In spite of its simple structure, this natural product exhibits potent antifouling activity against the larvae of the barnacle *Balanus amphirite* (EC<sub>50</sub> 0.13 µg/mL). Efficient synthetic access to this natural product and various synthetic analogues would promote useful contributions to the antifouling field. For this reason, we studied a short total synthesis of 3-isocyantheonellin and the synthesis of its analogues. In addition, we evaluated their antifouling activities to discuss the structure-activity relationship in terms of the antifouling activity. The results of the antifouling activities showed that the stereoisomer of 3-isocyantheonellin exhibited the same potent antifouling activity as the natural product and that some analogues belonging to the isocyanate group also exhibited potent activity, although slightly lower than that of 3-isocyantheonellin. In addition, the isocyanate compounds showed a low mortality rate in high concentration (LD<sub>50</sub> > 100 µg/ml). These findings suggest that the isocyanate compounds exhibit high antifouling activity without significant toxicity.

### **Critical speeds for fouling removal from a silicone coating**

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In order to comply with forthcoming regulations on tin containing antifoulings the Royal Dutch navy is currently running experiments with various alternative systems, among them silicone based fouling release coatings. Knowing that adhesion on fouling release coatings is generally poor, the Navy has asked TNO to investigate more specifically the speeds at which natural fouling communities detach and are removed from the coating surface. Tests were carried out with one silicone based fouling release coating in two different experimental set-ups.

In one set-up the coating was applied onto two large (diameter 80 cm) steel disks that were submersed for 6 to 10 weeks at the TNO raft and subsequently rotated in a large tank containing natural seawater. Disks were inspected after various rotation intervals and the degree of fouling removal observed. One of the disks was provided with a zinc anode for passive cathodic protection. After various rotation intervals the disks were inspected for the degree of fouling removal.

The same fouling release coating was also applied on to steel rotor panels (8 x 15 cm) for rotation studies at the TNO rotor system at four different speeds (10, 15, 20 and 25 kn). After various exposure periods at the TNO raft panels were collected and subjected to various rotation intervals at four different speeds. After each interval the degree of fouling removal was again determined.

Fouling organisms present at the disks and rotor panels were mainly barnacles, diatoms and microbial slime, occasionally (brown) algae and ascidians were observed. In both disk and rotor tests macrofoulers were relatively easily removed in contrast to diatoms and slime. In disk tests 1-hour rotation resulted in barnacle removal at 17 – 18 kn. whereas after 3 hours barnacles were removed at 12 – 13 kn.

Tests with rotor panels have revealed that below 15 kn barnacle removal from this coating is rather difficult whereas at 20 kn a rotation period of 40 minutes is quite effective. At 25 kn also a large part of the slime layer is removed.

### **Pepticoat: Protein technology for control of fouling**

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TNO Industrial Technology, Corrosion Prevention and Antifouling, PO Box 505, 1780 AM, Den Helder, The Netherlands.

This poster gives a description of a fundamental research project carried out in The Netherlands. The objective of the project is to develop an environmentally friendly fouling control technique base on protein technology. Main scientific targets are 1) to find new active proteins that interfere with adhesion rather than kill fouling organisms; 2) to develop advanced coating technology giving long-term stability and performance of new active proteins and 3) finding a breakthrough in expression and large-scale production of active proteins.

Partnership for this project was newly formed and consists of antifouling partners (TNO Industrial Technology, Sigma Coatings) on the one hand and protein technology partners (Groningen University, ATO BV, TNO Food and Nutrition and Genencor International) on the other hand.

### **Hydrodynamic Evaluation of Ship Hull Coatings**

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A field device has been developed to hydrodynamically evaluate standard static immersion test panels (0.254m x 0.305m). The instrument uses a floating-element and underwater video camera that are mounted in a wet well that has been built into the stern section of a 7 m powerboat hull. The test panel is aligned flush to and becomes an integral part of the boat hull. Drag and velocity are measured synchronously with video of the test panel to evaluate hydrodynamic performance and fouling. Data are presented for copper antifouling, silicone fouling release, and epoxy surfaces of varying roughness.

### **In situ atomic force microscopy studies of wettability of polymer surfaces**

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Elucidation of behavior of polymer surfaces in contact with aqueous environments is one of the prerequisites to achieving thorough understanding of bioadhesion and fouling release. This presentation will describe some novel insights into wettability of polymer surfaces obtained with the aid of *in situ* atomic force microscopy (AFM), which is capable of nanoscale visualization of solid liquid interfaces. Special emphasis will be made on recent developments in *in situ* tapping mode AFM, which opened the way to minimization and control of probe-sample forces over the range of several orders of magnitude, and to the studies of viscoelasticity and its role in adhesion. The phenomena and systems to be discussed will include: dynamics of silicone elastomers in contact with water, incomplete wetting of glassy hydrophobic polymers, and wetting of surfaces patterned at the nanoscale by self-assembling block copolymers. The possibilities of using these insights to rationally design surfaces with desirable bioadhesion and fouling release characteristics will be discussed.

### **State of the Art Procedures for Optimum Coating Longevity in Shipboard Ballast Tanks**

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Annual corrosion control costs have led the U.S. Navy maintenance community to institutionalize state-of-the-art surface preparation, coating, and inspection procedures for seawater ballast, potable water, and other critical internal tank and void areas. This new direction, in full practice for approximately three years, has proven to be beneficial in drastically improving the longevity of internal ship tank coating systems. This paper will discuss how the US Navy has implemented such practices.

### **An account on fouling invaders in Greek waters**

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Alien species have been reported several times from Greek waters, but their observation was only accidental, and due to general faunistic studies, or monitoring projects, none of which have had as objective to record the exotic species. In this study we've sieved through the literature and accumulated most of the existing information on invading species with a possible fouling way of introduction, laying the foundations for an oncoming study on fouling which will be carried out for the next three years.

In Greek waters, out of a total of 76 exotic species, 8 have possibly been transferred through ship fouling. According to our sources (mostly grey literature) these belong to Chlorophyta and 2 major animal phyla. The green algal species *Codium fragile* is now a very common species in the Mediterranean, and also in the Aegean Sea. It seems that it came through shipping after WWII, and now it is a successfully established species. Among barnacles, the Brazilian giant *Megabalanus tintinnabulum* has been certainly introduced via shipping. However, since its occurrence was only noted on ship hulls (at Pireaus port), and no systematic study has been carried out *in situ*, its finding is considered accidental. Molluscs is the best-studied group, and therefore displays much more records. The Indo-Pacific *Brachidontes pharaonis*, the Indian Ocean origin *Anadara demiri*, and the Red Sea species *Pseudochama corbieri* are fouling organisms, which have been presumably introduced via shipping. Other exotic fouling molluscs which are also reported from areas with ports (mostly Saronikos Gulf) and have been presumably introduced via shipping are the Atlantic species *Crepidula fornicata*, *Petricola pholadiformis*, and *Siphonaria pectinata*.

Of the above only *Anadara demiri* and *Siphonaria pectinata* have exhibited an invasive behaviour in Rhodes, Thessaloniki (near port) and Saronikos Gulf (near port) respectively. The rest are known to have a very limited, if not accidental, occurrence. Systematic work is expected to reveal a vast number of invaders in Greek ports.



### **Corrosion behavior of 316L in glycol / seawater mixtures**

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The corrosion trends of 316L stainless steel immersed in glycol / seawater mixtures have been examined. Potentiodynamic scans were performed on welded and flat plate specimens in glycol seawater mixtures. Initial results indicate that addition of glycol does not affect the cathodic reactions occurring on the metal. However, anodic scans indicate that as glycol concentration is increased, the pitting potential also increases. Therefore, glycol addition may increase the pitting resistance of 316L in seawater; additional data suggest that both propylene and ethylene glycol at concentrations greater than 65% inhibit microbial growth.

### **Chemical control of bacterial epibiosis in the red sponge *Mylae adherence*: phylogenetic analysis of benthic bacterial isolates and their susceptibility to sponge derived compounds.**

On On Lee. Pei-Yuan Qian, Department of Biology, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, SAR Hong Kong, China

In this study, the antifouling mechanism of the red sponge *Mylae adherence* was elucidated. The comparison between the culturable bacterial community on the sponge with indigenous bacteria isolated from an inanimate reference site in the close vicinity showed a significant difference. Unlike the predominance of  $\gamma$ -*Proteobacteria* among the culturable bacteria obtained from the reference site, a significant portion of culturable bacteria on the sponge surface belonged to  $\alpha$ -*Proteobacteria*, Gram-positive and *Cytophaga-Flexibacter-Bacteriodes*, suggesting that *M. adherence* possesses the ability to modify its surface bacterial community for its own benefit. Results also suggested that the effect of the surface-associated bacteria of sponges on the larval settlement of major fouling organisms, tubeworm *Hydrodies elegans*, did not have any relationship with their phylogenetic affiliation. A significant portion of isolates, including *Tenacibaculum mesophilum*, *Vibrio furnissii*, *Shewanella algae*, *Kocuria rhizophila*, *Micrococcus* sp., *Vibrio tubiashi*, *Vibrio campbellii* and *Vibrio alginolyticus*, showed inhibitory effect on larval settlement, indicating that *M. adherence* might employ an indirect inhibition of larval settlement of *H. elegans* by microfouling control. The conditional seawater sample from the sponge was potent in killing the larvae in a relatively short time. This may suggest that the sponge can protect itself against macrofouling also by a direct control.

### **Integrated Condition Based Maintenance Systems for Monitoring and Evaluation of Ballast Tank Coatings Integrity and Life Prediction.**

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Thomas E. Dail and Seelinger, Andrew, Naval Sea Systems Command, 05M1, 1333 Isaac Hull Ave. Stop 5131, Washington Navy Yard, DC, 20376-5131

Preservation of tanks and voids on US Navy ships expends over 25% of maintenance funds annually. The MIL-P-24441 system that has been installed in the vast majority of tanks and voids has a 5 – 7 year service life. Two major thrusts have been involved to reduce maintenance costs of tank and void preservation including 1) replacement with high solid epoxy coating systems that are approximately 98% solids, are edge retentive, and have a service life of twenty years have recently been employed and 2) implementation of condition based maintenance technology via electrochemical *in situ* sensors and remote optical inspection technologies for routine assessment of the “state of preservation” of shipboard tanks and voids. The present paper reviews the various improvements in technology for condition monitoring of advanced coatings with sensors and the various optical inspection techniques including the Insertable Stalk Imaging System (ISIS), the Remotely Operated Paint Inspector (ROPI) and the Corrosion Detection Algorithm (CDA). Each of these is described briefly and the relative impact on U.S. Navy maintenance and state of readiness are discussed.

### **Fouling prevention in the Royal Australian Navy: Where we are now, and where we are headed**

John A. Lewis, Maritime Platforms Division, Defence Science & Technology Organisation, GPO Box 4331, Melbourne, Vic 3001, Australia

Although the settlement and growth of marine organisms on boat hulls has vexed mariners since they first set sail, there have been several periods of intensified activity in the search for effective methods of biofouling control. The first coincided with the advent of iron ships in the 19<sup>th</sup> century, and resulted from the incompatibility of protective copper sheathing with the iron. This led to the first copper-based antifouling paints. The second followed World War II, was exemplified by the 1952 Woods Hole treatise “Marine Fouling and its Prevention”, and stimulated research that ultimately led to the development of tributyltin (TBT) copolymer paints effective for 5 or more years. However, in recent times, methods of biofouling control have attracted unprecedented attention, catalysed by concerns about the impact of organotin biocides in the marine environment. The challenge was to find effective tin-free products to meet the prospective ban on organotins, now realised with the adoption by the IMO last year of the “International Convention on the Control of Harmful Anti-Fouling Systems on Ships, 2001”, which bans the application of paints containing organotins from 1 January 2003. New challenges are now being faced: concerns on the impact of some other antifouling biocides; regulatory processes aimed at preventing new environmental impacts; and recognition of hull fouling as a significant vector for the translocation of marine pest species.

Defence in Australia has faced the recent challenges with a comprehensive program to evaluate the performance of alternative antifouling systems, while also monitoring the environmental impact of existing systems. Attention has focused on both new biocidal systems and non-toxic fouling release coatings. The outcomes have been promising. When the program started in the mid-1980s, tin-free products could not match the performance of tributyltin (TBT) copolymer coatings in either polishing action or long-term antifouling effectiveness. However, “new technology” copper-based products can offer both, and are now widely applied in place of TBT systems. Silicone fouling release coatings are also providing effective fouling control in some applications. Looking to the future, there remains considerable scope for improvement in fouling control technology, particularly if the ideal of environmentally benign, yet totally effective systems of biofouling control is to be achieved.

### **Hull fouling as a vector for the introduction of exotic marine species to Australia**

John A. Lewis, Maritime Platforms Division, Defence Science & Technology Organisation, GPO Box 4331, Melbourne, Vic 3001, Australia

In recent years, a number of prominent exotic marine species have established and spread in inshore waters of southern Australia. These have included the giant fanworm (*Sabella spallanzanii*), the northern Pacific seastar (*Asterias amurensis*), Japanese kelp (*Undaria pinnatifida*), and broccoli weed (*Codium fragile* ssp. *tomentosoides*). While the initial focus was on ships’ ballast water as the responsible vector for these and other introductions, a review of past introductions, a series of recent fouling-linked incursions into northern Australia, and an investigation of fouling presence on present day shipping have confirmed hull fouling to pose a continuing risk vector for the introduction of invasive species that is equal if not greater than that posed by ballast water. Two fouling species arriving in recent times have become troublesome species to boat owners: the Caribbean serpulid tubeworm, *Hydroides sanctaecrucis*, in Cairns, and the barnacle *Megabalanus tintinnabulum*, which fouls seawater intakes of vessels in south-eastern Australia. Two other species of concern in northern Australia are the black-striped mussel, *Mytilopsis sallei*, and the Asian green mussel, *Perna viridis*. Both have been detected on the hulls of fishing or illegal entry vessels in northern Australia, but inspection and management actions have so far prevented their successful establishment in local waters.

