Project No. NMP4-CT-2005-011827

AMBIO

ADVANCED NANOSTRUCTURED SURFACES FOR THE CONTROL OF BIOFOULING

Instrument Type:	Integrated Project
Thematic Priority:	Nanotechnology and nanosciences, knowledge-based multifunctional materials and new production processes and devices (NMP)

The Publishable Final Activity Report of the AMBIO Integrated Project

Period Covered by Report:	March 1st 2005-Feb 28th 2010	Date of Preparation: April 14, 2010
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Project Coordinator: Professor James A. Callow

Project Coordinator Organisation: University of Birmingham, UK

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http://www.AMBIO.bham.ac.uk

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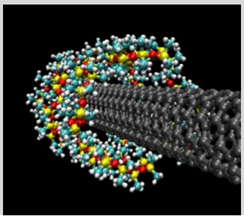

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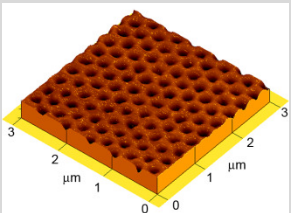

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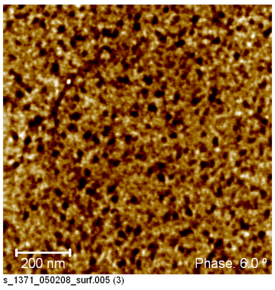
Preface and Executive Summary

AMBIO ('Advanced Nanostructured Surfaces for the Control of Biofouling') is an R&D Integrated Project funded by the EC, through its 6th Framework Programme. The 5-year project, started in March 2005, is highly interdisciplinary, operating at the frontiers of diverse disciplines, including nanotechnology, polymer science, surface science, coating technology, hydrodynamics and marine biology. The project integrated 31 Partners from industries, universities and research organizations and a significant number of end-user 'stakeholders' was involved. Twelve EU Member States were represented as well as Turkey, Israel and Norway. AMBIO demonstrates the strength of the EC's large Integrated Project concept, in that, for the first time in Europe, the efforts of a critical mass of researchers, with diverse skills, and representing several sectors and stakeholder organizations, was concentrated on the challenge presented by the need to introduce novel, non-biocidal technologies to control the economically and environmentally important problem of biofouling. At the conclusion of the project I am proud to say that we can recognize many significant impacts which will be elaborated in detail in this report; a summary is provided here:

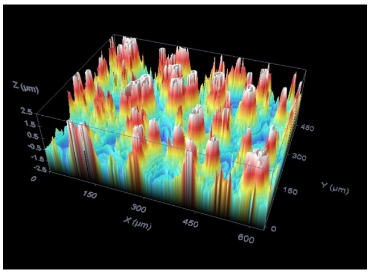
- Approximately 500 different nanostructured coatings, representing 64 generic coating chemistries were prepared at laboratory-scale and evaluated for their antifouling and fouling-release performance. Of these, 15 were down-selected for testing in a range of field and representative end-user tests. Several coatings showed promise in these trials, and have either been commercialized, or have the potential to be so after further development.
- A range of surface-sensitive tools, including novel methods developed within the project, were applied to the study of nanoscale properties of coatings and how these change during immersion.
- Fundamental advances were made in the understanding of the influence of surface nanostructure on the settlement and adhesion of fouling organisms. In particular there is a growing recognition that an appropriate level of heterogeneity and pattern, in topography, or in surface chemistry, may be more effective than a homogeneous surface, leading to the concept of 'ambiguous' coatings.
- Novel methods for nanostructuring surfaces were developed with potential benefits for many technologies other than antifouling.
- Fundamental advances were made in understanding the relationship between the structure and properties of a coating and its biological performance.
- Hydrodynamic properties of several candidate nanostructured coatings were established.
- Novel imaging methods including digital holography and imaging Surface Plasmon Resonance were developed and applied for the first time to the analysis of how fouling organisms explore surfaces and how coating properties affect this.
- There was extensive knowledge and technology transfer between Partners working in different disciplines and between academia and industry. New cooperative, trans-national relationships were established between Universities and companies, and between academic Partners from different institutions. Some of these have spawned new enterprises and cooperative projects.
- Through the Training Associate scheme, 5 young scientists have been trained to appreciate the importance of interdisciplinary investigations in the solution of applied problems.
- Patent applications have been submitted for 5 novel coating technologies
- 70 papers were published in international, refereed journals thus contributing to the scientific knowledge base.
- Through 531 items of individual dissemination, audiences in the coatings industry, the research community, and the general public have been informed about nanotechnology and its potential for accelerating the introduction of 'green', sustainable technologies to solve an applied problem.

Professor James Callow
Coordinator

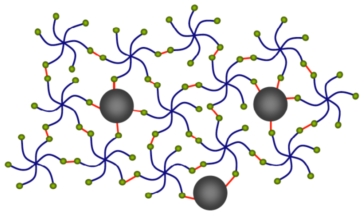
Some images illustrating the range of nanocoatings tested in the AMBIO project



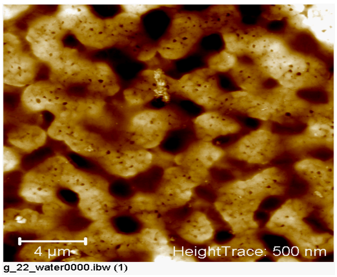
Rubbery coatings based on block copolymers of polystyrene and butadiene showing nanoscale structure of soft (dark) and harder (light) segments(BASF)



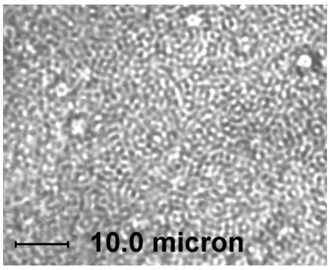
Confocal microscopy image of sol-gel coating incorporating nanoclay platelets (TNO).



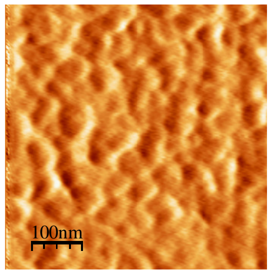
Schematic of a network created from Star-PEG prepolymers using nanosilica as crosslinker (Sustech).



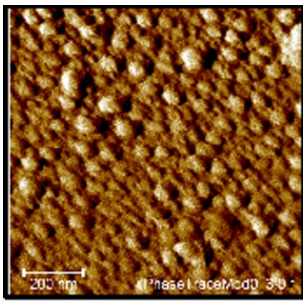
Structure of coatings made from copolymers of polypropylene and ethyl vinyl acetate (GYTE).



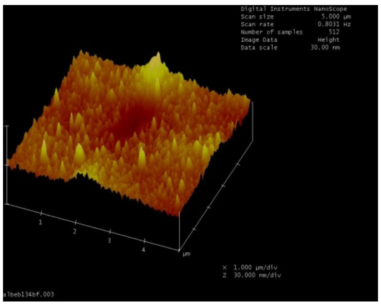
Blended polyphosphazenes under optical microscopy showing surface structuring through phase segregation (Polymer Labs).



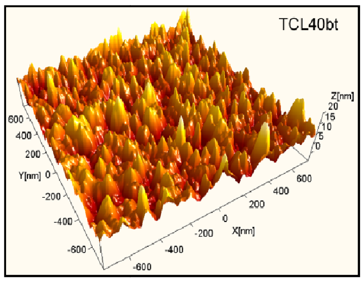
Nanostructure of fluorosilane coating elctrodeposited on stainless steel substrate (CIDETEC)



AFM image of amphiphilic (fluorinated/PEGylated) nanocoating (University of Pisa)



AFM image of the surface structure of a silicone coating filled with multi-wall carbon nanotubes (UMH)



AFM image of a silicon-oxide coating showing surface nanostructure (TEER).

1.Introduction

1.1 The biofouling problem

'Biofouling' is the colonisation of submerged surfaces by unwanted organisms such as bacteria, barnacles and algae, and has detrimental effects on shipping and leisure vessels, heat exchangers, oceanographic sensors and aquaculture systems.

The increase in frictional drag caused by the development of fouling on **hulls of ships** can reduce speed in excess of 10% (Townsin, 2003[1]). A vessel with a fouled hull burns 40% more fuel which has an impact on fuel costs and additional greenhouse gas production (estimated to be 20 million tonnes per annum). The estimated saving to the shipping industry through the use of antifouling coatings is estimated to be ~20 billion Euros per year. Fouled hulls are also implicated in the spread of 'alien species' around the world, potentially threatening the balance of sensitive ecosystems.

The influence of biofouling on coastal and **oceanographic measuring instruments**, which are routinely used in marine and coastal research and monitoring programmes, is very strong and the earliest stages of biofouling, within a few days of immersion, significantly affect data quality and instrument performance. There is a need to protect the instruments from biofouling so that they are able to gather better quality data and require less maintenance. Currently there are no effective coatings to control this problem, the only solution involves expensive manual cleaning by divers.

Biofouling of **intake structures, screens, seawater piping systems and heat-exchanger tubes** in desalination and power plants causes an overall decline in plant efficiency at great economic cost. For example the presence of a biofilm on transfer surfaces of heat exchangers cooled by seawater reduces the heat transfer rate by 20 to 50% and incurs a global expenditure of over $15 billions per annum to control the problem.[2] The majority of current measures to control biofouling involve the use of biocides.

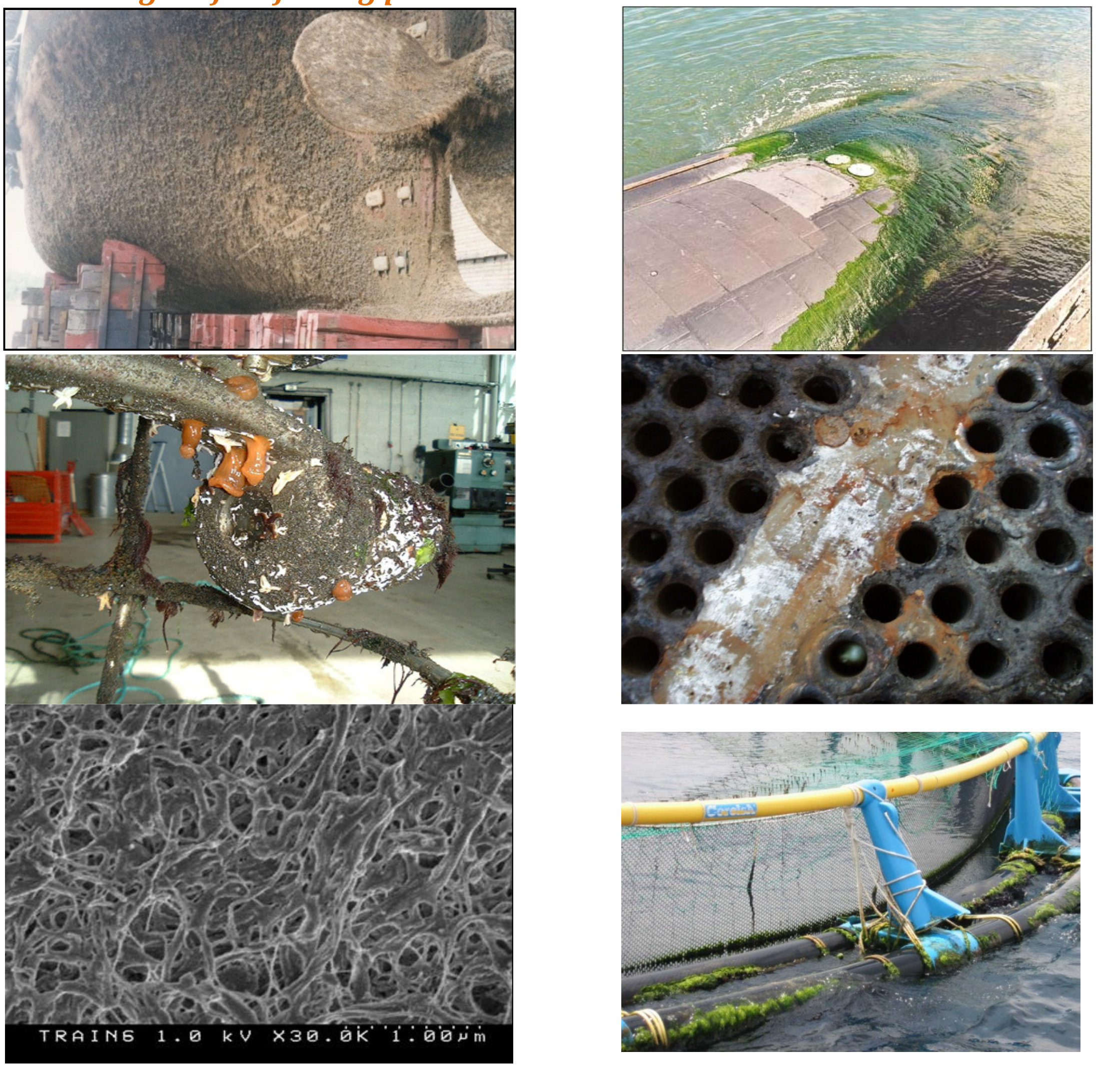
In the area of **membrane technology**, microfiltration and ultrafiltration membranes are used for drinking water production and wastewater treatment. The primary limitation to the more widespread adoption of membrane filtration is fouling with microorganisms and organic molecules which leads to a significant decline of the permeate flux, higher energy consumption, and eventually, failure to meet the regulatory standards. Frequent cleaning of the membranes is costly and may damage the membrane materials/barrier layers.

Biofouling is a major problem throughout the European and global **aquaculture industries**. Biofouling on farm infrastructure greatly reduces the efficiency of materials and equipment. Problem areas include immersed offshore-structures such as cages, netting and pontoons, on-shore equipment and structures such as pipelines, pumps, filters and holding tanks. Cost estimates for small shellfish producers indicate that biofouling leads to annual costs of €96000 per year, per farm.

1 Townsin, R.L. (2003) The ship hull fouling penalty. Biofouling 19 (supplement) 9-15.

2 Azis PKA, Al-Tisan I, Sasikumar N (2001) Desalination **135** : 69-82.

Some images of biofouling problems

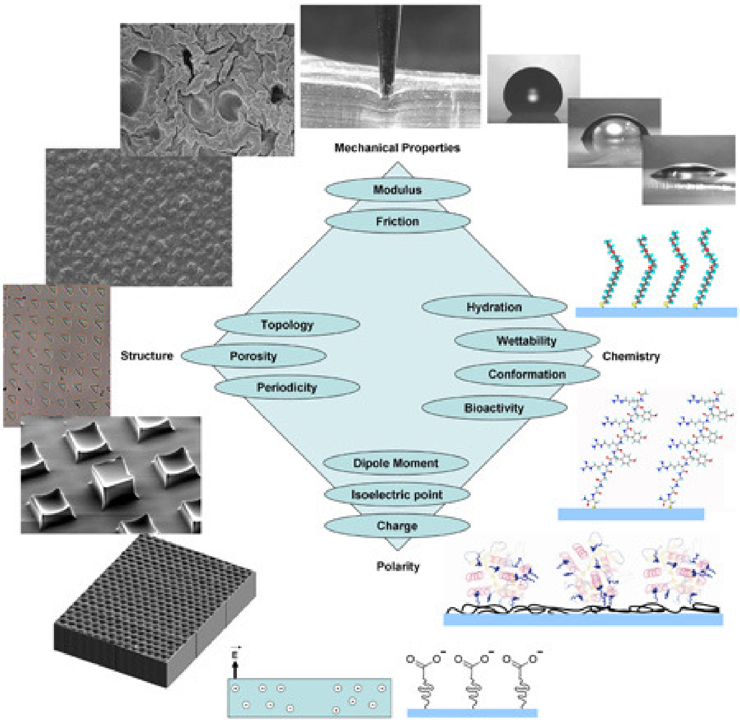


Top left, fouling of ship hull by barnacles (international Paints); top right, fouling of submarine by green algae (UoB); centre left, fouling of a turbidity sensor (OCN); centre right, microbial fouling and corrosion in heat exchanger pipework (KIMAB): bottom left, fouling of membrane filter (ZENON); bottom right, fouling of fish farming structures.

1.2 Current technologies and novel solutions

The two main approaches to creating commercial fouling-resistant coatings are a) 'antifouling coatings' (i.e. no settlement (attachment) of the colonizing larvae, spores or cells) and, b) 'fouling-release' (i.e. organisms release under hydrodynamic forces because they are weakly adhered). 'Antifouling' coatings are typically based on the controlled release of biocides, to kill the colonising organisms. With the increasing environmental restrictions placed on biocides (e.g. the EC's Biocidal Products Directive 98/8/CE) the registration of new active ingredients for use in antifouling paints is a very protracted business, increasing the cost and time required to develop a new coating. The emphasis in technological innovation is therefore now on non-toxic coatings that do not release materials into the environment and which function through their physico-chemical surface properties, either to deter organisms from settling, or which reduce their adhesion strength. The development of such coatings and an understanding of how they work may be accelerated through nanotechnology.

Biofouling is the outcome of surface colonization and adhesion processes used by the responsible organisms. The critical biointerfacial processes resulting in fouling are nanoscale/microscale in dimension: it follows therefore, that surface properties to control biofouling need to be on the same length scales. The figure below summarises the range of interfacial properties that are considered to be relevant to the performance of fouling-resistant coatings against marine organisms. An area of particular interest in recent years is the impact of surface patterning (nano- and micro-scale) on fouling organisms. Surface patterns may be purely topographical, chemical, or combinations of the two since they are often inter-related, and can be generated by either top-down' or 'bottom-up' approaches. The former are most suitable for small scale surfaces that enable specific hypotheses to be tested in laboratory studies. The latter are more suited to practical coating designs through, for example phase-segregating polymer blends or self-assembling block copolymers. The importance of studying surfaces underwater is also becoming more important, especially for those surfaces that reconstruct in water, since it is the hydrated surface that the settling organisms/cells encounter.



*The range of physico-chemical coating properties that can influence settlement and adhesion of fouling organisms. From, Rosenhahn, A., Ederth, T., and Pettitt, M.E. (2008) Advanced Nanostructures for the control of biofouling: the FP6 Integrated Project AMBIO. Biointerphases, **3**, IR1-IR5.*

1.3 The AMBIO Project Mission

The AMBIO project addressed a strategic need to strengthen research excellence in the application of nanosciences to help solve the applied problem of aquatic biofouling, within relevant European industry.

The overall goal of the project was to provide a combination of fundamental and application-oriented research that will lead to the development of novel coatings that will prevent or reduce the adhesion of fouling organisms through the physico-chemical properties of the surface, rather than the release of biocides. The research on nanoscale interfacial properties of different surfaces and how organisms adhere will allow understanding how anti-biofouling systems can work at the nanoscale. To achieve this goal the project aimed to take advantage of the new opportunities for designing and manipulating antifouling surfaces provided by nanotechnology. Nanostructuring of a coating controls many surface and bulk properties that are relevant to an antifouling, 'non-stick' surface, such as surface energy, charge, conductivity, porosity, roughness, wettability, friction, modulus, physical and chemical reactivity, and compatibility with organisms.

An **additional goal** of the project was to improve our understanding (theoretical and empirical) of how surface properties influence the adhesion processes of fouling organisms. This was achieved by hypothesis-driven experimentation that takes advantage of new technologies for creating surfaces with controlled and precisely known nano- and micro-scale properties.

2. Project Execution

2.1The AMBIO Consortium: a multidisciplinary approach

AMBIO operated at the frontiers between diverse disciplines, including nanotechnology, polymer science, surface science, coating technology, hydrodynamics and marine biology. The project integrated 31 Partners from industries, universities and research organisations. Twelve EU Member States were represented as well as Turkey, Israel and Norway. The Integrated Project concept facilitated the efforts of a critical mass of researchers, with diverse skills, and representing several sectors and stakeholder organizations, concentrated on the challenge presented by the need to introduce new technologies to control biofouling.

Figure right: countries involved in the AMBIO Consortium.

Table1: List of Participants* (N.B. Original Partners 21 and 26 withdrew)

No.	Participant Name	Short name	Country
1	University of Birmingham	UoB	UK
2	Institut National Polytechnique de Lorraine/CNRS	INPL/CNRS	France
3	Netherlands Organisation for Applied Scientific Research	TNO	Netherlands
4	University of Pisa	UniPi	Italy
5	International Paint (part of Akzo-Nobel)	Akzo-Nobel	UK
6	University of Dundee	UNIVDUN	UK
7	Gebze Institute of Technology	GYTE	Turkey
8	University of Mons-Hainaut	UMH	Belgium
9	Centro de Tecnologias Electroquimicas	CIDETEC	Spain
10	Linkoping University	LIU	Sweden
11	Newcastle University	UNEW	UK
12	Institute of Metals and Technology	IMT	Slovenia
13	Polymer Laboratories Ltd	POLYMER	UK
14	Institut für Polymerforschung, Dresden	IPF	Germany
15	University of Heidelberg	UHEI	Germany
16	Biolocus	BioLocus	Denmark
17	Zenon	ZENON	Hungary
18	Corrosion and Metals Research Institute	KIMAB	Sweden
19	Ship Design and Research Center	CTO	Poland
20	Argus Chemicals	Argus	Italy
22	Laviosa Chimica Mineraria	LAVIOSA	Italy
23	TEER Coating Ltd	TCL	UK
24	Wallenius Marine	WALL	Sweden
25	KEMA Nederland BV	KEMA	Netherlands
27	Oceanographic Company of the Netherlands	OCN	Netherlands
28	BASF-Aktiengesellschaft	BASF	Germany
29	Val Videregående Skole AS	VAL VGS	Spain
30	SusTech GmbH	SusTech	Germany
31	Nanocyl S.A.	Nanocyl	Belgium
32	Israel Institute of Technology	Technion	Israel

2.2 Project Objectives

The technical objectives of the project were formulated as 4 key questions:

- Which nano-designs show good "antifouling" properties against a range of test organisms?
- How does nanostructure influence adhesion of organisms?
- How do coatings respond to the aquatic environment and how do nanofillers influence this?
- Which design concepts show most promise as durable antifouling coatings for a range of "real-world" applications?

2.3 Methodologies and Approaches

To answer these questions the project R&D strategy involved 6 Sub-Projects, arranged in 3 overlapping phases: progression from one phase to another being regulated by key Milestones (Figure below). An additional Sub-Project (7) dealt with Integrated Project Management.