**Use of automated image processing coupled with an artificial neural network based classifier for identifying fouling organisms on ship hulls.**

Lieberman Stephen H., He Li-Ming, and Timothy Adam, Space and Naval Warfare Systems Center San Diego, 2361, 53475 Strothe Rd., San Diego, CA 92152

Invasive (or non-native) species have been introduced inadvertently into many marine and fresh water systems via ship movements. The major transport pathways that have been identified include ballast water, tank sediments and ship hull fouling. To date, most monitoring and control programs have focused on ballast water as the dominant pathway for transport of invasive species. However, recent studies suggest that historically, as well as presently, hull fouling may represent an important pathway for transport of invasive species.

Most information on invasive species and hull fouling organisms is based on diver inspections of hulls. This method is costly, potentially dangerous, and often subjective. Improved methods are needed to more effectively conduct underwater hull inspections, objectively quantify the abundance and diversity of fouling organisms, and more specifically identify non-indigenous species.

In this study we report on the investigation of the use of automated image processing/image-understanding algorithms coupled with artificial neural network based classifiers for identifying fouling organisms on ship hulls from digital images. The methodology is based on a four-step process that includes: 1) image acquisition, 2) image pre-processing, 3) feature extraction, and 4) object classification. Initial results will be presented from studies in which an artificial neural network is used to automatically classify various types of fouling organisms isolated via the standard digital image processing methodologies. Once individual objects are identified in the images, then an array of object properties (e.g., size, shape, color, texture, etc.) is used as an input array to train an artificial neural network to discriminate and thereby identify certain classes of organisms. After the network is trained by example using many images of organisms that have been previously identified, then the trained network is used to automatically classify organisms in new images based on the unique differences in the array of object properties. Preliminary results will be presented for the application of this approach to common hull fouling organisms with special attention to classification and discrimination of target non-indigenous species.

### **Microbiologically Influenced Corrosion in Tanks, Holds and Cargo Spaces**

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Case histories of microbiologically influenced corrosion in tanks, holds and cargo spaces will be reviewed with an emphasis on the role of fungi in the corrosion process. Fungi are the most desiccant-resistant microorganisms and can remain active at water activities that inhibit bacterial growth. Fungi are ubiquitous in atmospheric and aquatic environments where they assimilate organic material and produce organic acids including oxalic, lactic, formic, acetic and citric. Since water is a product of the microbial mineralization of organic substrates, it is possible in some cases for fungi to generate a water phase for further proliferation. The concentration and spectrum of acids produced by fungi can change during growth. Fungi can influence corrosion via numerous mechanisms including the following: 1) local acid production under colonies, 2) reduction of bulk pH in a liquid medium, 3) direct degradation of coatings, 4) dissolution of protective greases, 5) under deposit corrosion, 6) metal concentration cells and 7) microbial uptake of fuel additives, including corrosion inhibitors.

### **Development of Underwater Hull Systems Assessment Vehicle and Sensors**

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The Naval Surface Warfare Center, Carderock Division, (NSWCCD), has developed an underwater ship hull assessment system (ROV-DT) to monitor and document the condition of US Navy ships. This system is capable of: measuring paint thickness; evaluating cathodic protection systems; assessing hull damage; performing acoustic silencing diagnostics, and measuring magnetic signatures. Over 30 surveys have been performed since 1990 on U.S. Navy ships, including aircraft carriers, cruisers, destroyers, submarines, frigates, and swath hulls. The majority of these deployments have been focused on the examination of the thickness of the ship's underwater ablative antifouling paint to determine optimal time for drydocking. This process supports the U.S. Navy initiative to extend time between drydock repainting from 5 to 12 years.

The ROV-DT system is comprised of a Remotely Operated Vehicle (ROV) and sensors developed for acquiring specific hull system measurements. The requirement for the sensors and actuators used on ROV-DT to work underwater has required custom design or modification of terrestrial systems. The primary sensors utilized are a paint thickness probe, a hull thickness probe, and cathodic protection potential monitoring.

Additional features of ROV-DT include a windows based navigation display, 3-D interface, has been developed for use with acoustic navigation systems. This interface permits the ROV to be represented on a 3-D hull form of the ship being evaluated, with accurate representation of ROV's position relative to the ship. Additional data can also be represented on the 3-D form, including maintenance and position information.

The use of remote systems for acquiring hull maintenance data results in significant cost savings to the US Navy as well as supporting extended operating cycles.

### **Incorporation of Bioavailability of Copper in Risk Assessments and Setting Water Quality Standards.**

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In many countries, it has already been recognised that it is only the "bioavailable" fraction that is important for copper toxicity in marine and freshwater environments.

In freshwater, the bioavailability of copper has been shown to be affected by several water quality parameters such as pH, hardness and most importantly, dissolved organic matter (DOM). From the extensive data available, a model has been developed to predict the toxicity of copper to fish and invertebrates. The model, termed the biotic ligand model (BLM) can simulate changes in metal bioavailability and toxicity over wide ranges of ambient water chemistries.

For the marine environment there are less data available, however an initial risk assessment has already been conducted using measured total dissolved copper in several European waters. To further refine this risk assessment an environmental fate programme has recently been commissioned in the UK to determine the bioavailable fraction of copper in sites of high antifouling activity. This programme will determine the speciation of copper in marine waters and expose several marine species to the same speciated complex in laboratory flow through systems. Thus, the bioavailability of copper can be directly related to field scenarios of high antifouling paint activities. As part of this study the validation of a marine biotic ligand-type model is also possible.

### **New methods for neurotransmitter and receptor studies on *Balanus improvisus* cyprids.**

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Barnacle cyprids are tiny, hard and tough creatures that pose a challenge to those of us who want to study their internal enigmas. In our work we are mainly focusing on the cement apparatus, i.e. the nerves to the gland, the gland itself and the cement proteins. We are studying the cement release, and various specific ways to inhibit this release. If we learn more about the mechanisms controlling cement release this will likely improve our understanding of the barnacle settling process.

Exocytosis of cement proteins from the cyprid cement glands is crucial for the settling and metamorphosis. Nerves, their transmitter substances, and specific receptor proteins govern the process. In our attempts to understand how the cement release is regulated, we have focused our efforts on the characterisation of the communication between the nerve and the receptor proteins. A promising way is to visualise the cement gland by confocal microscopy. A number of non-toxic fluorescent probes are available with different biochemical possibilities and are able to detect for example, thiol groups, amount of intracellular calcium, and changes in pH. By this technique, the cement vesicles can be made fluorescent and visible through the microscope in a living and responding cyprid. It is now possible to follow single cement vesicles and the technique offers an opportunity to study pharmacological and physiological mechanisms behind the cement release *in situ*.

### **Inhibition of cyprid attachment by the combination of (-) menthol and copper *Omadine*<sup>®</sup> biocide.**

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(-) Menthol has been demonstrated as an inhibitor of the settlement of the cyprids of the barnacle, *Balanus amphitrite* Darwin, and effective against hard fouling organisms in marine exposure tests. Copper *Omadine* biocide is as an effective compound against soft fouling marine organisms and moderately inhibitory to hard foulers. This study examines the effect of combining these two compounds in an effort to develop effective antifouling systems. In the standard cyprid assay in which test compounds were added into the seawater medium, copper *Omadine* biocide and (-) menthol inhibited cyprid settlement with an EC<sub>50</sub> 1x10<sup>-7</sup> mg/ml and 1x10<sup>-3</sup> mg/ml, respectively. When (-) menthol was added simultaneously to seawater containing copper *Omadine* biocide, there was a significant increase in the inhibitory effect on the settlement of cyprid larvae. To further examine the effects of the combination of the two compounds, a modified assay was developed wherein the test compounds were incorporated into an ultra-pure nontoxic VYHH resin at various concentrations and were used to coat the bottom of petri dishes. After drying the resin, the seawater containing the cyprids was added to the petri dishes and the total number of attached and metamorphosed larvae were counted 24 hours later. This new test system allowed the examination of the biological performance of antifoulants in a coating matrix as part of the screening method. When both compounds were incorporated into the VYHH resin, the results showed that the combination produced a greater degree of inhibition than either copper *Omadine* biocide or (-) menthol alone. Marine field exposure tests using coatings which combine (-) menthol and *Omadine* biocide showed effective inhibition of fouling attachment. These results demonstrate that combinations of copper *Omadine* biocide and (-) menthol could produce effective fouling control and that a modified cyprid assay on coated plates as a screening system may serve as a useful tool to study the dynamics involved between the coating and the bioactive agents.

\*Copper *Omadine* biocide products are not registered by the U.S. EPA and are not available for sale in the United States.

## **On the Antifouling Properties of Menthol and Related Compounds. Results from Poseidon's Natural Bioproducts Screening Program.**

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The Natural Bioproducts Screening Program was established in 1990 to search for naturally occurring biochemicals of terrestrial and marine origins with pharmaceutical and industrial applications. The search for antifoulants was a major target for the screening program. In this report, we describe the efficacy of (-)-menthol as an effective antifoulant against hard fouling organisms. The primary screening method used was the settlement assay using cyprids of the barnacle, *Balanus amphitrite Darwin*. The assay showed an effective antisettlement effect with an EC<sub>50</sub> of 0.004 mg/ml. The stereochemistry played an important role in the biological activity of menthol. When (+)- menthol and (±) were tested, we observed a major reduction in the effective concentration to 0.01 mg/ml for both isomers. These data confirmed that the naturally occurring isomer is the biologically active form to elicit the inhibitory action on barnacle settlement. (-) Menthol was found to be moderately inhibitory in diatoms and in a panel of 40 marine bacteria normally associated with barnacles. This may suggest that the antisettlement effect is primarily against hard fouling organisms. (-) Menthol also showed very low toxicity against marine organisms. For example, in the nauplii of *B. amphitrite* and the brine shrimp (*Artemia salina*), the LD<sub>50</sub> was found to be 0.60 g/l and 0.75 g/l, respectively. This compared favorably against tributyl tin, which has an LD<sub>50</sub> of approximately 1 ug/l. When tested against mysids and fish larvae, an LD<sub>50</sub> of 1.5 g and 10 g/l respectively were observed. The toxicity data demonstrated the nontoxic effect of (-) menthol in various marine organisms. The structure-activity relationship studies also showed that specific conformations at the C-3 and C-8 positions of the menthol molecule are required to produce optimal inhibition. The attachment of large functional groups at these positions reduced the biological effect. However, smaller functional groups, such as chlorine, ketone and hydroxyl groups, significantly enhanced the antisettlement effect. Panels containing (-) menthol incorporated into various coatings at concentrations of up to 10% were tested under total immersion in a marine exposure platform for up to 1.5 years. The data demonstrated that (-) menthol could produce significant antifouling effects under field conditions. These studies demonstrated that (-) menthol and related compounds represent a new class of natural products that can be used in the future to create eco-friendly, nontoxic marine coatings.

## **General defense mechanisms against bio-coating of the integument in non-cetacean marine mammals**

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Fishes use the numerous ingredients of their skin mucus for protection against different microbial or parasitic invaders of the epidermis, which, additionally, reduce hydrodynamic drag. Non-cetacean marine mammals, however, lack such multifunctional protein and glycoconjugate mixture, although their skin surface is the biotope for micro-organisms, such as, for example, bacteria and fungi. In this connection, a specific defense strategy against this microbial challenge, and/or a proliferation control of the microflora present seems to be a basic need of mammalian skin biology in the aquatic medium. This is especially important, moreover, regarding that in the pinnipeds several skin diseases have been recognized which are primarily of infectious etiology. Recent studies of pinniped skin have demonstrated now that mucus analogous functions can be exerted on the skin surface, at least in part, by secretions of the apocrine tubular glands. These glands are generally present in the common integument of medium-sized and large mammals as normal constituent of the hair follicle complex, that, besides the hair-producing follicle system, also regularly implies sebaceous glands. The apocrine gland type can only be found, however, at primary hair follicles and not at secondary hair follicles that produce wool hairs. The reactive substances elaborated by the apocrine glands for antimicrobial and/or microbistatcal purposes on the skin surface are several free sugars:  $\alpha$ -D-mannose,  $\beta$ -D-N-acetylglucosamine,  $\alpha$ -D-galactose,  $\alpha$ -L-fucose, and N-acetylneuraminic acid. All these sugars are liberated by microbial activities from glycoproteins and glycolipids that are the main ingredients of apocrine gland secretions. Most of these sugars have the ability to inhibit the adherence of different bacteria and fungi to the stratum corneum cells so that attacks against epidermal integrity are impeded, and a general biological protection mechanism becomes obvious. The ability to produce apocrine gland secretions that contain specific terminal sugars is also present in terrestrial mammals and, thus, may be looked upon as an effective prerequisite for successful adaptation to aquatic biotopes. Independent of this typical quality of mammalian apocrine glands, the possession of an outer body cover that is equipped with a dense wool hair coat may also prevent micro-organisms from settling at the epidermal surface. Aquatic mammals without a dense undercoat, nevertheless, still exhibit primary hair follicles with apocrine tubular glands and their effective secretion type.

### **Fouling and ships' hulls: how spawning events may result in exotic species spread.**

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Organisms fouling ships' hulls are continually in transit worldwide. Although effective antifouling paints incorporating organotins have considerably reduced the biomass of attaching organisms, these paints have a limited period of effectiveness often less than the ships' inter-docking period depending on the sea temperature and abrasion whereas alternative paints have shorter practical periods of usage. As a result treated vessels, that have been immersed over several years, allow fouling communities to develop and become distributed to areas beyond their native distribution. The process of establishment in new areas is not fully understood. In this account we propose that even short rapid turn-around of vessels with mature biota can result in production of sufficient zygotes, following synchronized spawnings, to form a founder population. These events may be induced by changes in temperature or salinity that may be expected on entry into a port, according to season. The diversity of taxa in transit on ships' hulls throughout the world also includes commercial molluscan species. There is a possibility that these may also have the potential to transmit diseases or pests to port regions where aquaculture is practiced. Several factors are currently operating that may act in the further enhancement of exotic species establishment. For example, due to urban congestion, many berthing regions in ports are now situated further downstream where there are more marine conditions. Many ships are now generally larger, and so faster, than in the 1960's. These have a high frequency of port visits thereby increasing the number of spawning opportunities with a larger inoculum size. With trade expansion and the development of new trading routes, according to political events and changes in climate, new pathways for invasion will emerge. Greater controls on industrial discharges, improved treatments of urban wastes and better management of waste runoff into rivers as well as a phasing out of organotin antifoulants, will mean a reduced toxicity in port regions. These mechanisms are likely to enable more effective colonization, perhaps with a smaller inoculum so creating opportunities for establishment that were not present before in over a quarter of a Century. Some of these invaders will have consequences for the environment, economies and human health.

### **The communication network in biofilm and planktonic cultures of marine bacteria**

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The adhesion of marine bacteria onto immersed surfaces leads to a biofilm formation. Presence of biofilms has undesirable consequences in term of material corrosion, process degradation, and consequently an increasing cost for the offshore industries. The concerted answer of the bacteria included in a biofilm, in response to its environment, could be mediated by cell to cell communication signal molecules. For the Gram-positive bacteria, these molecules have different chemical structures as N-acyl-homoserine lactones (HSL), substituted 4-quinolones and diketopiperazines.

The aim of this study is to study the signal molecules in planktonic and biofilm cultures of Gram-negative marine bacteria using biosensors and liquid chromatography coupled with an ion-trap mass spectrometry detection. For this purpose, bacteria were grown to stationary phase in liquid culture and in biofilm onto glass filters. The cell-free supernatants of the liquid cultures and the lysis medium of the biofilms were submitted to a dichloromethane extraction. The organic phase was evaporated to dryness and the residue was resuspended in acetonitrile. The extract was fractionated onto a C18 column using a methanol/water gradient and the eluted solutes were analysed using ion-trap MS<sup>n</sup> detection. A biological confirmation of the cell to cell communication signal molecules present both in crude extracts and LC fractions was done using different *E. coli* HSL biosensors. These biosensors answer to a range of signal molecules by a bioluminescence emission.

The method was set up using synthetic HSLs and *Pseudomonas aeruginosa* PAO1 strain, and applied to *Vibrio tapetis* and several unknown forming-biofilm marine bacteria. Different HSLs have been identified, among other, the C4-, C6-, C8-, C10-, C12-, C14-HSL and the 3-oxo substituted HSL as the the 3-oxo-C6-, 3-oxo-C8-, 3-oxo-C10-, 3-oxo-C12- and the 3-oxo-C14-HSL. Three diketopiperazines, cyclo(□Ala<sub>L</sub>.Val), cyclo(L.Pro<sub>L</sub>.Tyr) and cyclo(L.Phe<sub>L</sub>.Pro) have been also identified. The biological activity of these molecules has been confirmed using biosensors. The production of signal molecules in biofilm versus suspension of single or mixed bacteria was analysed.

Applications of this method to monitor the antifouling strategies based on the limitation of bacterial biofilm formation by interference with the bacterial communication network as well as to study the relationships between marine bacteria in biofilms is discussed.

### **Shear forces necessary to remove newly settled fouling organisms from test surfaces: data from a precision flow cell.**

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Glass, fiberglass and newly formulated coatings were tested in a precision flow cell to determine shear forces necessary to remove newly settled tube worms (*Hydroides elegans*), barnacles (*Balanus amphitrite*) and algal spores (*Ulva fasciata*). 2.5-by-7.5 cm coupons, either uncoated or bearing experimental foul-release coatings, were immersed in sea tables for 4 - 5 days to accumulate a biological film and then exposed to competent larvae (barnacles or tube worms) or algal spores (alga). When the fouling organisms had settled upon the coupons, the coupons were placed into the test chamber where they were held by suction with their surfaces flush with the chamber floor. Seawater flow in the chamber was incrementally increased while the attached organisms were observed and videotaped through a dissecting microscope at 50X (except for the algal spores). From glass slides and coupons coated with Intersleek coatings, neither newly settled barnacles nor tube worms were removed even at the maximum forces generated in the cell, 110 Pascals. Preliminary data indicate that 30-50% of metamorphosed tube worms were released from other experimental coatings at maximum shear forces. Presence of algal spores required observation at high magnification (400X), and thus coupons were subjected to a single flow rate, removed, and observed for presence of the spores. Silicone coatings with certain additives proved to be more resistant to firm attachment by the spores: up to 50% were removed at shear forces as low as 40-50 Pascals. Data will be presented on other coatings currently being tested.

### **Antifouling compounds against Barnacle *Balanus amphitrite* Larvae from the Marine Sponge**

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Excessive growth of marine sessile organisms along water intake pipes constricts and impedes the inflow of cooling water in power plants. Generally, inside wall of the pipes are coated with cuprous oxide paints to avoid the organisms from growing, however, the use of such paints is considered to be limited in near future because of their toxicity to natural organisms. Therefore, non-toxic antifouling substances are urgently needed. In this study, to discover antifouling substances from Japanese marine invertebrates, extractions from marine organisms were tested for their antifouling activity and toxicity against barnacle (*Balanus amphitrite*) larvae. And antifouling substances were isolated with bioassay-guided method and determined mainly with NMR spectral data.

Fractions were extracted with hot methanol and chloroform from 118 marine invertebrates. Thirteen fractions showed an antifouling activity without strong toxicity.

The sponge *Acanthella* sp. collected off Atami, Shizuoka prefecture was extracted with MeOH followed by solvent partition. The active fraction was separated by silica gel column chromatographies, gel filtration, and ODS HPLC to afford several terpenoids having antifouling activity. The structure of new antifouling compound 10-formamido-4-cadinene was determined mainly by NMR spectral data and chemical transformation.



## **Experiences with TBT-free Antifouling Paints**

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Wallenius Lines has applied tin-free antifouling paint since 1996 and since then accumulated fairly extensive experiences on the tin-free paint types available on the market. The paint types are normally generically grouped into CDP, SPC and Fouling Release, FR. These types have typical characteristics and performances making them more or less suitable for different applications and service periods. The use of CDP will give the lowest paint cost, but also a short service life. Additionally CDP normally contains rather strong boosting biocides. The latest tin-free SPC coatings match the performance of TBT SPCs. Several tin-free systems for five-year service life have been applied. FR coatings have been applied on two vessels with good results so far. The effective service life of FR coatings should exceed five years. A long service life will be required to make their use economical. The correlation between hull roughness and fuel consumption is difficult to establish from full-scale measurements, due to a lack of accuracy in the measurement systems and different operating environments. An environmental study of a sample of tin-free antifouling showed that the CDP coatings have the highest environmental impact due to their boosting biocides. SPC has a more stable biocide release than CDP and contains weaker biocides, while FR coatings has no impact on marine life.

## **New metal free biocides for anti-fouling paints. ECONEA™ 028 a safe alternative for the future.**

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From 2003 the world wide ban on use of organo-tin containing anti-fouling paints installed by the IMO will become effective.

In many cases tin will be replaced by other metals with known anti-fouling effects metals but which remain persistent in the environment.

About 8 years ago, the Plant and Material Protection Division of Janssen Pharmaceutica NV started a research and development program aimed at finding innovative metal free biocides for use in anti-fouling paints.

A number of compounds were selected in laboratory screening models and then tested in raft trials around the world to create a broad range of fouling conditions . The most promising substances were subsequently applied in anti-fouling paint patches on ships operating in different parts of the world.

Finally a new compound ECONEA™ 028 was selected and proved to have excellent hard fouling activity.

To assure that this active ingredient will not cause negative effects in marine and fresh water environments, a full battery eco-toxicology and environmental fate studies were undertaken on the parent and all significant degradation products.

ECONEA™ 028 breaks down within hours in seawater and within a few days in fresh water. Its degradation products were identified and all were studied for their toxicity and environmental fate. They prove to be harmless in both the water and sediment compartments.

The degradation products of ECONEA™ 028 appear to have typically a 100 to 1000 times higher safety margin when compared to the parent compound.

All E fate and eco-toxicology data were introduced in the worst case scenario model of the San Diego harbor developed by SPAWAR.

Also risk calculations for worker exposure in shipyards have been done

Registration application for ECONEA™ 028, a hard fouling compound, has been filed for with US-EPA.

A registration file under the new Biocides Product Directive (BPD) in Europe will be submitted soon. Submissions in other parts of the world will follow thereafter.

## **Poly(ethylene glycol) and Fluorocarbon Modified Polymers for Biofouling Resistance and Biofouling Release**

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We describe the preparation of side chain modified polystyrene based surface-active block copolymers (SABC) for use as marine fouling resistance/release applications. Modifying moieties such as poly(ethylene glycol) (PEG) and fluorocarbon segments are used. Initial testing of these materials includes determination of surface properties and protein adsorption. We also present the preparation and testing of these materials as marine fouling resistant/release coatings using a novel bilayer methodology that optimizes mechanical properties through use of an elastomer (SEBS) primer layer and controls surface chemistry through use of the SABC's. This method has potential as a cost-effective method for improved benign marine fouling resistance/release coatings. Variations in side chain as well as SABC architecture are studied to elucidate structure-property relationships as well as maximize overall performance of the bilayers.

## **Management of a biofouling threat**

O'Brien Chris, Marine Biosecurity Group, Ministry of Fisheries, New Zealand

This presentation will outline the organisational and legislative structures that underpin the management of marine biosecurity in New Zealand, and illustrate their use in the management of a serious biofouling threat.

New Zealand's indigenous biodiversity – native species, their genetic diversity, and the habitats and ecosystems that support them, is of great value to the quality of life of New Zealand's citizens and their sense of identity as a nation. Furthermore New Zealand's economy relies heavily on primary production, tourism, and the underpinning clean green image it portrays to the world. As a consequence, biosecurity (which relates to the exclusion, eradication, and effective management of pests and unwanted species) is taken very seriously and is well supported by a strong legislative base in the form of a Biosecurity Act; and other organisational structures including a dedicated Minister for Biosecurity, and various councils and forums dedicated to biosecurity matters.

The Ministry of Fisheries is the lead agency for marine biosecurity in New Zealand. On March 2000, a fishing vessel with the invasive seaweed *Undaria pinnatifida* on its hull sank near a remote New Zealand island. Using the Biosecurity Act, the Ministry of Fisheries ordered the vessel to be moved to reduce the risk of undaria getting from the vessel to the island. Although attempts to salvage the vessel were unsuccessful, the powers of the Biosecurity Act enabled an adaptive management approach to be undertaken whereby a monitoring and eradication programme was put in place. This programme appears to have eradicated undaria from the vessel.

## ***Pselactux spadix* – a weevil attacking marine timber structures**

Oevering, P. and Pitman, P.J.

Not submitted

### **Consideration of Bioavailability in Assessing Exposure and Effects of Antifouling Agents**

Paquin, Paul R., Mathew, R., HydroQual, Inc., Mahwah, New Jersey, Santore, R., HydroQual, Inc., Camillus, New York and Di Toro, D. M., HydroQual, Inc., Mahwah, NJ and Manhattan College, Bronx, NY.

A variety of surface coatings are employed to prevent the growth of biota on ship hulls, growth that would otherwise result in the fouling of these surfaces. However, in addition to the benefit that is realized from this use, there is also a related need to assess the potential for adverse effects on aquatic life that could possibly result from the leaching of the active ingredient from the applied coating to the water body. A general approach for estimating the mass loading rate of the antifouling agent to the water body and its distribution within the water body will be described in the context of performing an exposure assessment. An example of how a mass balance-based water quality model may be applied in this step in the analysis will be presented. The focus will then shift to copper, and to how bioavailability not only may be considered, but should be considered, in further evaluating the potential for effects. The biotic ligand model (BLM) of acute toxicity will be described in this regard. The BLM, the subject of ongoing development efforts in recent years, provides a way for the analyst to consider metal speciation and interaction of the metal with the organism at the site of action of toxicity when assessing the potential for effects. Analyses will be presented to illustrate the utility of the BLM in the completion of a rational assessment of metal availability and effects under site-specific conditions. Although the approach and analyses to be presented will place emphasis on marine settings, they are equally suitable for application in a freshwater setting as well.