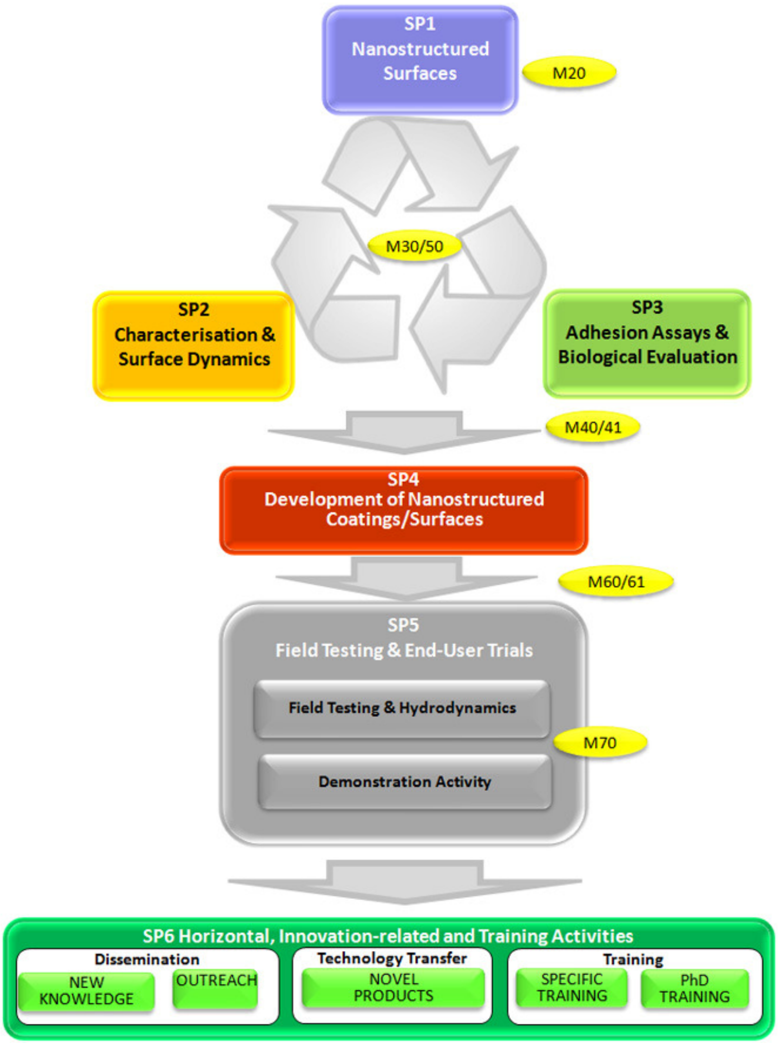


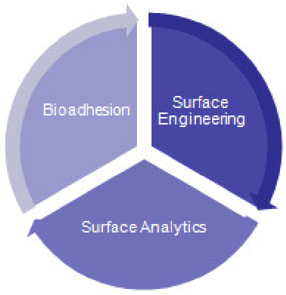
Figure: The general structure of the AMBIO project

3. Achievements:

3.1 Phase 1: 'Experimental'

3.1.1 Technical Operation

In the first 4 years of the project, 3 parallel Sub-Projects closely coordinated and integrated their activities with the overall goal of producing a short list of candidate coatings that could be further developed and tested in Phases 2 and 3. The elucidation of structure/property/performance relationships was at the heart of this phase of the project since such understanding will assist future attempts to develop rational design criteria for novel coatings.



Sub-Project 1 initially involved 16 Partners and was designed to produce a diverse range of nanostructured coatings that might be anticipated, on a priori grounds, to have potential, either as practical antifouling/fouling-release (AF/FR) coatings, or as 'model' coatings to improve fundamental understanding of the impact of surface nanostructuring on fouling organisms.

Sub-Project 2 involved 18 Partners and was responsible for the characterization of surface and interfacial (water-side and substrate-side) properties using state-of-the-art surface-sensitive tools including environmental AFM, SEM, angle-resolved XPS, Sum Frequency Generation and AT-FTIR spectroscopy, contact angle and surface energy determination and other characterization tools such as XPS depth profiling, nanoindentation.

Sub-Project 3 involved 5 Partners and was responsible for conducting settlement and adhesion bioassays on the experimental coatings using bacteria (freshwater and marine), algae, and barnacles. The results were used in conjunction with objective **selection** criteria, to progressively down-select coatings for further development in the project.

The integration of the results of these 3 Sub-Projects was performed in a specific Integrative Work Package.

3.1.2 Milestones

Progress within this phase was monitored and regulated by 4 key Milestones:

M20-based on discussions at the Nanostructured Surfaces Workshop (month 1), decisions were taken on which nanostructuring strategies were to be adopted by Partners and working plans for the coordinated exchange of test surfaces were developed.

M30-after 18 months there was an evaluation of progress and a reprioritization of Partner strategies and funding, with the result that certain, unproductive lines of investigation were discontinued.

M40/41-after 24 and 36 months, coating candidates to enter Phase 2 were identified.

M50-the initial duration of SP1 was 36 months. After 30 months there was an evaluation of progress and an extension of support for Sub-Project 1 activities for a 4th year, for 4 Partners with the most promising technologies.

3.1.3. Achievements of Phase 1 and their impact

1 In the first 2 years of the project a total of 64 nanostructured coating designs (i.e. generic chemistries) intended for future practical application, were produced at laboratory scale and submitted for surface characterization and biological performance testing. Twenty-four of these coating candidates were down-selected for further study at the end of Year 2. The selected coatings fell into the following generic categories:

- Silicone-based nanocomposites (filled with CNTs, nanoclays and quaternised copolymers) (UMH/Nanocyl)
- Nanohybrid sol-gel coatings incorporating clay nanofillers (TNO)
- Fluorinated silicone blends and amphiphilic, nanophase-segregated blends of fluorinated polymers with silicones and other elastomers (UniPi)
- Olefinic copolymer blends and fluorinated methacrylate blends (GYTE)
- Copolymers of vinyl chloride and vinylisobutylether, and of polystyrene and butadiene, both incorporating hydrophilic or hydrophobic nanoparticles (BASF)
- Nanophase-segregating rubbery coatings based on polyphosphazenes (Polymer Labs)
- Coatings incorporating immobilised proteolytic enzymes (IPF)
- Silicone elastomers surface-modified with fluorinated groups by vapour deposition (IPF)
- Silicon oxide, and diamond-like carbon coatings deposited by vapour deposition (TEER, UNIVDUN)
- Fluorosilane electrodeposition coatings (CIDETEC)
- Hydrogel materials, including StarPEGs and PEG-methacrylates (Sustech, LiU)

Impact:

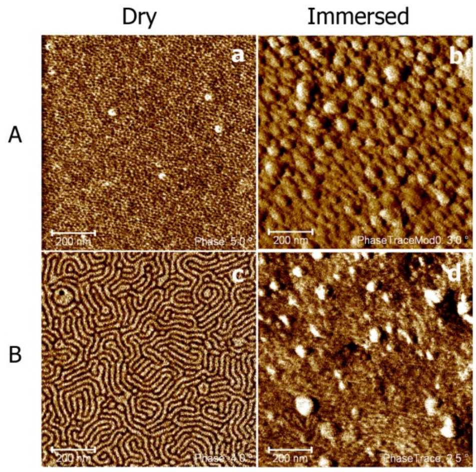
- *The relevance of a range of novel coating concepts to the design of antifouling coatings has been established and the results have been made available to the scientific community through a wide range of publications and other dissemination activities.*
- *Coatings that performed well provide a source of prototypes for practical antifouling technologies*

2 Surface nanopatterning of coatings incorporating low surface energy or amphiphilic copolymers, provides effective fouling-release coatings.

Systematic studies were performed by Partner 4 (UniPi) to improve understanding of the surface and bulk structure, composition and energetics of coatings based on random copolymers and block copolymers with different low surface energy ingredients, (perfluorinated chain segments, polysiloxane graft chains or polysiloxane blocks with amphiphilic side groups). Effective fouling-release coatings were obtained from blends of polysiloxanes with fluorinated-PDMS copolymers, their nanoscale surface segregation properties being demonstrated by angle-resolved XPS (Partner 2, INPL). More advanced coatings, showing good results in laboratory and some field tests, were obtained using amphiphilic, PEGylated-fluorinated block copolymers combined with elastomeric materials, either by depositing bilayer films on SEBS, or by blending with PDMS. AFM tapping mode imaging performed by Partner 28 (BASF) (below) illustrates the generation of well-defined nanostructures resulting from the thermodynamically induced phase segregation of the mutually incompatible components. This creates a compositionally ‘ambiguous’ character to these coatings. The images also show that the precise structure is dependent on coating composition and immersion also causes significant surface reorganization. In the Figure, coating A, with the more regular nanomorphology under water, showed the best fouling-release performance in laboratory tests at the University of Birmingham (Partner 1), while coating B, with the less regular surface nanostructure, performed less well.

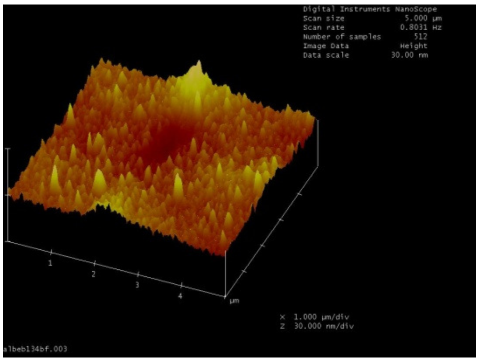
Impact:

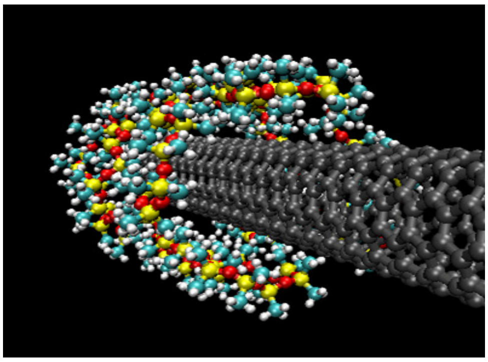
- *6 publications in refereed, international journals (#10,29,31,42,51,57)[3]*
- *Although the principle of using amphiphilic copolymers to create a complex surface that fouling organisms find it difficult to adhere to, is not new, the papers cited are the first freely-available publications to establish clear structure/property/performance relationships for such coatings.*
- *Initial exploitation of formulated coatings through a filed patent [4]*



AFM tapping mode, phase images of amphiphilic, fluorinated/PEGylated styrene-based copolymers. The left hand column shows morphologies of dry films after annealing at 120°. The right hand column shows the same coatings after immersion for 7 days in artificial seawater. The two coatings, A and B differ in the degree of polymerisation of the polystyrene (S_n) and the relative lengths of the fluorinated-PEGylated polystyrene block (Sz_m). Coating A was $S_{26}Sz_{23}$_90, and coating B was $S_{81}Sz_{19}$_90. Both coatings illustrated contained 10% by weight of SEBS in the top layer and were deposited on a pure SEBS underlayer. The scale-bars are 200 nm.

3 Controlled nanoscale roughness of novel polysiloxane nanocomposite coatings incorporating small amounts (0.05-0.1%) of multiwall carbon nanotubes made by Partners 8, UMH, and 31, Nanocyl, enhanced fouling-release performance in laboratory tests. A partial mechanistic explanation for this effect has been obtained. Dynamic molecular modelling and other studies have established that there is a strong affinity between the polysiloxane chains and the CNTs (Fig. below, right). AFM and other surface sensitive techniques have established that this changes the dynamics of surface reorganization of the PDMS chains underwater (Fig. below, left) resulting in a characteristic rugosity that enhances fouling release, although the mechanistic basis of this performance is not clear. The fouling release properties appear to be independent of any changes in bulk properties, specifically modulus. The strong affinity between the PDMS chains and CNTs is also responsible for two important properties, a) thixotropy, which influences the ease of application to a surface, and b) the CNTs are not released from the matrix, which is a significant feature in relation to any potential ecotoxicological issues associated with carbon nanotubes.





Impact:

- *These studies, detailed in 4 publications, make a seminal contribution to the growing literature on understanding the molecular level organization of nanocomposites (Papers #16,17,34,52).*

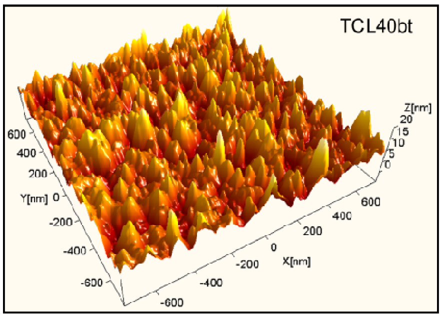
[3] Numbers #1 etc. refer to the papers in the list of refereed publications (see Appendix 1 to this report)
[4] For a list of filed patents see Section 5 of this Report

- *Patents filed* [4]
- *A premix of PDMS and pre-dispersed MWCNTs (BioCyl™) is commercially available from Partner Nanocyl. This allows for the preparation of fouling-release paints by coating manufacturers.*

4 The properties of novel nanocomposites based on CNT-filled polysiloxanes have been optimized (Partner 31, Nanocyl). Production and processing conditions have been optimized to minimize the formation of large CNT aggregates and thus to enhance the quality of dispersion of CNTs. The affinity for silicone matrices of a range of CNTs with different surface properties has been defined. Diameter, length, degree of graphitisation, morphology and specific surface area of the CNTs do not have a strong impact but, introduction of surface oxygen atoms has a major effect. Parallel surface tension measurements demonstrated that the major factor influencing the affinity for silicone is the hydrophobic character of the CNTs. The work on dispersion has been published (Publication #52)

Impact: The results improve the competitive position of Nanocyl as a supplier of different types of CNTs, and have significance for the commercialisation of nanocomposite materials based on polysiloxanes and CNTs, for biofouling and other industrial applications (e.g. flame retardency).

5 Thin, nanorough SiOx-like films (right) deposited by Partner 23 (TEER) using vapour deposition methods (PACVD), have good antifouling and fouling-release properties for bacteria and algae in laboratory tests. Structure/property/performance relationships have been partially elucidated and operating parameters controlling performance were optimised for practical application.



Impact:

- *Such thin films have not previously been explored for antifouling purposes: those produced in the project provide a source of novel prototypes for application to optical windows and heat exchangers.*
- *3 papers published in international refereed journals(Papers #22,27,61)*
- *Exploitation through a filed patent* [4] *and direct commercialisation*

6 Diamond-like carbon coatings deposited by physical vapour deposition (Partner 6, UNIVDUN) were effective in reducing bacterial attachment in laboratory tests. The interactions have been extensively modelled to determine the optimal coating parameters in terms of surface energy components, and the effect of 'doping' DLC films with silicon, nitrogen and fluorine on surface energy and fouling resistance to bacteria has been determined.

Impact:

- *Papers #28,56, 66*
- *The modelling studies contribute to understanding the design criteria for this type of coating and optimisation.*
- *The hardness, and durability of DLC thin layers suits them for application on heat exchangers where thermal transfer is important.*

7 New processing techniques using clay nanofillers have been applied to sol-gel technologies and tested for novel applications in marine antifouling (TNO). Depending on the compatibility and the shape of the nanoparticle, the coating morphology can be tuned to occur at nanometer, micrometer and intermediate levels, thus influencing biofilm formation.

Impact: Although sol-gels are an established technology, they have rarely been used for marine antifouling applications. The work in AMBIO has led to a patentable technology and a paper (Paper #62)).

8 Films with controlled topography and hydrophobicity made from polyolefinic homo- and copolymers, and fluoroacrylate-methacrylate copolymers (Partner 7, GYTE) showed fouling-release properties against soft-fouling species in laboratory tests. An interesting correlation was obtained between contact angle hysteresis and the adhesion strength of *Ulva*, a soft-fouling alga: coatings with high hysteresis reduced adhesion strength.

Impact: Such materials have not been investigated for antifouling applications before and this class of materials deserves further study: their potential within the AMBIO project was limited by their poor fouling-release properties against hard-fouling organisms such as barnacles. The relationship between high contact angle hysteresis and reduced adhesion strength is a novel observation and contradicts previous dogma in the literature.

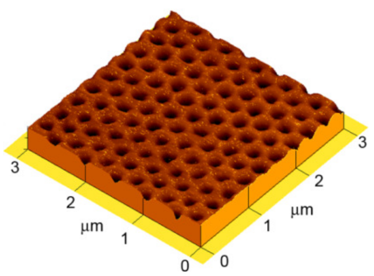
9 Thin, hydrophobic fluorosilane layers electro-deposited over suitably prepared metal substrates with specific nanoroughness characteristics (Partner 9, CIDETEC), show good antifouling and fouling-release properties against bacteria in laboratory tests.

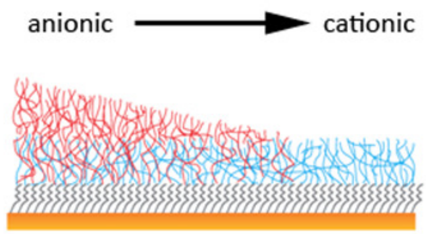
Impact: The relevance of these surfaces to the control of biofouling is limited by their relatively poor resistance to macrofouling species. However, their effectiveness against bacteria, plus their high thermal transfer suits them for application on heat exchangers. Further investigation for applications in other areas, e.g. in the biomedical and food processing areas is also warranted.

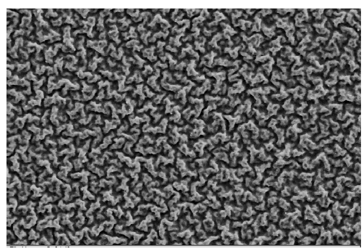
10 Two analytical reviews of the chemical and physical settlement cues presented by the nanoscale properties of a surface were published (Paper #12 and Callow and Callow[5])

Impact: In order to design environmentally benign, non-fouling and/or fouling release coatings on a rational basis, design rules need to be developed which define the material properties that have to be fulfilled for an antifouling or a fouling release coating. Such knowledge acquisition relating to fundamental physical and chemical phenomena requires the study of biofouling on model surfaces with systematically varying properties. These reviews contribute to the conceptual framework for further studies on settlement cues used by fouling organisms and were important in guiding the work outlined in Item 11.

11 The sensitivity of marine fouling organisms to surface topography, wettability, lubricity, charge and hydration has been established through the use of a wide range of well-characterised model systems prepared by Partners UHEI, LIU, IPF. The surfaces were created from self-assembled monolayers, polyelectrolyte multilayers, bioinspired polymer brushes and other covalently-coupled surface films,and gradient surfaces that vary systematically in such physico-chemical properties. Bioassays of performance were conducted by Partners UoB, TNO, UNEW.







[5] JA Callow and ME Callow (2010) Nano- and micro-structured polymer surfaces for the control of marine biofouling. In: Arzt, E and del Campo, A. Eds. Generating micro/nanopatterns on polymeric surfaces. Wiley.

Images of some of the model surfaces created in AMBIO; left, polymer brush bioinspired 'honeycomb' structures created by chemical photolithography (UHEI). Centre, hydrogel charge gradients (LIU). Right, hiererchical, self-assembled polyelectrolyte multilayers (UHEI)

Impact:

- *Taken together this substantial body of work constitutes an advance in fundamental understanding of the importance of surface nanoscale cues in influencing the settlement behaviour of fouling organisms. This is relevant to the development of design rules that define the most important materials properties required for a new generation of antifouling fouling-release coatings.*
- *The results are represented by 13 papers (#1,9,18,19, 20,33,37,38,45,47,64,69,70)*

12 A specific example of the effects observed, comes from studies between UHEI and UoB on the influence of interfacial hydration properties (Papers #18, 45, 69, 70). SAMs were formed from oligoethylene glycols of different chain length, and polyethylene glycol brushes. All surfaces had similar wettability (approx. 30^{o}) but dramatic differences in settlement of spores of the green alga *Ulva* were seen, PEG being totally repellent to spore settlement. These differences can be ascribed to the different hydration energies of oligoEGs and the steric repulsion of loosely packed PEG chains forming a diffuse interface. Further discussion of this is presented as a review in Paper 70.)

Impact: This work on oligo- and poly(ethylene glycol) (OEG and PEG) functionalized surface films is important for 4 reasons: a) experiments on spore settlement on OEG and PEG coatings help to understand the mechanism of non-fouling of highly hydrated interfaces; b) these studies defy the common assumption that surface wettability—as measured by water contact angles—is an unambiguous and predictive tool to determine the fouling behavior on the surface; c) this system is a good example for ''interfacial systems chemistry'' since it connects the behaviour of unicellular marine organisms with the antifouling properties of a hydrated surface coating with structural and electronic properties as derived from ab initio *quantum mechanical calculations using the electronic wave functions of oxygen, hydrogen, and carbon; d) although OEG and PEG per se are not an appropriate material for a durable marine coating, incorporation of these functionalities is of interest and the basis of attempts to develop amphiphilic or 'ambiguous' coatings.*

13 Proof of principle has been obtained for bioactive nanocoatings containing adhesive-degrading enzymes. Many marine fouling species use proteins and glycoprotein polymers to attach to surfaces. The project has successfully explored strategies for the use of immobilized proteolytic enzymes to prevent marine biofouling by hydrolyzing these adhesive proteins. The enzyme-containing coatings showed very promising antifouling properties by reducing the settlement and the adhesion strength of spores of *Ulva linza*, the adhesion strength of diatom cells and the settlement of barnacle larvae.

Impact:

- *This demonstration providers a sound basis for further applied work on enzyme-containing coatings.*
- *Papers #24,25*

14 Novel strategies to graft maleic anhydride (MA) copolymer films onto poly(dimethylsiloxane) (PDMS) precoatings have been developed by Partner 14 (IPF).

Impact:

- *The results show that the impact of the plasma treatment on the physical properties on the topmost surface of the PDMS is critically important for the characteristics of the layered coatings. Coatings which combine the advantageous bulk properties of polymeric materials with surface-selective chemical conversions, are required in numerous advanced technologies.*
- *Paper #26*

15 Several novel nanofabrication methods have been developed by UHEI (Partner 15) that collectively enhance the range of technologies that may be used to create defined surface structures at nano- and

micro-scales. Examples include: a) a novel method based on carbon templating for producing structured polymer brushes of controlled nanomorphology, without the need for time-consuming and complex surface chemical initiation (Paper #44); b) A novel form of chemical photolithography combining surface-initiated polymerization (SIP) with electron-beam chemical lithography (EBCL), which enables the fabrication of full-coverage 3D polymer brush nanostructures of variable shape and pattern (Papers #18,19), c) a novel method for producing tunable, hierarchical self-assembled micro- and nano-structured surfaces from pH-amplified polyelectrolyte multilayers (Papers #39, 64).

Impact:

- *SIP-ECBL and carbon templating constitute advances in the technology for generating nanostructured surfaces with sophisticated properties for research purposes (e.g. antifouling research) and will find utility in industrial applications such as optical sensor devices and microfluidics.*
- *9 papers in refereed journals (# 6,7,18,19,39,40,44,64,65)*

16 A novel hydrogel coating (PEG-methacrylate) has been developed by Partner 10 (LIU)and tested against a range of marine organisms in controlled laboratory assays, raft trials and end-user trials. The same polymer has also been used in a novel method for producing a biosensing gradient matrix.