### **The biology of the wharf borer *Narcedes melanura***

Pitman, P.J., Jones, E.B.G., and Jones, M.A.

Not submitted

## **OSPAR and EC - Methodology for the Selection and Prioritization and the Risk Assessment of Hazardous Substances and Antifoulings in the Marine Environment**

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In October 2001 the International Convention on the Control of Harmful Anti-Fouling Systems on Ships was adopted by the Contracting Parties of the IMO (IMO-International Maritime Organization) and it contains under Annex I provisions for a ban on Organotin - based Anti-Fouling Systems by the year 2003(Application) / 2008 (Phase Out) and under its Annexes II and III the requirements on data and risk assessment (Initial and Comprehensive Proposal) for any other Antifouling which might be subject for further discussion and regulation. The OSPAR- Convention (OSPAR-Oslo Paris Convention for the Protection of the North-East Atlantic) developed and established a selection and prioritisation procedure for hazardous substances in the marine environment. This procedure comprises a Risk-based Ranking which might also be used for the selection of less-hazardous and preferably non-hazardous substances, antifouling agents and alternative antifouling products. The EC (European Community) recently finalized the updated version of the "Technical Guidance Document on Risk Assessment" by incorporating a methodology for the Marine Risk Assessment. This method will also apply to Biocidal Products, including Antifouling Agents, which are to be registered and authorized under the EC-Regulation on Biocidal Products (EC-Directive 98/8/EC). The methods comprise Local (e.g. harbours), Regional (e.g. estuaries, coastal areas) and Open Sea (large scale, global) scenarios for exposure and effects assessments. The Local and Regional Risk Assessments are based on the "Quotient Method"(PEC/PNEC-Ratio) including Bioaccumulation and Secondary Poisoning whereas the Open Sea Risk Assessment is based on a PBT-(Persistence/Bioaccumulation/Toxicity) Risk Assessment. Both, the OSPAR Selection/ Prioritization Procedure and the EC /OSPAR-harmonized Risk Assessment methodology could provide guidance and criteria for the further development of less-or preferably non- hazardous antifouling agents.

### **Investigations into the release of epoxy from clear silicone coatings**

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The physical and mechanical factors controlling release of epoxy bonded metal studs on two candidate clear silicone coatings were investigated using laboratory tests similar to those developed by Kohl and Singer (1999). It was found that increasing coating thickness from 0.05 to 1.5mm will decrease failure stress by 1000% and that by increasing the loading rate from 0.01in/min to 0.15in/min, will cause a 300% increase in failure stress. Other tests performed found a dependence of failure stress on amount of applied moment and that variations in recorded stresses may be due to non-uniform stress distributions. An outline for future research that will correlate laboratory tests to hydrodynamic release is presented.

### **Fouling on Cylindrical Surfaces: Edge and Depth Effects**

Rittschof, Dan, Cai Y-X and Sin TM, Duke University Marine Laboratory and TMSI National University of Singapore

We quantified settlement on PVC cylinders ranging in outer diameter from 1.3 cm to 30 cm. The questions asked were: 1) do cylinder dimensions impact settlement? and 2) does settlement vary with depth? PVC pipes of 1.3 cm, 5 cm, 20 cm and 30 cm o.d. were mounted on a raft so that they extended perpendicularly from the surface to a depth of 50 cm. Included for comparison were a 30 cm-wide PVC panel, a size used in industry coatings tests, and a 7 mm o.d. polyphenolic rod used in academic studies. We determined the density of fouling organisms in 7 cm square (0.7 cm by 10 cm) areas down the long axis of the surfaces. On cylinders, sampling was at 0°, 90°, 180° and 270°. On the panels, 6 sample series were taken, one on the midline of each side and one on each side at the edges. Cylindrical shapes and edges of panels had similar high levels of fouling with highly correlated but significantly lower levels of fouling on the midline of the flat surface. Intensity of fouling was highest from 10 to 30 cm below the surface. Flow patterns around cylinders may provide more effective delivery of larvae. Cylinders may have utility in certain kinds of testing schemes.

### **Pharmaceuticals as Antifoulants for Barnacles**

Rittschof, Dan, Lai C. H., Kok L. M., and Teo, S. L. M.

Duke Marine Lab, Nicholas School of the Environment and Tropical Marine Science Institute, National University of Singapore.

We hypothesized that Pharmaceuticals, with their known synthesis, chemical properties and primary mechanism of action would be an efficient place to start in order to discover new antifouling agents. The hypothesis is that very potent biologically active molecules such as pharmaceuticals should disrupt the very sensitive and complex cascade involved in metamorphosis. We tested 18 compounds for toxicity and settlement inhibition of barnacles. Our interest was in supporting or negating the test hypothesis. Compounds were chosen that impact ion metabolism, signal transduction, and neural pathways in vertebrates. The upper limit for toxicity and settlement inhibition was set at 25 ug/ml in solution assays for toxicity and settlement of barnacles. The lower limit was set at 40 ng/ml. The upper level of potency was chosen because compounds that are this potent have practical potential. The lower level was chosen to save time and materials. Over 80% of the compounds tested had significant effects in this range. Anti-inflammatory and compounds that alter neurotransmitter concentrations or that block opioid receptors were extremely potent with effective concentrations at or below tens of ng/ml. Results with feeding and non-feeding stages indicate that developmental stage and route of entry of the drugs are both important. The next step is to determine if a selected subset of test compounds is effective against other macrofouling species.

### **Effects of Copper in Heavily Impacted Coastal Embayments: Chemical Speciation and Toxicity in San Diego Bay**

Rivera-Duarte Ignacio, Rosen Gunther, Chadwick David B., Lapota David, and Zirino Alberto, Space and Naval Warfare Systems Center, Environmental Sciences Division, Code 2361, 53475 Strothe Road, San Diego, CA 92152-6325 U.S.A.

San Diego Bay is a coastal embayment heavily impacted by anthropogenic inputs. The primary source of copper to bay waters is leaching from antifouling paints. Copper concentrations in the bay are anomalously high, and some of them exceed EPA's chronic water quality criteria of 3.1 ppb dissolved copper, with extensive areas in the bay reaching 3.5 ppb Cu. The largest concentrations, however, are measured in enclosed marinas within the bay, with up to 6 ppb copper (i.e., Shelter Island). In spite of these anomalously high concentrations, toxicity of copper in San Diego Bay is minimal, with EC<sub>50</sub> values ranging from about 10 ppb at the mouth of the bay up to 34 ppb in the back of the bay. Copper toxicity (EC<sub>50</sub>) values are determined following exposure to sensitive life stages (embryo-larval development) of bivalves (*Mytilus galloprovincialis*) and echinoderms (*Dendraster excentricus*), and are 10-times to 20-times larger than the respective total copper concentrations. In contrast to the disparity between toxicity and total copper concentration, a direct relationship is observed between toxicity and copper complexation capacity (CuCC) in those same waters. CuCC is obtained from the response of the copper ion-selective electrode to a copper titration of the original seawater, and ranges from about 7 ppb at the mouth of the bay, to 25 ppb in the back of the bay. The control of chemical speciation over the toxicity of copper is also indicated by the "natural" activities of free copper ion (pCu) measured in the bay, which are consistently below the toxic copper activities (pCu<sub>tox</sub>) at the EC<sub>50</sub>, indicating that a minimal pCu must be reached in order to have toxic effects on the developing embryos. These distributions attest to the importance of chemical speciation and complexation in controlling the effects of copper to organisms in heavily impacted coastal embayments. This work also indicates that whole-basin modeling with respect to sources and sinks of copper, toxicity, and chemical speciation is necessary in order to elucidate the toxic effect of this metal on the environment.

### **Visible Light Cured Coatings for Corrosion Control**

Angela M. Ross, Naval Surface Warfare Center, Carderock Division, 9500 MacArthur Blvd., West Bethesda, MD 20817, USA

Under the Navy's Small Business Innovative Research (SBIR) funded by ONR visible light cured coatings have been developed for use as a ballast tank touch-up repair coating. Spectra Group Limited Incorporated formulated corrosion resistant coatings consisting of oligomeric acrylate resins combined with different combinations of monomeric diluents, various fillers and other materials which provide a balance of critical properties. A blend of photoinitiators including Hnu470 (photoinitiator developed and patented by Spectra Group) achieves tack-free cure in one minute or less using pulsed or continuous visible or UV light sources. Unlike traditional anticorrosion coatings, these coatings are environmentally friendly in that no volatile organic compounds (VOC's) are released or generated. The coatings are capable of application to minimally or poorly prepared surfaces, curing at 50°F or below, with a minimum of three years service life. They were developed to have high impact resistance, corrosion resistance, and good adhesion when used for surface repair applications on Naval vessels while docked or underway. A variety of visible light cured coatings formulations developed by Spectra Group have undergone an extensive laboratory screening process. The coating formulations have successfully passed ASTM test procedures which include crosshatch adhesion, impact, salt fog, cohesion cabinet, long term salt water immersion testing, and electrochemical impedance spectroscopy (EIS) testing. About 15 candidate, epoxy acrylated formulations were selected for application in the ballast tank of three different Trident class submarine platforms. These formulations were cured using a safe, visible light source. These formulations were applied over grit blasted to a near white finish (SSPC SP10), needle gun prepared steel surface (SSPC SP11), intact anticorrosion system (AC), and intact AC system (MIL-P-24441 Type III and Sigmaguard BT high solids coating) with or without rust bleed in the ballast tank of the three Trident class submarine platforms. Some of the formulations were unpigmented (pale yellow color), and some were pigmented either gray or orange. Out of the 15 formulations tested, five formulations showed no sign of adhesion failure or coating deterioration after 2 to 3 years of service.

### **Ships as Vectors: Assessing the Role of Hull Fouling in Biological Invasions**

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Ships are a dominant vector for the introduction of aquatic and marine organisms throughout the world. Although ship-mediated transfer of organisms has been occurring for many centuries, the rate of biological invasions associated with shipping appears to have increased exponentially during the past 200 years. This increase in detected invasions is correlated to obvious increases in the number, size, and speed of ships over time. Despite the clear importance of shipping as a vector for species transfer, the relative contribution of hull fouling to the total number of ship-mediated invasions is difficult to estimate. Today, a great deal of emphasis is placed on ballast water and sediments as the primary source of invasions from ships. Among ships, it is evident that the greatest number of species and individual organisms are transferred currently in the ballast tanks, and some of these species clearly become established. However, species that become established often have planktonic life stages and benthic life stages, which can occur respectively in ships' ballast materials or on ships' hulls. Thus, many invasions associated with ships may result from either component (ballast or hulls) of this vector. Quantitative analysis of hull communities, as well as the correlation between shipping practices and invasion patterns, can help resolve the relative importance of hull fouling in contemporary invasions.

### **Antifouling Property of the Ascidian *Eudistoma viridae* from Gulf of Mannar Southeast Coast of India.**

Ramasamy M. Santhana & A. Murugan, Suganthi Devadason Marine Research Institute, 44-Beach Road, Tuticorin – 628 001, Tamil Nadu, India.

Though Tributyltin based antifouling technology was so successful, it is considered as the most toxic compound ever deliberately introduced into the natural environment. International Maritime Organization (IMO) has proposed a total ban of TBT based paints by the year 2008. Extensive research is being carried out worldwide on antifouling compounds from natural resources especially marine. The sedentary marine invertebrates possess unique secondary metabolites, which exhibit antifouling properties. So investigation was carried out on the ascidian *Eudistoma viridae* collected from Gulf of Mannar Southeast Coast of India for antifouling property. The microbial sensitivity assay showed antibacterial activity of the methanol extract of the ascidian. In the byssal thread bioassay with *Perna indica*, the extract inhibited the byssal production and attachment. The EC50 value of extract is 100 µg/ml and LC50 value is 250 µg/ml. Toxicity studies indicate that this ascidian extract did not cause irreversible damage to *Perna indica*. The results indicate the possible potentialities of this extract as a natural eco friendly antifouling agent.

Biomass and succession pattern of fouling diatoms and invertebrate larvae of Thoothukkudi coast, India  
Ramasamy Santhanam\*, Arasan Srinivasan and Chellappan Kavitha, Fisheries College and Research Institute, Tamil Nadu Veterinary and Animal Sciences University, Thoothukkudi 628 008, India

The Thoothukkudi coast, a segment of Gulf of Mannar in India is known for its diversified fisheries resources including the world famous pearl oysters, sacred chanks and sea cow. While its fishing harbour operates more than 500 mechanised fishing vessels, its major port berths cargo vessels originated from other countries. In order to assess the status of fouling in fishing crafts, an investigation was made on the biomass and succession pattern of the fouling diatoms and invertebrate larvae of this coast during Jan – Dec. 2000. While the number of diatom species varied from 3 to 8, its species diversity index from 0.8 to 2.1, the values of which were invariably corresponding to species composition. The biomass of fouling invertebrate larvae was mainly contributed by the larvae of cirripedes (*Balanus* and *Lepas*), bryozoans (*Membranipora*), tubeworms (*Serpula*), bivalves (*Crassostrea*) and cnidarians (*Obelia*) in that order. While the density of net phytoplankton varied from 12000 to 32000 cells/m<sup>3</sup>, the fouling invertebrate larvae from 7000 to 15000 organisms/m<sup>3</sup>. Since the net phytoplankton and larval ratio is only approximately at 2:1, it is quite possible that the larvae depended not only on the net phytoplankton (200µm) but also the nanophytoplankton for their food source. This is evident by the chlorophyll pigment content estimated in the seawater samples. An interesting succession in the diatom and larval populations was also observed as follows:  
Pennate diatoms                      Centric diatoms                      Obelia medusae                      Serpulid larvae                      Oyster veligers  
Cyphonautes larvae.