Impact:

- *Although the coating did not provide good performance in field tests (probably due to insufficient robustness), the proof-of-principle that hydrogels have good intrinsic antifouling properties is established by this work.*
- *The hydrogel contributes beneficial physical properties to cast membranes for water treatment, which has commercial potential*
- *Because of the protein-resistance properties of PEG the hydrogel gradient matrix can be used as a template to evaluate non-specific binding events to prototype protein microarray sensors*
- *4 Papers in international refereed journals (#20,36,37,60)*

17 Novel thermoresponsive hydrogel polymer films based on copolymers of poly(*N*-isopropylacrylamide) (PNIPAAm) and N-(1-phenylethyl) acrylamide have been developed (Partner 14, IPF). Aspects of their mode of action have been elucidated through electrokinetic methods (Paper #32) and their performance against fouling organisms was tested (Paper #50).

Impact: Although these particular hydrogels were not found to be effective for marine antifouling, coatings based on thermoresponsive ('smart') hydrogels remain important in the biomedical field and this background study on a novel copolymer hydrogel contributes to the understanding of the mechanisms by which such coatings act. Furthermore, the methodology provides a tool for unravelling electrohydrodynamic phenomena at composite interfaces formed between hard surface and soft polymer coatings in cutting edge technologies as, for example, in micro- and nanofluidics.

18 Novel, chemically-modified nanoclays have been developed, and are commercially available (Laviosa)

Impact: Although these nanoclays did not enhance the fouling-release properties of experimental nanocomposites produced within AMBIO, they provide a commercial source of novel materials for other types of application in the nanocomposite industry.

19 Novel methods have been developed by the TECHNION for characterising wettability properties of surfaces and nanomaterials. A theory-based, alternative approach to those currently used for measuring the surface tension of complex, heterogeneous surfaces has been developed. The novelty in this approach comprises experimental aspects (horizontal vibrations system to measure the most stable contact angle concept) as well as theoretical aspects (new equation for the interpretation of contact angle data). In addition, a method has been developed for determining the surface energy of nano-particles, based on assessing the floatability of the particles on the interfaces of liquid mixtures of

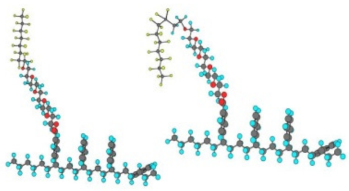
different surface tensions.

Impact:

- *Novel methods for surface characterisation by surface tension assessment enable testing of the possible correlation between biofouling and surface energetics, and contribute towards an improved understanding of the functional properties of nanomaterials and their application.*
- *1 paper published (Papers #53) plus 3 more in preparation*

20 Evidence for the reorganisation of the surface architecture of specific coating types after immersion has been published for several coating designs through the use of state-of-the-art, in situ surface characterisation tools such as environmental AFM, near-edge X-ray fine absorption structure (NEXAFS) and angle-resolved XPS (see also item 2 above).

For example, unequivocal evidence of surface reconstruction of the S-Zon side chains in amphiphilic coatings produced by Partner 4, UniPi was obtained by NEXAFS (schematic right). Reconstruction of the film surface underwater occurs as the hydrophilic CH_2CH_2O segments become more exposed to the outer surface, whereas the hydrophobic CF_2CF_2 segments are buried in the inner surface of the wet films.



Impact:

- *Many coating designs, such as those based on copolymer blends and amphiphilic polymers, undergo reorganisation under water. Antifouling/fouling-release coatings have to function in aquatic environments. Therefore to understand how they work it is important to know how their surface properties change after immersion since these are what the fouling organisms will be sensing.*
- *Papers #10,29,30,34,42,51,57*

21 Novel nanoporous monolayers with a range of length scales and controlled wettability characteristics have been developed using thiocholesterol self-assembled monolayers 'backfilled' with mercaptoundecanoic acid (Partner 10, LIU). These biocomponent SAMs have been used by Partner 32 (TECHNION) to test wetting theory and hypotheses on the influence of surface nanostructure on wettability. The method and results are published in Paper #48.

Impact:

- *Mixed SAM surfaces are used in many applications, e.g. to control biomaterials adhesion, fabrication of biochemical sensors.*
- *The measurement of surface wettability is important for the characterisation of surfaces and there is much debate on the appropriateness of various methods, the relevance of various predictive model equations, and the length scales at which surface heterogeneities may exert an influence. The published work contributes to this debate. Specifically the use of these novel nanosurfaces has demonstrated that:*
    - *measurements of stable contact angles correlate well with those predicted by the Cassie equation.*
    - *measurements of contact angle hysteresis can be used to characterise surfaces with compositional heterogeneity at the nanoscale.*

22 Theoretical analyses of the phenomenon of superhydrophobicity and its relevance underwater have been published and considerations of design optimisation established. Furthermore, a thermodynamic analysis of the conditions needed to establish superhydrophobic surfaces from low contact angle materials has been published (Partner 32: Technion).

Impact: in the development of antifouling coatings there is much interest in superhydrophobic coatings incorporating roughness since minimising the wetted area of immersed surfaces may reduce drag and the rate of biofouling. However, the conditions under which different wetting regimes may occur are controversial and not well-understood. Furthermore, it has been questioned whether superhydrophobicity is a stable condition under water. The thermodynamic analysis presented in paper #2 formulates the equilibrium stability conditions necessary to define superhydrophobicity underwater, and demonstrates that only roughness topographies that conform to a specific feasibility condition can support superhydrophobicity under water. Even then, the high contact-angle state may not be stable, and transition from the heterogeneous (Cassie-Baxter) wetting regime to the homogeneous (Wenzel) regime with a lower contact angle may occur. In addition, some generic design optimisation criteria are established. Paper #3 discusses the implications of this theory to biofouling. Furthermore, an important practical as well as fundamental question is whether superhydrophobic surfaces can be made from hydrophilic materials. This question is thermodynamically studied in paper #15, where the conditions under which this goal can be achieved are formulated.

23 Novel methods for characterising the structure, periodicity and unit cell size of irregular self-assembled topographies (in this case polyelectrolyte multilayers) have been established using 2D Fourier transform image analysis (Partner 15, Paper #64).

Impact: 'Top-down' nanostructuring techniques, such as various forms of lithography, reveal a high degree of symmetry, which makes their description (e.g. size of structure, periodicity, dimension of the unit cell) straightforward. The description and classification of natural structures or self assembled systems is much more difficult. The approach described enables classification of such self-assembled nanostructures.

24 Surface charge properties of the spores of *Ulva* have been established through the use of optical tweezers and electrets (Paper #41)

Impact: It is important to know the surface charge properties of marine organisms in order to interpret the influence of coating charge on antifouling performance.

25 Laboratory assay protocols with freshwater and marine bacteria, algae and barnacles were developed in order to provide data to enable the down-selection of coatings for more detailed study and development. During Phase 1, 64 generic coating types were tested, represented by 29,630 individual assays: 548 reports were sent to the coating originators.

Impact: Laboratory based assays, under controlled challenge and conditions, properly replicated and with a representative range of fouling organisms, provide a rapid, detailed and iterative evaluation of the intrinsic antifouling and fouling release properties of test coatings and thus permit the downs-selection of candidate coatings for subsequent field tests.

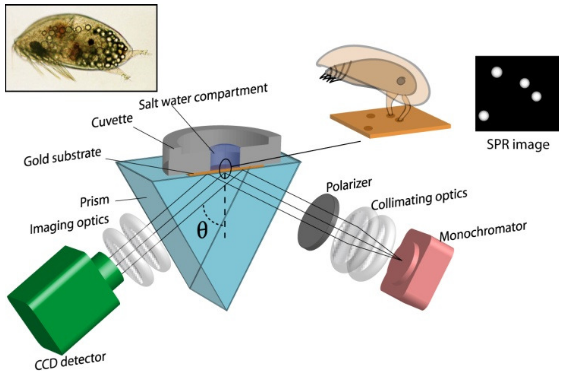
26 Novel bioassay methods have been developed for the evaluation of coating performance, including: a) automated apparatus to measure adhesion strength of barnacles (UNEW, Paper #11), (b) a flow channel to measure strength of attachment of settled barnacle larvae by hydrodynamic methods (UNEW), (c) bacterial adhesion assays (TNO, Paper #49).

Impact: The new competencies enhance European capabilities for quantifying adhesion of organisms to test substrates.

27 The novel application of digital holography to study the 4-D behaviour of algal spores in response to different surfaces has been established. The studies required the development of novel software to reconstruct thousands of holograms automatically (Papers #8,43).

Impact: The cited publications provide the first demonstration that spores of Ulva *can respond to surface chemistry without physical contact being made. This finding is fundamental to understanding how cells/organisms locate sites for settlement. A transportable version of the* *microscope has been developed to allow in situ, field observations in future work.*

28 Advanced physical imaging technologies (Imaging Surface Plasmon Resonance (right) and Confocal Raman microscopy) and have been applied to the *in situ* and real time analysis of cement deposition of barnacle cypris larvae. Under iSPR, footprints of cyprid temporary adhesive were imaged on coatings. The technique enabled the amount of proteinaceous adhesive to be quantified and compared between different coating chemistries. Under Raman microscopy, images for characteristic chemical functional groups were obtained. In addition to showing the morphology of the attachment apparatus, the images provided information on chemical composition, in particular the hydration state of the cement. These novel applications demonstrate the potential of this method for *in situ* studies of adhesion at the micro-scale (Papers #46, 54)



Impact: Barnacles are a model for research on permanent underwater adhesion and the wider process of marine biofouling. A detailed understanding of the adhesives secreted by the cypris larva for exploration and eventual permanent settlement, has potential to lead to novel antifouling solutions. It is envisaged that these techniques may be applicable to the colonisation stages of other fouling species.

29 Partner 6 (UNIVDUN) used the extended DLVO theory to derive a theoretical optimum surface energy of ~20 mN/m for coatings with minimal attachment of bacteria (Paper 5). Subsequent experimental observations with several different types of coatings (doped DLC, SiOx-like, metal-polymer composites), have supported the this theoretical analysis (Papers 22,27,28). Bacterial adhesion strength can also be modeled in terms of the work of adhesion ΔF_{Adh} which is derived from the individual polar and dispersive components of surface energy. Thermodynamically adhesion should be favoured if it results in a lowering of total energy of the system, i.e. ΔF_{Adh} becoming negative. Therefore bacterial adhesion strength should decrease if ΔF_{Adh} increases. Zhao et al. (Paper 28) estimated the polar and dispersive components of surface energy for Si- and N-doped DLC coatings and showed that bacterial adhesion strength decreased with increasing work of adhesion, which is consistent with thermodynamic theory. There was also a strong strong relationship between the polar components of surface energy ($\gamma+$, electron-accepting; $\gamma-$, electron-donating). At higher electron-donor values surfaces are more negatively charged and thus would be expected to repel negatively charged bacteria, leading to higher rates of removal.

Impact:

- *4 published papers*
- *Theoretical models have predictive value in developing new coatings to resist bacterial attachment*

30 Fundamental studies of the effects of surface texture on the selection of surface by barnacle larvae have established that attachment strength is a key factor in surface selection (Partner 11, UNEW)

Impact: the published paper (Paper #63) provides the first evidence of the link between settlement preferences and susceptibility to removal by force implying an adaptive response to select surfaces on which adhesion will be most tenacious.