The larvae of cirripedes i.e. *Balanus* and *Lepas* however showed year round occurrence and abundance. The factors responsible for the succession of these larvae have been determined and discussed. The influence of ballast water originated from foreign vessels and mariculture on the possible introduction of new species of fouling invertebrates through their larvae in this coast are also discussed.

## **Biofouling & its control strategy in the cooling water of Prototype Fast Breeder Reactor**

Satpathy K. K., Jebakumar K E & Kannan S E, Safety Engineering Division, Indira Gandhi Centre for Atomic Research, Kalpakkam – 603 102, India

Power plants located on the coastal areas make use of large quantity of seawater for their condenser cooling. A 500 MW (e) Prototype Fast Breeder Reactor (PFBR) the first of its kind in India, is to be located at Kalpakkam, east coast of India ( $12^{\circ} 33' \text{ N}$  &  $80^{\circ} 11'$ ) close to the existing Madras Atomic Power Station (MAPS). The PFBR will use about  $25 \text{ m}^3/\text{s}$  of seawater for its cooling water system (condenser & process seawater). The MAPS has been operating since 1983 and uses seawater for its cooling water system at a rate of about  $35 \text{ m}^3/\text{s}$  through a submarine tunnel ( $3.8 \text{ m } \Phi$ ,  $486 \text{ m}$  long &  $53 \text{ m}$  deep). The velocity inside the tunnel is about  $2.5 \text{ m/s}$ . In spite of intermittent chlorination ( $\sim 1 \text{ ppm}$  residual for  $0.5 \text{ h}/8 \text{ h}$ ), the cooling water system experienced severe biofouling particularly in the pre-condenser section. Using a Remotely Operated Vehicle, about 600 tones of marine organisms were estimated to be inside the tunnel. The growth inside the tunnel ranged from  $9$  to  $25 \text{ cm}$  with an average of  $18 \text{ cm}$ . This increased the pressure drop ( $\Delta p$ ) at the pump house from the design value of  $2.8$  to  $3.3 \text{ m}$  resulting in serious operational difficulty. A shock chlorination ( $2.5 \text{ ppm}$  for  $3$  weeks) removed about  $70 \%$  of the growth, which improved the  $\Delta p$  considerably. However, it has not been possible to overcome the biofouling problem at MAPS completely.

The PFBR is to have an off-shore Jetty and the seawater pipe ( $\sim 3 \text{ m } \Phi$ ) will be laid on a Jetty of  $600 \text{ m}$  long. From the experience of MAPS, it is expected that different sections of the cooling water system of the PFBR would experience serious biogrowth and thus will stand in the way of efficient operation. PFBR process seawater will have plate type of heat exchanger and expected to experience serious biofouling as compared to that of MAPS which has tube type. The major biofouling organisms assessed at Kalpakkam coastal water are green mussel & barnacle. Chlorine is decided to be the biocide for biofouling control in the PFBR cooling water, considering its easy availability at an economical rate and its proven effectiveness. To devise a precise and accurate biofouling control programme based on chlorination for the PFBR cooling water, a complete assay of cooling water with emphasis on chemistry of chlorination has been initiated. Results on chemistry of chlorination such as chlorine demand showed that the demand varied from  $0.4$  to  $1.5 \text{ ppm}$  ( $3 \text{ ppm } \text{Cl}_2$  dose &  $0.5 \text{ h}$  contact time). About  $50 \%$  of the demand occurred during a period of  $0.25 \text{ h}$  indicating that a good amount of reactive organic matter is present in the cooling water. Results also showed three distinct demand periods January to March (lowest), April to September (highest) & October- December (moderate). This revealed that the quantum of  $\text{Cl}_2$  injection can't be the same throughout the year. The demand also found to increase with time indicating the need for appropriate additional  $\text{Cl}_2$  addition during low flow period. The significance of chlorine demand in biofouling control is discussed in detail from techno-economic point of view. Due to the close proximity of PFBR to MAPS the possible influence of one cooling system on the other is also delineated. The paper also discusses various other methods of biofouling control methods vis-à-vis chlorine and it also brings out why does chlorine still rule the roost. Moreover, the paper critically analyses the R & D effort required in this direction considering the lesson learnt from the MAPS experience.



### **Microtopography of shell surfaces as a defence against fouling in molluscs.**

Scardino, Andrew<sup>1</sup>, de Nys, Rocky<sup>3</sup>, Steinberg, Peter<sup>1,2</sup>

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Biofouling rapidly covers most submerged surfaces in the marine environment. However, some marine organisms remain clean despite strong fouling pressure indicating a defence against the settlement and growth of fouling organisms. Mechanical, chemical and physical mechanisms may contribute to this defence. We investigated potential physical defences against fouling by comparing the surface properties of two bivalve molluscs, the blue mussel *Mytilus galloprovincialis* and the pearl oyster *Pinctada imbricata*. We measured the presence and thickness of the periostracum on four size classes of each species using staining and microscopy techniques. There are significant differences between thickness and coverage of the periostracum between species and between size classes for each species. We also measured the microtopography of the shell surface using atomic force microscopy (AFM). Three-dimensional plots of surface roughness showed a homogeneous corrugated surface structure for *M. galloprovincialis* with a uniform distance of 1-2 microns between ridges, while *P. imbricata* had a heterogeneous surface structure without a repeating structural pattern. To determine whether the shell surface had antifouling properties we subjected size classes of both species to long-term field exposure trials. We also manipulated the surface of the shell and tested the deterrent properties of the shell in field and laboratory trials. *M. galloprovincialis* was rarely fouled over a six month period. *P. imbricata* was fouled with the intensity of fouling being dependent on the age of the shell and the cover of the periostracum. We discuss the relationship between the structure and deterrent effect of the shell surface of both species.

### **Assessment of Trace Metal Emissions From Antifouling Paints During Underwater Cleaning Events and Passive Leaching**

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William R. Crawford III, Scuba Duba, Inc., 255 Marina Drive, Long Beach, CA 90803

The contributions of potential pollutants are routinely monitored to assess mass emissions from most regulated sources (i.e. boatyards and shipyards) in the Southern California Bight. Emissions from antifouling bottom paints applied to recreational vessels are an exception and virtually no monitoring of this source occurs on a regular basis. The problem is becoming exacerbated in harbors and marinas throughout southern California as water quality measurements for trace metals, such as copper, are indicating potential impairments in these waterbodies. When this occurs, state regulatory agencies are required to take action. However, stakeholders are concerned about the rationale and justification for requiring management actions when it is still unclear what the relative contributions of these potential pollutants are to water quality problems. The goal of this study was to measure the contributions of trace metals, including copper, from antifouling paints during underwater cleaning events and during passive leaching to quantify the emissions from this source. The relative emissions were compared between hard vinyl, modified epoxy, and biocide-free formulations. Passive leaching was characterized at multiple time periods after a hull cleaning event to measure the changes in leach rates as biofilms develop. Contributions during underwater hull cleaning events were measured after allowing for a month-long fouling. Moreover, some management actions available to stakeholders for reducing trace metal contributions include the use of “best management practices” developed by the underwater hull cleaning companies. This study assessed the differences in emissions with and without the use of these best management practices.

## **Silicone Nanocomposites as Minimally Adhesive Polymer Coatings**

Schmidt Daniel E. and Giannelis Emmanuel P., Department of Materials Science & Engineering, Bard Hall, Cornell University, Ithaca, NY 14853, U. S. A.

Biofouling of ship hulls is a significant problem. It leads to decreased speed and fuel efficiency and increased maintenance costs. Traditional solutions to this problem have involved the incorporation of toxic organometallic species into a paint-based hull coating. This technique is effective, but harmful to the environment. The resultant ban on the use of many of these systems has created a need for alternative systems to control marine fouling.

One such system that has been proposed is the minimally adhesive polymer surface (MAPS). The ideal system revolves around a tough, non-toxic, polymer coating that combines the appropriate surface characteristics necessary to retard biofouling (low surface roughness, porosity and surface energy, high molecular mobility) with chemical and physical stability in saltwater, appropriate film-forming characteristics, and good adhesion to a variety of hull materials. Such a material would then act in two ways: By retarding biofouling (“minimally adhesive”), and by fouling release (where organisms that *do* stick can be easily removed, ideally by simply bringing the ship to speed).

In this talk, we will focus on our development of polymer/layered silicate nanocomposites based on poly(dimethylsiloxane) (PDMS) elastomers, for use in anti-fouling and fouling-release applications. These systems, containing no more than 10% of an inorganic phase by weight, display significant reinforcement while retaining relatively low viscosities and remaining good film-formers. By contact angle, they display a more hydrophobic surface than unfilled silicones, and dielectric spectroscopy shows significant enhancements in polymer mobility, even below  $T_g$ . Additionally, in cooperation with Callow, Finlay et al at the University of Birmingham, it has been shown that such disparate properties as coating adhesion and microorganism settlement are very strongly affected by small changes in curing chemistry. Finally, we present data on systems containing commercially available PDMS-PEO block/graft copolymers, which not only improve dispersability of the nanoparticles, but also offer to improve fouling-release characteristics.

## **Enzymes as antifouling agents in marine coatings for ships and offshore constructions.**

Schneider Ib and Allermann Knud, BioLocus ApS. Danish Science Park. Agern Allé 3. DK-2970 Hoersholm. Denmark.

BioLocus ApS has taken a biological approach to give a non-toxic solution to the two major requirements for future marine coatings:

Safe for the environment  
Effective as anti-fouling agent in a marine paint.

By studying the biology behind the fouling process a solution became obvious. The organisms involved in the fouling process all use a biological mechanism (a form of glue) to settle at e.g. a ship hull.

As an example: barnacle larvae secrete a protein to settle as cypris larvae on a surface before the metamorphosis into the adult stage. This secreted protein (the glue) can be hydrolysed by enzymes. Similar polysaccharides secreted from the bacteria, giving rise to the slime-layer, can be hydrolysed by enzymes.

The protease “Alcalase” was shown to prohibit settlement of the cyprid barnacle larvae at a dose as low as 50 µg/ml seawater in a laboratory experiment.

Experiments were further performed to investigate the compatibility with known marine paint binders. From these experiments it turned out that a “natural” binder e.g. rosin were compatible with the “Alcalase”. It was demonstrated that the Alcalase was still active in the prototype marine paint formulated.

It was also demonstrated that enzymes are effective as anti-fouling agents in field experiments.

Marine painted panels containing enzymes were immersed into seawater. After being immersed for six months the panels were inspected. Only very few barnacles could be detected on the enzyme containing panels compared to the control panels without enzymes.

It is a well-known fact that enzymes, which are necessary part of all living cells, will be degraded in the environment and reused in the habitat as amino acids. Thus using enzymes, as anti-fouling agents, will fulfil the above-mentioned major requirements.

### **Three models to relate detachment of low form fouling at laboratory and ship scales**

Schultz Michael P.<sup>1</sup>, Finlay John A.<sup>2</sup>, Callow Maureen E.<sup>2</sup> and Callow James A.<sup>2</sup>, <sup>1</sup>Department of Naval Architecture and Ocean Engineering, United States Naval Academy, Annapolis, MD 21402, USA, <sup>2</sup>School of Biosciences, The University of Birmingham, Birmingham B15 2TT, UK

Since fouling-release coating systems do not prevent settlement, various methods to quantify the tenacity of adhesion of fouling organisms on these systems have been offered. One such method is the turbulent channel flow apparatus. The question remains how the results from laboratory scale tests relate to the self-cleaning of a ship coated with a fouling-release surface. The present paper relates the detachment strength of low form fouling determined in the laboratory using a turbulent channel flow to the conditions necessary for detachment of these organisms in a turbulent boundary layer at ship scale. A power-law formula, the ITTC-57 formula, and a computation fluid dynamics (CFD) model are used to predict the skin-friction at ship scale. The results from all three methods show good agreement and indicate that turbulent channel flow can be used to provide useful means of predicting the detachment of low form fouling at ship scale. Turbulent channel flow data for the detachment of the marine algae *Enteromorpha* are presented to illustrate the use of the three models.

### **Turbulent boundary layers on surfaces covered with marine algae**

Schultz Michael P., Department of Naval Architecture and Ocean Engineering, United States Naval Academy, Annapolis, MD 21402, USA

Turbulent boundary layer measurements have been made on surfaces covered with marine algae. These experiments were conducted in a closed return water tunnel using a two-component, laser Doppler velocimeter (LDV). The mean velocity profiles and parameters as well as the axial and wall-normal turbulence intensities and Reynolds shear stress are compared with flows over smooth and sandgrain rough walls. Significant increases in the skin friction coefficient for the algae-covered surfaces were measured. The boundary layer and integral thickness length scales were also increased. The results indicate that profiles of the turbulence quantities for the smooth and sandgrain rough walls collapse when friction velocity and boundary layer thickness are used as normalizing parameters. The algae-covered surfaces, however, exhibited a significant increase in the wall-normal turbulence intensity and the Reynolds shear stress, with only a modest increase in the axial turbulence intensity. The peak in the Reynolds shear stress profiles for the algae surfaces corresponded to the maximum extent of outward movement of the algae filaments.

### **Nontoxic phytochemical fouling control for the marine industry**

Seabrook, Guy and Lindberg, Bob, Magellan Companies, Inc., 1051 Planters Place, Mt. Pleasant, SC 29464 and Reltek, Inc., 640 Spears Road, Santa Rosa, CA 95409.

Significant, preliminary test results show promise for a safe, nontoxic antifoulant for the marine industry. Woodshole Oceanographic Institute conducted two separate trials with Magellan's patented technology. The first nine-month trial was the testing of one phytochemical on the equator, which controlled the growth of barnacles. The second nine-month test conducted off of George's Bank, MA, which controlled algae with less than 5% growth. Reltek, Inc. partnered with Magellan to combine the phytochemicals, then purify and concentrate the formula. A Fortune 500 paint manufacturer's marine coatings division has been blending and testing this innovative formula with marine coatings over the last ten months with very encouraging results. The photos of test panels shown at the presentation indicate a progressive improvement in fouling control on artificial surfaces with a nontoxic, environmentally safe product.

## **Environmental Loading of Copper From Antifouling Marine Coatings in San Diego Bay**

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Interest in environmental loading of antifouling (AF) biocides including copper, used to prevent marine growth on vessel hulls, has increased recently because of observed adverse effects on non-target organisms resulting from tributyltin (TBT) leaching from boat hulls and the impending International Maritime Organization ban on TBT-containing coatings. A major component of copper loading into many harbors and estuaries is from the release of cuprous oxide biocide into surrounding waters. Copper release rates from several AF paint formulations were measured by laboratory and in-situ methods from static and dynamic field-exposed panels in San Diego Bay. The panels coated with AF paints were exposed for over two years in natural seawater in San Diego Bay and measurements were made by three methods. In addition, direct in-situ Cu release rate measurements were made on the hulls of both Navy vessels and pleasure craft with a novel diver-deployed dome system used to obtain environmentally realistic loading rates. Copper release rate measurements revealed a large range of values for different paint formulations over time and with different measurement techniques varying from  $1\mu\text{g}/\text{cm}^2/\text{d}$  to  $35\mu\text{g}/\text{cm}^2/\text{d}$  with up to order of magnitude differences between formulations. One of the most important environmental variables is the biofilm or slime layer which can reduce Cu release by an order of magnitude over coatings with little or no biofilm. Direct in-situ on-the-hull release rate measurements of typical Navy AF formulations average about  $3.9\mu\text{g}/\text{cm}^2/\text{d}$  where intact slime layers were present (ranging from  $3\text{-}6\mu\text{g}/\text{cm}^2/\text{d}$ ), and are typically two-to-three-fold lower than laboratory measurements of the same paint system with a reduced slime layer. Temperature is another important variable. In laboratory studies a  $20^\circ\text{C}$  change ( $7\text{-}27^\circ\text{C}$ ) yielded a two-to-three-fold increase in Cu release rate.

With growing enforcement of the Clean Water Act through watershed management practices such as Total Maximum Daily Loading (TMDL) and Waste Load Allocation (WLA), an understanding of all the contaminant source loading terms is becoming more important. Copper loading estimates are provided using measured, modeled and estimated copper inputs. With environmentally realistic loading estimates, hydrodynamic/contaminant transport models can be used to project copper concentrations and dispersion and support the development of non-conservative models using various loading scenarios to support risk assessment requirements and develop rational regulatory strategies

### **Inspection method for identification of TBT-containing anti-fouling paints**

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In order to ensure the effectiveness of the international convention which prohibits the use of organotin compounds for anti-fouling paints of ships, it is essential to establish an inspection system to determine whether or not the paint applied on a ship contains the prohibited compounds. In the present study, a method for the identification of organotin containing anti-fouling paints in accordance with the following two-stage analyses is investigated. Firstly, X-ray fluorescence analysis (XRF) is applied, which could be used at the place of ship surveys or port state control (1st stage test). Using a portable instrument equipped with a silicon drift detector (SDD) and customized for ship inspection, analysis is automatically executed, providing an interpretation for detecting the presence of tin. In case that the existence of tin is confirmed by XRF, secondly, the sample is subsequently to be examined at a trustworthy analytical organization for further scientifically strict analyses, such as gas-chromatograph-mass-spectrometry (2nd stage test). Sampling device consists of a disc of approximately 20 mm, or 10 mm, in diameter and abrasive paper pasted on a flat surface of the disc. The device is pressed and slid on the ship hull to slightly scrape off the fragments of the paint from the hull surface onto the abrasive paper. Preliminary experiments revealed that sampling from a ship at a dockyard and subsequent XRF analysis successfully identified the presence of tin and that the resultant damage caused to the anti-fouling coating surface by the sampling was acceptably light.

**Barnacle Removal from Silicone Coatings in Shear and Pull off Tests.**

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The mechanics of barnacle release from silicone coatings has been studied in shear and tension as a function of coating thickness. Mechanical tests were performed on both transparent, single-layer silicone coatings and duplex silicone coatings. Release forces of both pseudobarnacles (epoxied studs) and Chesapeake Bay barnacles (*Balanus improvisus*) were measured; release behavior was determined by analyzing video recordings of the separation process of pseudobarnacles from transparent coatings (on glass). Release forces of both barnacles and pseudobarnacles decreased as coating thickness increased in both shear and tension (pull off) tests; forces in shear were generally lower than in tension. Pseudobarnacles separated by a peeling process in both shear and tension; peeling modes depended on the confinement ratio,  $a/h$ , where  $a$  is the baseplate radius and  $h$  is the coating thickness. *In situ* visualization of the separating interface identified the various peeling modes, including perimeter and void peeling during tensile release and shear waves during shear release. Fracture mechanics has been used to model the release processes and to account for several of the modes of release.

**Dehumidification for Ballast Tank Corrosion Control in a Tension Leg Platform**

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Dehumidification of the air in normally dry ballast tanks and other interior spaces is being used for corrosion control on the Morpeth Tension Leg Platform (TLP) in the US Gulf of Mexico. Corrosion is prevented by reducing the relative humidity inside the tanks to a point where liquid water does not exist on the steel surface in equilibrium with water hygroscopic salts and rust. Further, by reducing relative humidity to below 60%, biofouling from bacteria and fungi is eliminated in the tanks. This eliminates the need for interior coatings in these tanks, saving substantial capital investment and construction time. Dehumidification, combined with the fresh air circulation system, is used for the final drying of the tanks after installation, and to maintain a corrosion free environment in the tanks.

## Why Don't Barnacles Stick to Silicones?

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Model silicone foul release coatings with controlled molecular architecture were evaluated to determine the effect of compositional variables such as filler loading and crosslink density on pseudobarnacle and barnacle attachment strengths. Pseudobarnacle adhesion values correlated with filler loading in both condensation and hydrosilation-cured silicones. Variation of crosslink density of hydrosilation-cured silicones had an insignificant effect on attachment strength. However, the mode of failure upon detachment of the pseudobarnacle was dependent upon the crosslink density—samples with high crosslink density failed cohesively within the silicone. Barnacle adhesion mirrored pseudobarnacle adhesion in hydrosilation-cured systems.

One way to increase foul release performance without compromising coating physical properties is by incorporation of oil into the silicone. We examined the adhesion of six fouling organisms; the barnacle *Balanus eburneus*, the gastropod mollusc *Crepidula fornicata*, the bivalve molluscs *Crassostrea virginica* and *Ostrea sandvichensis*, and the serpulid tubeworms *Hydroides dianthus* and *H. elegans*, to silicone fouling-release surfaces. Macrofouling attachment strength varied among the fouling species and among the surfaces. Principal component analysis of the removal stress data revealed that the fouling species fell into two distinct groups, one comprising the bivalve molluscs and tubeworms, and the other the barnacle and gastropod mollusc. Adhesion of these groups was not obviously related to any of the surface physical or chemical properties measured for the silicone materials, including critical surface tension.

The series was further evaluated to determine the effect of oil type and coating type on organismal adhesion values. We found that not only are the main effects important in determining the organismal response, but the interaction term (oil type crossed with coating type) is highly significant for all organisms except oysters at the University of Hawaii test sites which is significant at the 90% confidence interval.

To determine the parameters responsible for organismal adhesion differences on these oil amended coatings, we evaluated the modulus, critical surface tension, contact mechanics of the coatings. Measurement of nanoadhesion forces on the coatings using high-resolution force spectroscopy will also be discussed.

### **On the generality of seaweed natural antifoulants**

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Many seaweeds have biologically active secondary metabolites or extracts which, when extracted from whole plants, inhibit settlement of fouling organisms. It is not clear, however, whether such compounds generally act as settlement inhibitors for these algae *in situ*, e.g., as natural antifoulants. We used a variety of approaches to assess the extent to which chemically rich Australian seaweeds use non-polar secondary compounds to deter fouling of their surfaces. First, we quantified (macro)fouling on these species at several sites over time. Variability in fouling among species, times and sites was considerable, but all seaweeds suffered some fouling. Second, we examined the morphology of the algae to investigate whether putative inhibitors were encapsulated/presented in such a way that they could be delivered to the surface of the thallus. Metabolite "delivery systems" varied considerably, with some structures suitable for presenting compounds at the surface of an alga, and others apparently preventing surface delivery of compounds. Third, we assessed the activity of crude non-polar extracts and some pure metabolites from the algae against propagules of a variety of fouling organisms. Test organisms included ecologically relevant epibiota such as the algae *Ulva* sp. and *Polysiphonia* sp.; the bryozoan *Bugula neretina*, and the commercially relevant barnacle *Balanus amphitrite*. In general, most extracts deterred most propagules for at least one of the concentrations tested, although extracts of two algae (*Delisea pulchra* and *Laurencia rigida*) stood out as most active. However, when we tested these same organisms against surface extracts of the algae, which remove metabolites from the surface of the thallus but not internally, most of the algae did not show evidence of chemical inhibitors. *Delisea pulchra* was the exception, with surface extracts from this alga having strong effects against most epibiota. Some assay organisms were deterred by surface extracts from other algae. However, except for *D. pulchra*, the pattern of deterrence did not correlate with deterrence by whole thallus extracts, suggesting that the effect was not generally due to the well known secondary metabolites from these algae. Overall, the results of these studies indicate that chemical deterrence of fouling may not be as common among seaweeds as has been suggested, and generalisations regarding natural antifoulants from seaweeds or other marine eukaryotes will require detailed data on the morphology, chemistry, and ecology of the organisms.

### **Environmental occurrence and behaviour of selected antifouling paint booster biocides**

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The environmental occurrence and behaviour of antifouling paint booster biocides used in the UK was assessed by conducting laboratory experiments and field measurements. Results showed that the biocides Irgarol 1051 and diuron were present in surface waters and sediments at detectable concentrations and that the Irgarol 1051 degradation product GS6575 and the diuron degradation products DCPMU and DCPU were also detected. Field based measurements and laboratory experiments showed that Irgarol 1051 and diuron persist in the water column due to a low affinity to partition onto sedimentary material and high resistance to degradation. Other biocides, such as chlorothalonil, dichlofluanid, and Sea-Nine 211 were all found to be rapidly removed from the water column and were less persistent. A preliminary study of biocide input during both normal use and foreshore hull hosing showed that hosing may be a significant point source input and also be a cause for future concern since much of this input is in the form of paint particles. Laboratory experiments showed that even labile biocides could persist in sediments when they enter in the form of paint particles. This study suggests that even rapidly degrading booster biocides could lead to environmental damage if associated with paint particles released into marinas unless activities such as hull cleaning are strictly regulated. The impact of biocides entering the environment in the form of paint particles should be fully evaluated in the risk assessment process.

### **Restrictions on the use of biocidal antifoulings, the Scandinavian case**

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The paper will deal with the Scandinavian and especially the Swedish policy on the use of antifouling. Sweden's history of restrictions on biocidal products started 1989 with the ban on TBT for vessels less than 12m length. In 1993 a risk assessment resulted in the ban on AF paints containing Diuron as well as Isothiazolin for pleasure craft. The use of antifouling was prohibited on vessels weighing less than 200kg with the latest restriction coming into force in 2001 with no approved biocidal products on the entire east coast of Sweden. Sweden has now defined 4 different antifouling application areas. The paper will review monitoring and resulting risk assessments leading up to the current regulatory situation. Need assessments and other documentation will also be reviewed and compared with the actual situation in 2002. Conclusions drawn from a major project to evaluate biocide free systems will be presented as well as opinions voiced in the boating press and by boat owners via internet etc.

### **Sessile organism communities on the artificial reefs made of coal - fly ash concrete blocks placed at depth of 80 m in the coast of Nagasaki, Japan**

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In Japan, 30% of coal - fly ash from coal-fired power stations is landfilled. It is vital to seek ways to recycle these materials. For this reason, a technology that uses coal - fly ash as artificial reefs was developed. An artificial reef made from coal - fly ash (30000 m<sup>3</sup>) was submerged to a depth of 80 m off the coast of Nagasaki, Japan. In order to capture fish using artificial reefs, it is essential that sessile organism communities form on the reef. But there is little information on sessile organism communities that form on coal - fly ash concrete submerged at a depth of 80 m.

In this study, at a depth of 80 m, coal - fly ash concrete panels (25 X 25 cm) were submerged from September 1998 to August 2001. Panels were raised to the surface each year to investigate sessile organism communities as well as the length of orifice for the barnacles. Also, at a depth of 1.5 m, sessile organism communities were investigated for coal - fly ash concrete panels, normal concrete panels, and PVC panels (15 X 15 cm each) that were submerged from May 2001 to February 2002. Panels were raised to the surface every three months to investigate sessile organism communities.