3.2 Phase 2: 'Development'

Phase 2 of the project mainly operated in Years 3 and 4 with a short extension into Period 5 and was concerned with a single Sub-Project, SP4, 'Development of Nanostructured Coatings and Surfaces'. The primary goal was to fully realize the potential of materials developed within Phase 1, providing a link between the fundamental part of the project and the field trial and end-use demonstrations in Phase 3. It enabled the formulation of selected practical coating prototypes at a scale appropriate to the final trials and end-user evaluations.

3.2.1 Technical Operation

In order to scale up promising experimental coating concepts and develop them into practical nano-structured coatings and surfaces a broad spectrum of scientific and technological expertise was required, which is reflected in the composition of the 14 partners primarily involved: in synthesis and scale-up of monomers/polymers (Partners 13 (POLYMER), 20 (ARGUS), and 28 (BASF)); in coating development and evaluation (Partners 3 (TNO), 5 (Akzo-Nobel), 17 (Zenon), 19 (CTO) and 23 (TEER), and in large scale production of nanomaterials (Partner 31 Nanocyl and 22 Laviosa). They were supported by partners with specialist expertise: Partner 4 (UniPi, self-organised polymers), 8 (UMH, nanocomposites), 6,9 (UNIVDUN, CIDETEC, thin coating deposition). The involvement of material producers and formulators provided a real industrial perspective. The ability to produce nano-coatings on an industrial scale while retaining the desired antifouling properties is absolutely critical in enabling solutions to the problem of biofouling in real-world applications.

Right: a 50 litre reactor used to produce kg quantities of copolymers (Argus).

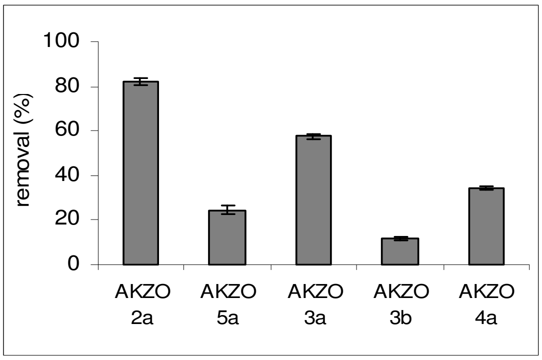
3.2.2 Milestones

M60/61-at months 36 and 48, coating candidates to enter Phase 3 were identified.

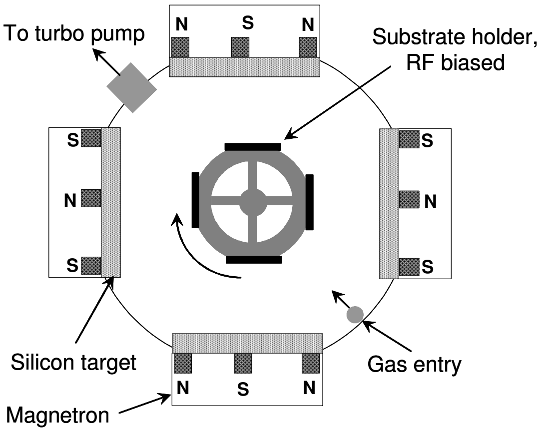
3.2.3. Achievements of Phase 2 and their anticipated impact

A total of 15 novel coating concepts from the experimental scale studies in Sub-Project 1, were successfully re-formulated and scaled-up to a level where they could be tested in field and end-user trials. Depending on the coating type**, critical coating properties** such as film-forming, stability, surface uniformity, surface tension, friction coefficient, wear resistance and roughness were studied and improved. **Accelerated ageing tests** were performed on appropriate coatings and **coating adhesion** parameters were assessed for substrates that are relevant to end-uses, e.g. glass, aluminium, stainless steel, primers, and nylon. In some cases appropriate tie-coat systems were evaluated. Suitable **application methods** for different end-uses were also established.

Some of the results of this formulation phase of the project are shown below:



In Phase 2, experimental coatings were reformulated to facilitate their application in field tests. The reformulated coatings were checked to ensure retention of original properties, using laboratory bioassays. The graph (left) illustrates the impact of reformulating the CNT-filled silicone coatings in terms of their fouling-release performance against Ulva. All coatings contained 0.05% CNTs but differed in respect of a) grade of CNTs, b) dispersion speed, c) solvent used. Data from UoB.



SiOx-like coatings deposited by PACVD were shown in Phase 1 to have good fouling-resistant properties, and were extensively field-tested. However, their adhesion to some substrates was poor, necessitating special tie-coats, and their mechanical properties were such as to to render them less useful for industrial applications where high durability is required. In an attempt to improve mechanical properties, ideally without reducing antifouling properties, during the formulation Phase Partner 23 (Teer) investigated the potential for ‘hybrid’ coatings, with higher levels of silicon, deposited by a combination of plasma polymerisation and magnetron sputtering. Hybrid coatings showed much better scratch and wear resistance than PACVD coatings whilst maintaining relatively high fouling-release performance against freshwater bacteria (Paper #61).

*Impact: This phase of the project was critical to the transition between ‘Research’ and ‘Development’ phases of the project. It enabled selected experimental-scale coating **concepts** to be translated into industrially-applicable formulations at a scale and quality (robustness etc.) to satisfy specific requirements of different end-users.*

3.3 Phase 3: ‘Exploitation

This Phase of the project was operated in Years 4 and 5 and contained both RTD and Demonstration Activities, organized within a single Sub-Project, SP5 Field Testing and End-User Trials. The Demonstration Activities were considered to be a logical part of Sub-Project 5 rather than being a separate Sub-Project, because they represent the culmination of a progressive approach towards evaluation of candidate coatings rather than a separate activity in their own right. The main objectives of the Sub-Project were:

- To make a quantitative and comparative evaluation of the antifouling efficacy of promising nanostructured technologies developed in SP4, through controlled field-scale testing.
- To determine the hydrodynamic drag characteristics of promising coating technologies developed for dynamic end-uses.
- To perform a range of Demonstration Activities in which coating prototypes were tested in appropriate “real-world” trials appropriate for each end-use application (ship and hull coatings, aquaculture systems, power plant inlets, heat exchangers, membrane filters, oceanographic instruments).

3.3.1 Technical Operation

Eight partners provided capabilities and evaluations for field-tests and end-user trials in specific sectors.

Partner 5 (AKZO) was responsible for marine and freshwater raft panel testing in the UK, Singapore and Sweden. AKZO also conducted some small-scale fish-net tests and end-user trials on pleasure craft in Hartlepool Marina, UK.

Partner 17, ZENON, conducted pilot plant and full operational scale testing on membrane filtration equipment.

Partner 24 (Wallenius), in conjunction with AKZO, performed patch testing on operational ocean-going vessels.

Partner 25 (KEMA) provided test facilities for heat exchanger tests and organized trials on operating installations in the Netherlands. KEMA, in conjunction with AKZO, also organized and monitored testing on power station inlets.

Partner 27 (OCN) carried out field testing on oceanographic instruments in Trondheim Fjord, and an end-user tests on an operational monitoring facility in Greece.

Partner 29 (VAL VGS) was responsible for field and end-user tests on fish-nets in Norway.

These partners also constituted the End-Users Reference Group (EURG), which played a key role throughout the project by providing a practical, end-user frame of reference for the coating developers. Specifically they designed the ‘EURG Matrix’ a compendium of the various requirements that need to be satisfied for practical, commercial coatings in the different end-user applications.

Impact: This is the first, publically funded, systematic evaluation of the field performance of a range of novel, non-biocidal, nanostructured coatings developed for antifouling applications in aquatic environments. The results from these evaluations contributed towards the incentive to patent some of the most promising coatings and eventual commercialization. It must also be remembered that all the coatings in this phase of the project were tested because they showed good performance in laboratory-scale assays. Even in those cases where coatings failed to perform well in field- and operational scale tests, the results are important in that they help to identify where improvements in coating design and formulation are necessary.

Evaluation of hydrodynamic performance of selected coatings

In addition to field testing activities, Sub-Project 5 evaluated hydrodynamic drag properties of candidate coatings through Partners 11 (UNEW) and 9 (CTO). Tests with axisymmetric bodies and flat plates demonstrated that nanostructured, condensation-cured silicone coatings containing amphiphilic fluorinated-PEGylated copolymer showed low frictional drag characteristics compared with commercial fouling-release coatings. Tests with coated propellers showed that the nanohybrid sol-gel coating (TNO8) gave a 4% increase in propeller thrust and hence efficiency compared with a reference coating.

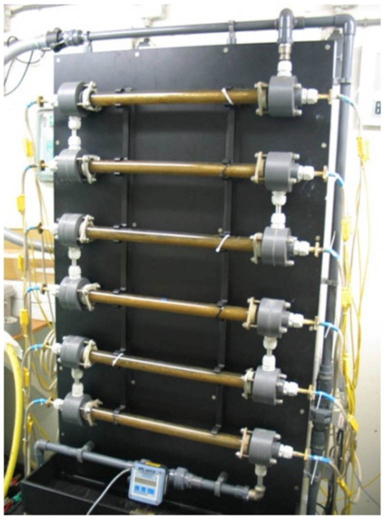
> *Impact: this is the first time that nanostructured coatings intended for marine applications have been subjected to thorough hydrodynamic evaluation. Reduced hydrodynamic drag is an important characteristic of coatings intended for commercial application to ship hulls. A 4% increase in propeller efficiency would generate significant savings in fuel consumption. Furthermore, the TNO sol-gel coating can be applied as a thin (<50 μm) coating, which could be important for maintaining the desired level of surface finish on a propeller*

Evaluation of field performance

The evaluation of field performance of coatings is a complex matter that has to encompass issues of a) the complexity of natural fouling communities and how this can be quantified; b) seasonal and geographic variation in fouling pressures; c) statistical considerations for producing robust data; d) for fouling-release coatings the activity of the vessel is important; static vessels, or those which are used infrequently and/or which never achieve speeds high enough to detach fouling organisms, may not demonstrate their full potential. In practice, in a commercial organization, the testing of prototype coatings involves trials over several years, different seasons, and in several different locations. Within the scope of AMBIO such a comprehensive evaluation was impossible; the test that were conducted therefore provide a 'snapshot' of potential performance that can be used to guide future more comprehensive evaluations.

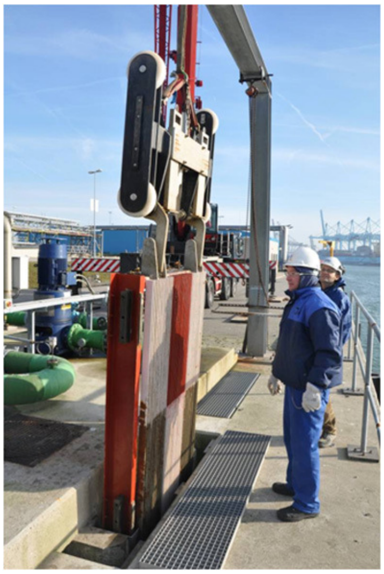
Some images of AMBIO 'field' and end-user test methods

Heat exchanger module and an individual coated plate (KEMA)



Testing of thermal transfer properties of coatings using TestRig apparatus (KEMA)

Panel testing from rafts (AKZO)



Inserting a coated trash rack into a power plant (KEMA)

Testing of fouling release coating performance by jetwash (AKZO)

Coated transmissometers ready for immersion (OCN)

Coating a yacht with test paint (AKZO)

Testing of coatings on fish net samples (VAL)

3.3.2 Milestones

M70-from month 48 onwards coating candidates for the Demonstration Activity were progressively identified.

3.3.3 Achievements of Phase 3 and their anticipated impact

The following coatings were evaluated through initial field tests. Those that showed sufficiently good performance to pass Milestone M30 were then tested in the Demonstration Activity.