At depth of 80 m, 8 classes and 21 species were identified. Sessile organism biomass assessed as wet weight were 44 g/m<sup>2</sup> to 2400 g/m<sup>2</sup>. Dominant sessile organism communities attached to the panels were barnacles. Length of orifice for the barnacles was 8 - 9 mm for *Megabalanus rosa*, and 4 - 5 mm for *Balanus trigonus*. At a depth of 1.5 m, coal - fly ash concrete panels were submerged for nine months. Number of barnacles identified on the coal - fly ash concrete panels were less in comparison to that of normal concrete submerged under similar conditions.

### **Inducing effect of microbial films on the larval settlement of the barnacle, *Balanus amphitrite***

Tomoyuki Jouuchi and Hitoshi Kitamura, Faculty of Fisheries, Nagasaki University, Nagasaki, 852-8521, Japan

The presence of a surface film of microorganisms (microbial films) has long been recognized as a prerequisite for the settlement of many fouling invertebrates. Although some reports have implicated microbial film with barnacle settlement, its inducing activity remains unknown. In this study, the inducing effect of microbial films formed in the sea and of laboratory cultured diatom films on the larval settlement of the barnacle, *Balanus amphitrite* have been examined. Films formed in the sea did not induce settlement. Uni-algal films of about 20 species of diatoms did not also show any activity for larval settlement. However, a few species of diatoms such as *Navicula ramossissima*, *Cocconeis* sp. exhibited high inducing activity. The inducing activity of the diatom, *Navicula ramossissima* increased with density. Activity decreased after lectin treatment, suggesting that settlement cues in the films could be sugar related compounds.



**Hull roughness experiment, Comparison with different coating type and extrapolation on ship full economy**  
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The importance of hull roughness to the performance and economics of ship operations was discussed by Townsin et al (1980). They found that fuel represented more than 50% of the operating cost on a new ship and rose to almost 90% on a 70's class ship due to hull roughening. Regulations that will require ships to change from the self polishing organotin paints to new generation copper based and silicone fouling release coatings have raised questions as to how these new coatings will perform. This research is designed to compare the antifouling, roughness and hydrodynamic characteristics of new antifouling coatings to the self polishing organotin paints. The research will be achieved by exposing 254 x 305mm coated panels to dynamic and static seawater conditions, monitoring for fouling, fouling adhesion, roughness and coating condition, and measuring drag and fouling release properties using a waterborne test facility.

#### **The ship hull fouling penalty**

Townsin Robert L, retired Head of the Department of Naval Architecture and Shipbuilding at the University of Newcastle UK, present address: 'Garfield', Whitley Road, Benton, Newcastle upon Tyne, NE12 8BP UK – presented by Colin Anderson, International Paints.

The ship resistance penalties of slime, shell and weed are discussed in turn. Methods to measure the hard paint roughness of anti-fouling are recapitulated. The determination of a satisfactory roughness parameter from correlations with measured roughness functions is described. This in turn, allows a relationship between ship added friction and roughness height to be found. This recapitulation allows a consideration of using the same route for a surface with filamentous fouling. Consideration is given to low surface energy coatings and their roughness idiosyncrasies. Finally, the determination of economic penalties is discussed, both for a particular ship and globally.

#### **Antifoulant Biocides – Why Laboratory Testing is not Enough (or Maybe Too Much)**

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Regulatory approval of antifouling biocides requires the completion of various laboratory tests designed to assess environmental safety. These tests are intended to determine the degradation rate of the parent compound and the identity and fate of any significant degradants, and are carried out under conditions designed to limit degradation to a single mechanism (e.g. hydrolysis or biolysis), to the exclusion of all others. Further studies may then be required to assess the safety of degradants identified in the individual studies.

While the required laboratory tests may have merit in providing a basic understanding of individual chemical and biological degradation mechanisms, they are not necessarily useful in determining which degradants will be of significance under actual use conditions. Indeed, they may be misleading. Due to the fact that a metabolite which appears to be important in a single-mechanism study may be quite insignificant when more than one degradation mechanism is active, this approach can lead to unnecessary and wasteful additional testing.

By designing and conducting a study under simulated end-use conditions, where all natural forces are in play, a more realistic environmental fate profile is obtained, where the truly significant metabolites become obvious, and further testing more justifiable.

We will present a case history, involving zinc and copper pyrithione, which illustrates the advisability of conducting supplemental environmental fate studies under simulated end-use conditions.

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### **Past and future of erodable polymers in antifouling paints.**

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The evolution of the international, environmental legislation is moving towards a total withdrawal of organotin compounds and to a severe limitation of the use of cuprous oxide and of organic molecules in antifouling paints. In the objective to develop new antifouling strategies without added toxic products, we have researched the discriminating factors of the efficiency of the existing erodable paints. Then, the specific parameters of erodable coatings which constitute the more efficient protection at the moment : erosion, hydration, biocides release and the common parameters to all coatings : mechanical and physico-chemical properties of surfaces (toughness, roughness, surface energy), as well as the biodiversity of the adherent bacteria, have been studied. Due to the poor literature in this field, specific analytical tools have been set up.

Results suggest a single discriminating factor, the erosion. This result confirms the interest of the erodable binder for the preparation of antifouling coating. The effects of the other parameters and particularly the role of biocides have not been established. The amount of released biocides was largely inferior to the lethal doses for bacteria and was similar for efficient or not paints. The thermodynamic characteristics of the paint surfaces (hydrophobic/hydrophilic character, Van Der Waals constituents ( $\gamma^{LW}$ ) and the Lewis acid-base character, showed strong differences. Roughness and toughness were also quite different from a paint to another. Moreover, if all the paints present a biofilm at their surfaces, it seems, first, that the biodiversity was larger in the case of non efficient paints and, second, that the adherent bacteria could be selected with regard to the physicochemical properties of paints. In spite of the constant development of non-stick silicone coatings, the biodegradable, erodable polymers keep being interesting because they enable the development of a new generation of antifouling paints, easy to apply, compatible with the existing protection systems and based on the use of non toxic molecules which can control the initial step of marine fouling, the bacterial biofilm.

### **Biogenic Neighborhood Effects in Recruitment Dynamics**

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The circumstantial observation that the composition of benthic assemblages on similar substrates seem to differ among microhabitats dominated by a single species, e.g. blue mussel beds or seagrass communities, led to the assumption that recruitment dynamics may be influenced by the presence of macroorganisms, i.e. the biogenic neighborhood.

In a field study artificial substrates were exposed to fouling within different microhabitats for 4 months and were afterwards compared to control assemblages that established outside but nearby the particular habitat, during the same time. This experiment revealed significant differences in larval recruitment and community structure, presumably generated by biogenic properties of the habitat.

A set of in-vitro experiments were conducted in order to test our hypothesis that chemical water conditions within microhabitats, due to exudation of secondary metabolites by the dominant species, could be responsible for the differing settlement patterns. Seawater samples from benthic assemblages were incubated with natural planktonic communities from Kiel Fjord and settlement patterns were assessed. Settlement behaviour of some colonizers, e.g. the blue mussel *Mytilus edulis*, corresponded closely to the recruitment patterns observed in the field study. This suggests that small-scale chemical water conditions generated by the presence of a dominant macroorganism contribute substantially to the complex abiotic and biotic processes determining recruitment patterns in benthic systems.

## **An Advanced Scanning Probe Microscopy Tool-kit for Studying Anti-fouling Surfaces**

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We report the development of a powerful new scanning probe microscopy tool-kit for the analysis of fouling release surfaces and biofoulants. This kit includes techniques include novel methods to measure JKR adhesion, elastic modulus and single molecule and micelle forces at soft interfaces. Single molecule studies provide new insights into surface polydispersity and long range bridging interactions between foulants and the underlying surface. We also describe a method to measure the infrared spectra of chemical functional groups on a nanometer length scale. The conformation of macromolecules at surfaces influences their activity. We have developed single molecule single molecule experiments that reveal such conformations and folding states, such as are relevant to the development of conditioning layers. We have applied these techniques to adhesion macromolecules. Thermodynamic parameters for folding stability and kinetics have been obtained. We compare these force dynamics of foulants with the molecular dynamics of a minimally adhesive silicone surface itself. Adhesion release can be enhanced by controlling the modulus of the substrate. We have recently developed new methods to measure the modulus of surfaces using AFM. We apply these techniques to examine the curing of both composite PDMS and natural polymer materials. When the modulus is a strong function of depth on a length scale of the AFM probe, special precautions must be taken. We also report recent strides in developing apertureless near-field scanning infrared microscopy (ANSIM) for analyzing at exceptional spatial resolution the chemical properties of polymeric films. This new tool positively impacts our ability to analyze the chemical composition of polymeric coatings because the instrument construction is made in parallel with careful theoretical modeling to characterize the spectroscopic performance.

## **Biofilm cues for generalist herbivores ? Settlement of the sea urchin *Heliocidaris erythrogramma* larvae in response to biofilms**

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Larvae of marine invertebrate herbivores settle in response to a suite of cues including conspecifics, host plants and biofilms. Bacterial biofilms in particular strongly influence the settlement of many marine invertebrate larvae. We hypothesize that cues for generalist herbivores will be biofilm derived while those for specialist herbivores are more likely to be derived from host plants. We tested this hypothesis with the sea urchin *Heliocidaris erythrogramma*, a generalist herbivore, investigating the role of algal cues vs. biofilms in the induction of settlement. We first tested algae and other common substrata from the habitat of adult *H. erythrogramma* as potential sources of settlement cues. We found that algae from the Corallinaceae, such as encrusting corallines, *Corallina officinalis*, and to a lesser extent *Amphiroa anceps*, caused high settlement rates of *H. erythrogramma* larvae in the laboratory. However, significant settlement also occurred on sand and rocks. We then investigated the settlement response of larvae to coralline algae treated with antibiotics or other procedures designed to remove bacteria. When the bacterial biofilm on the alga's surface was modified by these treatments, settlement rates were significantly reduced. Decreasing bacterial diversity (as opposed to abundance) had the strongest effect on settlement. Culture studies and molecular community analysis using denaturing gradient gel electrophoresis (DGGE) are being used to identify isolates that induce settlement in *H. erythrogramma*. This study contrasts with an earlier, analogous investigation of settlement cues for the co-occurring specialist herbivore *Holopneustes purpurascens*, which metamorphoses in response to host plant (algal) derived cues.

## **Development in Easy Release Antifouling Coatings Technology**

Webb Arthur A., and Foster Richard L., Naval Research Laboratory Center for Corrosion Science and Engineering 4555 Overlook Ave SW Washington DC 20375, Kaznoff Dr. Alexis I., Ingle Mark, Naval Sea Systems Command SEA 05M1 1333 Isaac Hull Avenue SE, Stop 5131 Washington Navy Yard, DC 20376-5131.

This paper summarizes the U.S. Navy's efforts in the development and performance evaluation of easy release coatings and a summary outlining the uses of these coatings in the fleet. Presented in this paper are the findings associated with these coatings to include physical and chemical properties which may enhance or detract the coating's performance properties.

**Low Solar Absorbance (LSA) Coatings Performance and Reliable Evaluation Techniques**

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This paper describes the technology, formulation and performance measurement of Low Solar Absorbance (LSA) coatings for shipboard camouflage. Discussed in this paper are the recent developments concerning the materials and measurement techniques associated with LSA coatings and their performance predictability as well as results of actual shipboard applications.

**New Tank and Void Coating Systems for Increased Life and Reduced Maintenance in Seawater and Compensated Fuel Service**

Webb Arthur A., and Bergh Jan O., Foster Richard L., Naval Research Laboratory Center for Corrosion Science and Engineering 4555 Overlook Ave SW Washington DC 20375, Brinckerhoff Beau E., Naval Sea Systems Command SEA 05M1 1333 Isaac Hull Avenue SE, Stop 5131 Washington Navy Yard, DC 20376-5131. Harris Tyler, Geo-Centers Incorporated  
Rockville Maryland

This paper discusses the initiative employed by the U.S. Navy regarding enhanced corrosion control efforts based on the implementation of solvent free, high build coatings in shipboard seawater and compensated seawater/fuel tanks. Discussion focuses on three key elements, 1) process control, 2) materials, and 3) documentation. Also discussed are the performance criteria and evaluation processes associated with candidate coatings which are intended for shipboard ballast tank corrosion control.

**Use of Composite Technology for the Replacement of Shipboard Metallic Components**

Webb Arthur A., Naval Research Laboratory Center for Corrosion Science and Engineering 4555 Overlook Ave SW Washington DC 20375, Ingle Mark, Naval Sea Systems Command SEA 05M1 1333 Isaac Hull Avenue SE, Stop 5131 Washington Navy Yard, DC 20376-5131.

This paper describes the U.S. Navy's successes in employing composite materials in an active process of controlling maintenance costs associated with corrosion control. Discussion includes the design elements associated with material selection and fabrication as well as process instructions associated with installation and general maintenance.