Coating	Field tests	Demonstration Activity
Amphiphilic, nanophase-segregated blends of fluorinated polymers with silicones (UniPi/AKZO)	Raft panels (marine), fish nets, instrument casings	Patches on ship and pleasure craft hulls, instrument casings, fish nets, power station inlets
Amphiphilic, nanophase-segregated blends of fluorinated polymers with styrene-ethylene-butadiene (UniPi/AKZO)	Raft panels (marine and freshwater)	Not selected
Hydrosilation-cured silicone nanocomposites filled with CNTs and quaternised copolymers (UMH/Nanocyl/AKZO)	Raft panels (marine), fish nets, instrument casings	Not selected
Condensation-cured silicone nanocomposites filled with CNTs and quaternised copolymers (UMH/Nanocyl/AKZO)	Not tested	Patches on pleasure craft hulls and fish nets
Nanohybrid sol-gel coatings (TNO)	Raft panels (NiBrAl) and optical windows	Heat exchangers
Olefinic copolymer blends and fluorinated methacrylate blends (GYTE)	Raft panels (marine and freshwater), fish nets	Not selected
Copolymers of polystyrene and butadiene (BASF)	Fish nets	Not selected
Silicon oxide deposited by vapour deposition (TEER)	Heat exchangers and optical windows	Optical windows and heat exchangers
Diamond-like carbon coatings deposited by vapour deposition (UNIVDUN, TEER)	Heat exchangers	Heat exchangers
Fluorosilane electrodeposition coatings (CIDETEC)	Heat exchangers and optical windows	Heat exchangers
Hydrogel materials based on PEG-methacrylates (LiU/Polymer Labs)	Raft panels (freshwater), instrument casings, additive to filtration membranes	Filtration membranes
Hydrogel materials based on Star PEGs	Tested as additive to filtration membranes	Filtration membranes

Testing Partners	Demonstration Activity Test Regime
AKZO	Test patches on 5 pleasure craft in Hartlepool Marina, UK; 7 months Coating of magnetic panels for ship test patching
VAL	Trials on 2m^2 fish nets in Torland, Norway, 8 months
KEMA	Trials of coatings applied to heat exchanger panels in NUON power station, Amsterdam, 3 months Trials of coatings on trash racks at Loders/Corklaan (Holland), 4 months
OCN	Tests of optical window coating on operational marine monitoring buoy in Greece, 10 weeks
Zenon	Trials of membrane modifying materials in production plants
Wallenius/AKZO	Magnetic coated test panels applied to 2 car carriers, November 2009

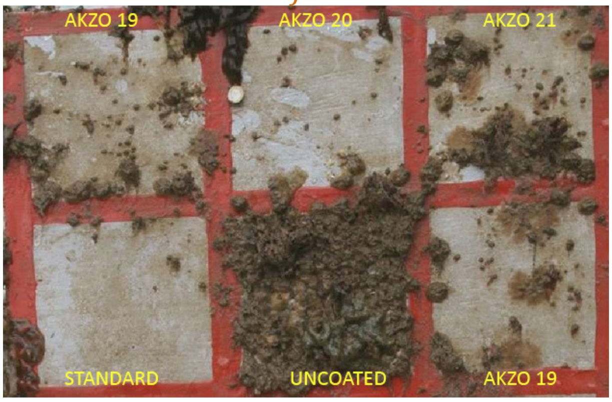
3.3.4 Summary of coating prototype performance and impact:

Coating Prototype	Application	Technical Performance	Exploitation Plans	Environmental issues	Economics	Remarks
Nanophase-segregated blends of fluorinated amphiphilic polymers with silicones (UniPi/AKZO)	Hull coatings, Fish nets, Power inlets Instrument casings	Good performance in laboratory and in field tests (comparable to commercial standards in all test regimes): ○ panels, up to 7 months in 3 locations ○ nets, up to 8 months ○ canisters, 5 weeks ○ Trash racks/power inlets, 4 months ○ Yacht test patches, 7 months Good hydrodynamic performance (low skin friction coefficients)	Patent filed by AKZO (Section 5). Continued work to formulate a commercially relevant coating to be carried out by AKZO.	The perfluoroctyl component of the fluorinated/PEGylated copolymer will soon become unavailable due to concerns over bioaccumulation	Cost likely to be comparable to premium commercial fouling-release coatings incorporating fluoropolymers	Some reformulation work required to replace perfluoroctyl (C8)
Condensation-cured silicone nanocomposites filled with CNTs (UMH/Nanocyl/AKZO)	Hull coatings, Fish nets, Power inlets	Good performance in laboratory tests but performance worse than commercial standards in all field test regimes.	Patent filed (Section 5). Predispersion of CNTs in silicone (Biocyl™) commercially available	Risk assessment must eventually address potential environmental concerns over CNTs	Cost likely to be comparable to premium commercial silicone-based fouling-release coatings	Require further development work to solve problems of coating formulation, application and consistency
Condensation-cured silicone nanocomposites filled with quaternised copolymers (UMH/Nanocyl/AKZO)	Hull coatings, Fish nets, Power inlets	Good performance in laboratory tests but performance worse than commercial standards in all field test regimes	Limited opportunity for immediate exploitation	Quaternised component may be an issue under the Biocidal Products Directive	Cost likely to be comparable to premium commercial silicone-based fouling-release coatings	Require further development work to solve problems of coating formulation, application and consistency
Silicon oxide-like coatings deposited by vapour deposition (TEER)	Optical windows	Good performance against bacteria and algae in laboratory tests. Field performance on optical windows was good (5-10 weeks immersion).	Patent filed (Section 5) Available now as commercial coating for optical windows.	None known	Commercial, cost-effective production of coated windows is possible (€20 per	

					window). Cost-benefit analysis suggests 50% savings on maintenance costs if adopted.	
Silicon oxide-like coatings deposited by vapour deposition (TEER)	Heat exchangers	For heat exchanger applications the durability and heat transfer properties were good, but no significant effect on fouling release properties	Patent filed (Section 5)	None known	Cost of the order €550/m^2	Scale-up of process required for application to commercial heat exchangers. More durable formulations now available. Alternative advantages foreseen in increased lifetime/corrosion protection and use of less noble materials for heat exchanger manufacture, but will require 5-10 years 'proof of principle' before commercialisation contemplated
Diamond-like carbon coatings doped with Si and N, deposited by vapour deposition (UNIVDUN, TEER)	Heat exchangers	Good performance against bacterial biofilm formation in laboratory tests. Passed durability test and showed good thermal transfer properties. Biofouling was not reduced in the field tests.	Available in principle as commercial coatings for heat exchanger manufacture.	None known	Costs of the order €550/ m^2	Scale-up of process required for application to commercial heat exchangers. More durable formulations now available. Alternative advantages foreseen in increased lifetime/corrosion protection and use of less noble materials for heat exchanger manufacture, but will require 5-10 years 'proof of principle' before commercialisation contemplated
Fluorosilane electrodeposition coatings (CIDETEC)	Heat exchangers	Good performance against bacterial biofilm formation in laboratory tests. Showed good thermal transfer properties but biofouling was not reduced in the field tests.		None known	Material and process costs low	Scale-up of process required for application to commercial heat exchangers. More durable formulations now available. Alternative advantages

						foreseen in increased lifetime/corrosion protection and use of less noble materials for heat exchanger manufacture, but will require 5-10 years 'proof of principle' before commercialisation contemplated
Nanohybrid sol-gel coatings (TNO)	Propellers Optical windows Heat exchangers	Good performance against biofilm formation in lab. tests. Performed well on static NiBrAl raft panels (39 weeks), comparable to commercial standard. 4% increase in propeller efficiency in hydrodynamic tests. Moderate field performance on optical windows. Showed good thermal transfer properties but biofouling was not reduced in the field tests.	Patent filed. Has potential for commercial application to propellers by manufacturers.	None known	Material and process costs low	Operational trials required on propellers
Hydrogel materials based on PEG-methacrylates as membrane additive (Zenon/Polymer Labs)	Membrane filtration	No improved biofouling performance and anticipated benefits to physical performance of membranes were not realized in Demonstration Activity	No direct exploitation anticipated in view of limited improvements in performance	No environmental implications	No anticipated benefits	
Hydrogel materials based on Star PEGs as membrane additive (Zenon)	Membrane filtration	No improved biofouling performance and anticipated benefits to physical performance of membranes were not realized in Demonstration Activity	No direct exploitation anticipated in view of limited improvements in performance	No environmental implications	No anticipated benefits	

Some selected Results from the Field Tests and Demonstration Activity



In field tests of coated panels on rafts in Sweden, the amphiphilic coating incorporating zonyl-acrylate in silicone (top centre) performed as well as the commercial standard (Intersleek 900, bottom left) after 18 weeks immersion. The uncoated control panel (bottom centre) shows heavy fouling (International Paint).

Condition of instrument canisters after 5 weeks immersion.The front and rear assemblies were coated with the amphiphilic zonyl acrylate/silicone blend coating; the centre instrument was uncoated and is covered by an extensive growth of mussels and brown seaweed.

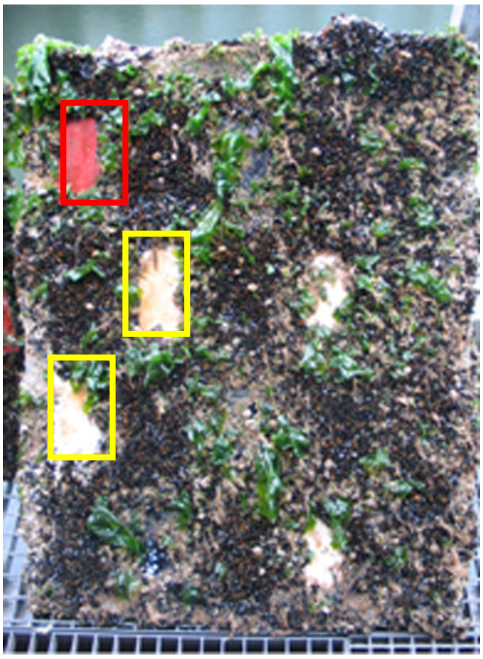
Before hosing

After hosing

Amphiphilic coating with 1% copolymer

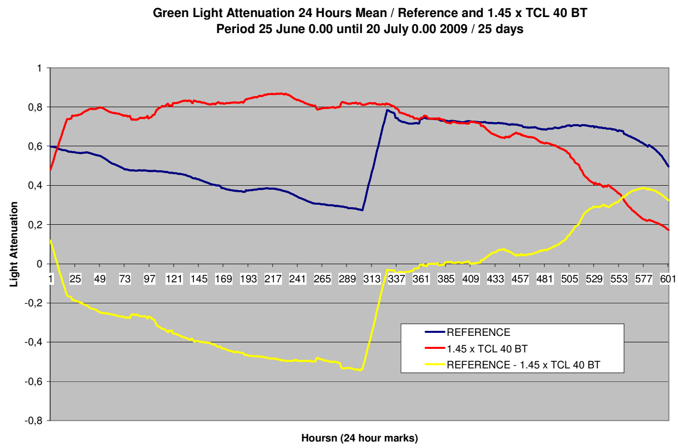
Uncoated control

In fish net trials conducted by Partner 29 (VAL), after 31 weeks immersion the nets were extensively fouled but after hosing the fouling was almost totally removed from nets coated with amphiphilic zonyl acrylate copolymer coatings (UniPi/AKZO), a performance comparable to nets coated with the commercial Intersleek 900 standard. Uncoated nets were still extensively fouled after washing (see images above).