**Experimental study of drag resistance on sea water immersed surfaces using a laboratory scale rotary set-up.**

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Ship performance and ship hull roughness are closely related. An increased hull roughness will give an increased drag resistance and hence higher bunker costs. The hull roughness is a combination of a number of factors such as rust, paint remains, weldings, hull defects, fouling etc. For several years Hempel's Marine Paints has conducted both static and dynamic tests in the evaluation and optimisation of biocide based and fouling-release paint products. The dynamic testing is performed on rotary set-ups either located in the laboratory or at sea sites. In the laboratory set-ups it is possible to investigate the polishing and the leaching behaviour of antifouling paints as well as to evaluate the drag resistance on immersed surfaces. One of the laboratory rotary set-ups has been equipped with a torque meter to the rotor shaft. From recording of the torque on the rotor shaft it is possible to evaluate the drag resistance acting on the rotor cylinder spinning in the water tank. In this work a comparison between different immersed surfaces has been conducted. A number of PVC rotor cylinders with varying surface roughness have been prepared by sand blasting and used to map the correlation between drag resistance and surface roughness. Different painted surfaces have been compared to the reference surfaces by varying parameters like the type of the paint (both biocide based and fouling-release paint), thinning of the paint before spraying and the spraying conditions. In one experiment also the drag resistance of a commercial tin-free paint is mapped as a function of time exposed to 30 knots in artificial sea water of 30 °C. To our knowledge this is the first attempt to investigate the drag resistance of modern tin-free biocide based and fouling release paints using a rotary set-up. The results obtained from this work will be compared to other published data obtained from e.g. towing tank experiments.

## **On the Ecology and Natural History of Macrofaunal Organisms Fouling Vessel Surfaces**

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While macrofouling assemblages found on vessel surfaces comprise a wide variety of taxonomic groups and life history types, they share a number of common features that facilitate their ability to colonize those surfaces. For example, once larvae attach to the surface, they quickly metamorphose and affix themselves with very good powers of adhesion. Most species are generalized suspension feeders and there is little evidence that food is a factor limiting growth and survivorship. The vast majority of species have rapid growth rates, often become reproductively viable within weeks to months and have high and/or continuous reproductive output; all of which act to enhance the fouling process. Some species have relatively limited larval dispersal capabilities and are likely to settle within a short distance of the parents. Larvae of others are attracted to conspecific adult populations, settle gregariously, or are able to settle on newly disturbed surfaces. Most species do not display a high degree of substrate preference when settling. The net result of these traits is the ability of the species to rapidly build-up local populations and therefore reducing the probability that other species will settle and out-compete them for space. Rapid population growth also enhances the probability of survival from predators and/or physical disturbance.

The vast majority of the invaders found on vessel surfaces are normally resident to harbors and estuaries. The species, therefore, are >pre-adapted= to being exposed to a relatively wide range of chemical, physical and biological conditions. Their eurytopic nature aids in their tolerance to environmental conditions as they are being transported across the oceans and from port to port. To assist in survival during transit, fouling species often have squat profiles which reduce drag and have the ability to strongly attach themselves to vessel surfaces. Some species can survive long periods of time without feeding and have the ability to isolate themselves from the external environment with shells (e.g., molluscs) or tests (e.g., barnacles) during transport.

Embayments and harbors provide ideal recipient habitats for the maintenance of both resident and introduced species which then can act as sources for colonizing new areas. These habitats are ideal because of (a) the abundance of habitable areas (e.g., pilings, docks, breakwaters), (b) physical conditions within the areas often tend to retain larvae produced by adults, and (c) they often have reduced numbers of predators residing within them. In addition, recent experimental studies have found that successful invasions appear more likely in habitats with reduced resident species diversity and areas which receive high frequencies or magnitudes of natural and/or human-induced disturbance. Harbors and embayments frequently have low numbers of resident species and are continually disturbed by human-activities such as degraded water quality. Once established, the invaders rapidly build up local populations that can be dispersed to new localities on vessel surfaces. Other dispersal mechanisms include adults attached to flotsam or as larvae transported in the water column by currents.

Comparative life history studies of several of invasive and resident ascidians in southern New England coastal waters indicate little difference in growth and reproductive rates between the two groups. In addition, invaders appear equally or less vulnerable to predation than similar resident species. Native predators do not limit the invader=s distributions any more than they limit the distributions of resident fauna. In fact, some invaders may be chemically defended from predators and it is surprising that they have not invaded habitats not currently utilized by residents. Long-term studies on the invaders reveal that they are more positively influenced, than residents, by the warming of winter seawater temperatures. With the moderation of winter water temperature over the past 25 years in Long Island Sound, invaders reproduce earlier than residents and are more likely to persist and dominate coastal habitats. Therefore, increasing coastal ocean temperatures coupled with enhanced global transport of species, may be contributing to the observed accelerated invasion rate in these ecosystems.

### **Peculiarities of barnacle adhesive cured on non-stick surfaces**

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In order to define the properties which influence non-stick behaviour of surfaces we need to understand the qualities of the adherent - namely the barnacle or its adhesive - and the qualities of the joint between the surface and the adherent. The main scope of this study is to improve the understanding of why barnacle bonding to certain foul-release surfaces is weak.

These investigations dealt with the interface barnacle adhesive/ surface of diverse materials. Barnacle adhesive was investigated by various microscopic techniques. Electron microscopy revealed a filamentous structure of the adhesive. The formation of adhesive threads on non-stick surfaces differed from easy-to-attach substrates. Close weaven networks - suggesting a progressed cross-linking process - were seen on surfaces that had no foul-release properties.

Differences in the adhesion force of barnacles on the used materials corresponded with the adhesive's consistency. Low adhesion forces referred to high water contents of the adhesive. It is assumed that barnacle adhesive with low adhesion strength remained in a partially bridged state, not proceeding further cross-linking.

### **A bioassay system for the semi-high throughput screening of compounds for antifouling activity**

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Identifying and developing new active ingredients for use in antifouling coatings is a very demanding task: candidates must not only be highly effective against major fouling organisms, but also environmentally acceptable, cheap, easy to produce and compatible with other coating ingredients. A fruitful approach is to evaluate as many different chemicals as possible.

Learning from the fields of medicine and pesticide development we have developed a bioassay system for the semi-automatic screening of compounds for barnacle settlement inhibition (*Balanus amphitrite*) and diatom growth inhibition (*Amphora coffeaeformis*). Tests are carried out in 96-well microtiter test plates, enabling to test many samples simultaneously. Test plates are automatically prepared from 1000 ppm DMSO stocks by a robotic liquid handling station. Primary screening is in two replicates in one concentration (usually 1 ppm), while secondary screening is in automatically prepared dilution series (4 or 6 concentrations, 3 replicates). Diatom film formation is monitored by fluorescence measurements using an automatic plate reader, taking just one minute per plate. A fixed number (10±1) of laboratory cultured barnacle cyprid larvae is added manually to each well containing 100-150 µl filtered seawater. After 24 hours incubation the plate is rinsed to remove all non-settled cyprids, following a standard washing procedure. The number of permanently attached cyprids/juvenile barnacles is counted manually or by automatic image analysis. Up to 500 samples can be screened daily. Examples of screening results will be given. The set-up can easily be adapted for other assays such as diatom settlement and larval toxicity.

### **Nontoxic Fouling Release Coatings: Prospects for Improvements**

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Nontoxic fouling release coatings are based on weak bonding of marine organisms rather than toxicant release. An ideal nontoxic fouling release coating would offer a combination of physical, mechanical, geometric, and kinetic barriers to adhesion such that fouling organisms could not bond effectively. Thus, the hull, ballast tank, heat exchanger water inlet, or other area of a ship with this “ideal” fouling release coating would either not foul or would self-clean under minimum water flow. The attainment of an economical, effective fouling release coating would be a major achievement in protecting sensitive estuarine environments that are currently contaminated with Sn, Cu, or organic toxicants from marine paints. This presentation addresses progress toward achieving the challenging goal delineated above. What are the criteria that are important in providing negligible adhesion? In an underwater coating, the complete set of factors is not yet clear. Wetting behavior, surface topography and morphology, fillers, bulk modulus, coating thickness and other factors play a role in adhesion. However, the anticipated long life requires fouling release coatings to be tough and easily repaired, but there is evidence of an inverse relationship between toughness and fouling release. What is the special combination that is best? How can we develop the “ultimate” fouling release coating? Results on polydimethylsiloxane and oxetane based coatings will be discussed and analyzed for clues.

### **The study of offshore fouling in China**

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Biofouling on ships' hulls and other man-made structures is a major economic and technical problem around the world. Due to the increase of hydrodynamic loading, hindrance of underwater inspection and influence of corrosion characteristics, extensive and intensive work on marine fouling in offshore areas has been conducted for safety operation over the past several decades with the growth of the offshore oil and gas industry.

In China, the studies of offshore fouling are conducted in the Bohai and the northern South China Seas. The relevant results show that the type and extent of fouling assemblages on offshore installations varied with time, latitude, water depth, distance from coast, and type of marine facilities, i.e. floating or fixed.

For example, the major species of fouling organisms in Bohai Sea were *Garveia francisana* and *Corophium* sp. in the early stage, and then the fouling communities were gradually dominated by *Mytilus edulis*, *Sagartia rosea*, *Ostrea denselamellosa*, *Hiatella orientalis*, *Membranipora grandicella*, *Hydroides ezoensis* and *Balanus uliginosus*. Unlike those in the Bohai Sea, the fouling assemblages in the northern South China Sea were composed of pedunculate barnacles, hydroids, acorn barnacles, common and pearl oysters. With increasing distance from shore, pedunculate barnacles and hydroids became more and more important, and the species number and biomass of littoral species decreased greatly. Moreover, pedunculate barnacles were only distributed on floating objects. On the fixed marine structures, fouling communities were characterized by hard foulers, such as acorn barnacles, common and pearl oysters.

Future strategies for effectively assessing the potential impact of marine fouling on offshore facilities and for establishing appropriate cleaning (or prevention) procedures are proposed also at the end of this paper.



### **Ether linked, Side Chain Poly(ethylene glycol) and Fluorocarbon Containing Polymers With Controlled Architecture for Biofouling Resistance and Release**

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Current research in marine fouling resistance/release applications is focused on low energy materials and biocompatible materials. Of interest in these two areas are fluorinated materials due to their extremely low surface energy, surface activity, self assembly, and self healing natures and poly(ethylene glycol) (PEG) which shows remarkable biocompatibility. We present here the preparation of well defined architecture block copolymers with pendant fluoroalkyl or PEG side chains by both anionic and controlled radical polymerizations. As recently shown, the ester group which is commonly used to link side groups to the main chain is hydrolytically unstable over extended periods. For this reason we instead focus on ether linked side chains to overcome this problem. Biofouling resistance and release are determined for the materials and comparisons are made where appropriate. Protein adsorption and surface properties are also determined and presented in terms of the biofouling properties.

### **Biodegradation-based Polymer Surface Erosion and Surface Renewal for Foul Release at Low Ship Speeds**

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Non-toxic foul release provides an environmentally friendly and sustainable technical solution to control of micro-and/or macro-biofouling on ship hulls. Silicone-based coatings have been used for foul release at high or moderate ship speeds (> 15 knots). To remove the fouls from slow ships (<15 knots), the macro-fouls in particular, biodegradable polymers may be used to make the coating surface self-renewable. Synthesized by microorganisms as carbon and energy storage under controlled conditions, the biodegradable polymers (polyhydroxyalkanoates, PHAs) are natural thermoplastics or elastomers depending on the substrate fed to the microbial cells. PHAs are gradually decomposed into CO<sub>2</sub> and water in the environment. Because of their hydrophobic property and no hydrolysis in sterile aqueous solution, PHAs do not dissolve into water, but erode at the polymer surface (2-5 micrometer in depth) catalyzed exclusively by microbial enzymes (depolymerases) that are attached on the solid surface. The thin-layer surface erosion behaves like a self-renewable coating surface, which approaches a constant renewal rate at a relative hydraulic speed as low as 3 knots. A turbulence eddy model is used to describe the effect of energy consumption per mass of liquid on the turbulent shear stress and the surface renewal rate. Furthermore, the polymer biodegradation or surface renewal rate can be controlled in a broad range by blending the material with other polymers such as cellulose acetate (CA) and Poly (ε-caprolactone) (PCL). Because a complete miscibility between a PHA and a CA leads to very slow biodegradation or surface renewal, partial miscibility or compatibility between a PHA and a PCL was studied. The biodegradation of binary blends of PHA/PCL at different composition was quantitatively monitored with weight loss and Raman spectroscopy.

### **Intraregional transport of marine biological invaders: a case study from California**

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In the past decade, several large bays and harbors, including San Francisco Bay, Chesapeake Bay, Pearl Harbor, and Port Phillip Bay in Australia, have been surveyed for invasive species. All of these waterways are exposed to international shipping, and to ballast water dumping, and were found to be highly invaded. To our knowledge, no thorough survey had been done of an embayment not connected to an international port. Elkhorn Slough, an estuary 70 miles south of San Francisco in the Monterey Bay, is exposed only to regional boat traffic, mostly small fishing vessels, and little, if any, ballast water dumping. In 1998, we spend some 50 person-hours surveying the slough for macroinvertebrates. Fieldwork and a literature review revealed 56 exotic species at the slough, a surprising diversity considering there are few direct international transport modes for invaders. While some of these invaders may have been brought directly to the slough from Japan and the Atlantic Coast of the U.S. with cultivated oysters, many others are associated with boat-hull fouling and were likely transported indirectly from San Francisco Bay or other West Coast harbors with thriving populations of exotic species. Indeed, the invasive species in Elkhorn Slough appear to be a subset of the invasive fauna of San Francisco Bay, suggesting that bay may be acting as a stepping stone for secondary invasions to regional embayments such as Elkhorn Slough.