Above: Stainless steel panels with test coatings immersed at a power station inlet, after 2 months. Performance of the amphiphilic coating (UniPi/AKZO, yellow boxes) is comparable to the Intersleek 900 commercial standard (red box).(image fromKEMA)

Above: top imge shows fouling of optical window after 5 weeks immersion. Bottom image shows reduced fouling of optical window coated with TEER's SiOx-like coating, after 7 weeks immersion

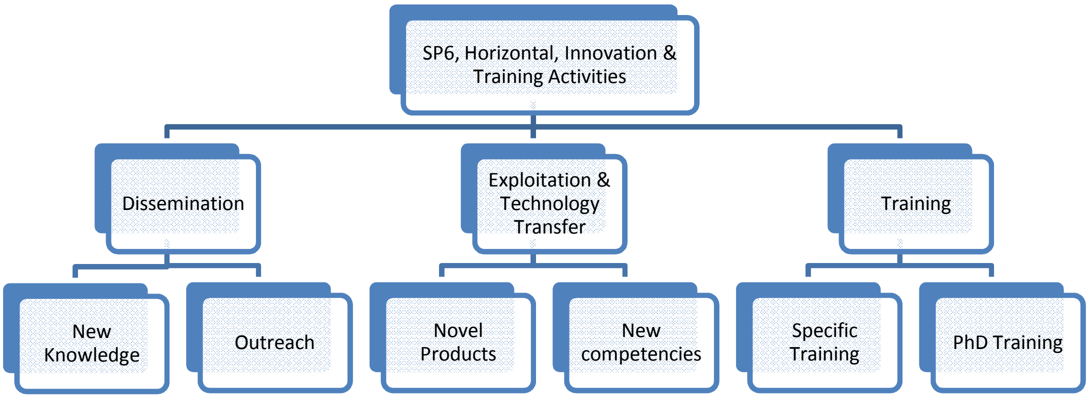


Transmission performance of windows: uncoated (blue), coated with SiOx (red). The yellow line shows the difference between the two treatments (negative values indicate better performance than the uncoated control). The performance of the uncoated window was so poor that it was manually cleaned on day 12, hence the sharp rise in transmission.

Sol-gel coatings intended for propellers were applied to NiBrAl panels and immersed in the UK. After 10 months the performance of the TNO sol-gel coatings (centre right and left) was equal to the Intersleek standard (white, left). Heavy fouling on the uncoated control (right). (International Paint).

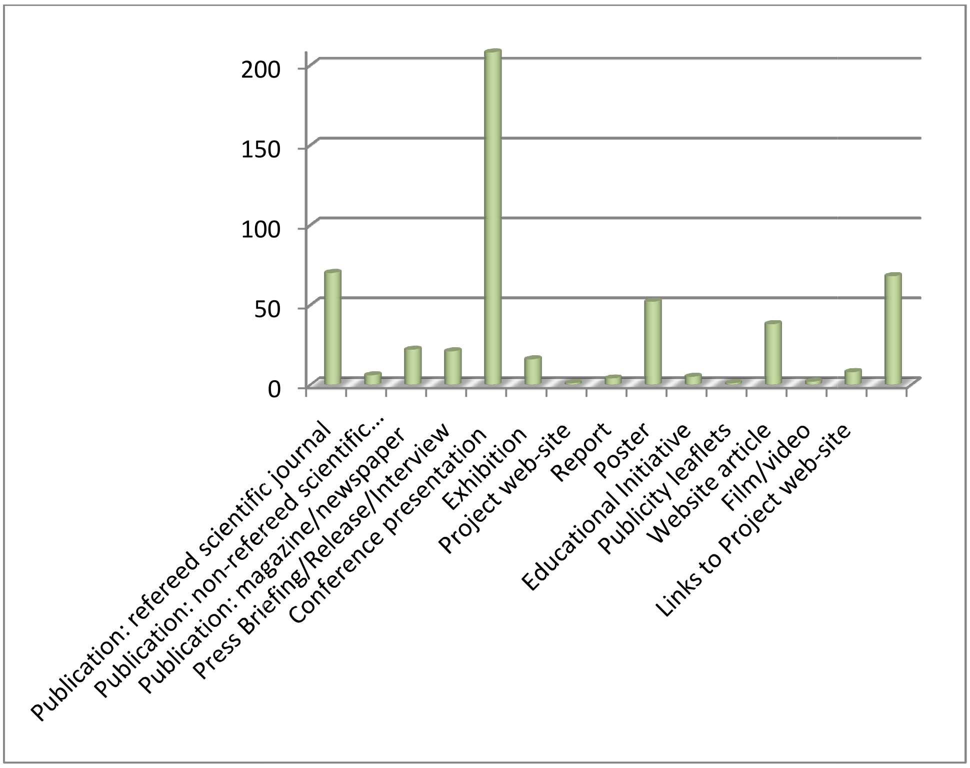
3.4 Sub-Project 6 Horizontal, Innovation-related and Training Activities

Activities of this horizontal Sub-Project applied across the whole project, and over the whole 5 years. The actions fall into 3 main areas:



3.4.1Dissemination

Partners in the project made 531 items of individual, or collective dissemination aver the 5 years. The major categories are identified in the Figure below (data contained in separate Final report on the Plan for Utilising & Disseminating Knowledge (PUDIK)).



Dissemination of New Knowledge:
The majority of dissemination has been in furtherance of the project's mission to **Transfer New Knowledge to Research and Technology Sectors,** through Publications in Refereed International Journals, Conference Presentations and Posters. Many other articles for magazines/trade journals and displays at Exhibitions also disseminated the work of the project within this sector.

A number of specific Dissemination events were aimed at audiences in the Research and Technology sectors. These were either organized by, or on behalf of AMBIO, as Consortium-level events.

- A symposium "Progress and Perspectives in Nanostructured Coatings for Biofouling" was held in September 2007. The symposium included 5 external speakers in addition to members of the Consortium. Invitations were issued to selected external attendees (e.g. members of the AAG, trade organisations and the media).
- Three Partners gave oral and/or poster presentations on the work of AMBIO to the 54th International AVS Symposium, Special Topical Conference on Marine Biofouling, Seattle 14-18 Oct 2007
- Four Joint Workshops involving members of the US Navy (ONR) and AMBIO projects were co-organised by AMBIO (Maui, Hawaii, December 2005; Jacksonville Florida, December 2006; Sedona Arizona, December 2007; St Petersburg, Florida, December 2009).
- Partners (UoB, AKZO, UniPi, Nanocyl, IPF), contributed to a specific AMBIO session at the European Coatings Congress, Nuremberg, April 2009.
- Partners (UoB, CNRS, UNIVDUN, GYTE, BASF, TECHNION) made contributions to ENF 2009, Prague June 2009 as a coordinated Consortium activity.

'Outreach' Actions:
Regarding 'Outreach' activities to disseminate the work of the project to wider audiences, analysis of the PUDIK database showed that 79 items of dissemination were directed towards the **general public and informed lay audiences**, through articles in the general media, press releases, exhibitions and web articles. ***For example,*** the Coordinator participated in a Press Briefings to ENF2009 (Prague, June 20089) and the World Conference of Science Journalists (London, July 2, 2009). The project has also been invited to participate in 'NanoTV'. This is an EC-sponsored organization that makes short video news releases (VNRs) from EC-funded projects. The VNRs will be distributed through established networks to different television stations and programmes in all EU Member States. The VNRs are also made available on the European Research Media Centre website (www.youris.com). The decision was made to focus the AMBIO contribution on the amphiphilc, nanopatterned coatings prepared by UniPi/AKZO and at the time of writing this report the programme is in production.

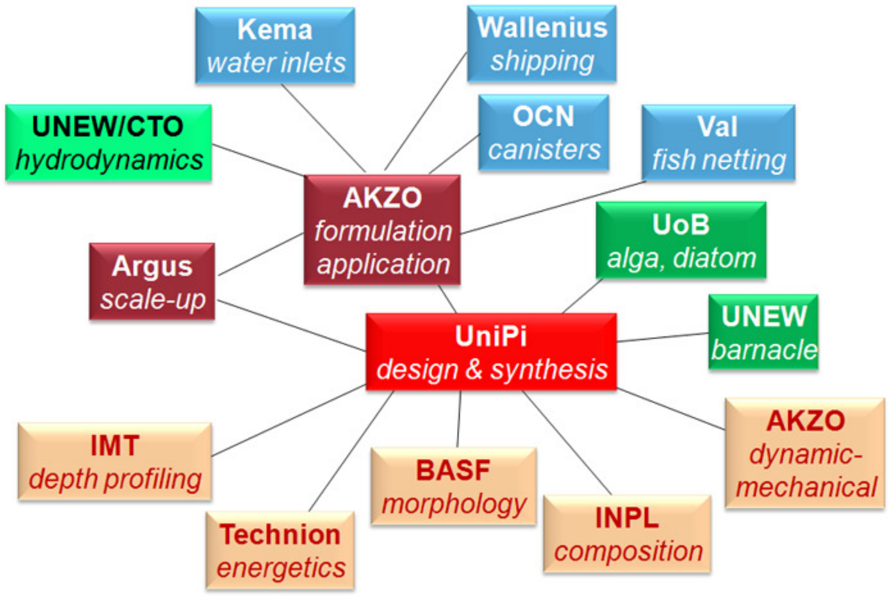
Another mechanism for disseminating the work of the project to wider audiences involved the AMBIO Associates Group, an invited group of companies, trade associations, classification societies, PR and consultancy organizations. Members of this group were invited to a special dissemination event, and will be sent a final report.

Nanoforum	University Marine Biological Station Millport	Umicore SA	BioGea Servicios Medioambientales
IMAREST	CEFAS	Altex Coatings Ltd	Ciba
Frost & Sullivan	Marine Tech	Society of Maritime Industries	European Boat Association
Imerys	Elzly Technology Corporation	RINA	Der Norske Veritas
PRA Coatings Technology	Poseidon Ocean Sciences	Institute of Biology	Chelsea Technologies Group
Qinetiq	University of Twente	SI Laboratories	Nippon Paint
Defence Science and Technology Laboratory			

A 'user-friendly' illustrated brochure has been prepared for general dissemination purposes. It identifies the background and mission to the project and the main achievements.

3.4.2 Knowledge and Technology Transfer Actions

Knowledge transfer seeks to organize, create, capture or distribute knowledge and ensure its availability for future users. The integrated and coordinated activities within the AMBIO project facilitated the extensive transfer of know-how between Partners and sectors. For example, the diagram below illustrates the level of cooperation between Partners associated with just one coating technology originated by the University of Pisa. No less than 14 different Partners shared their expertise to enable the complete characterisation, biological evaluation, scale-up, formulation and field testing of this one coating! Beyond the project, knowledge transfer to the scientific community was facilitated by the publication of 70 papers in publically available, refereed, international scientific journals and 208 presentations to international conferences, including the European Coatings Congress (2009), the 13th and the 14th International Congresses on Marine Corrosion and Fouling.



Technology transfer is the process of sharing of skills, knowledge, technologies and methods of manufacturing to ensure that scientific and technological developments are accessible to a wider range of users who can then further develop and exploit the technology into new products, processes, applications, materials or services. The AMBIO project integrated industries, universities and research organisations into a coordinated, interdisciplinary programme. Fifteen companies were involved ranging from suppliers of nanomaterials through to coating production. The industrial supply chain built into the project thus increased the chances of durable impacts through technology transfer from the project to industrial production. Specifically, companies involved in the manufacture of coatings, or coating materials in AMBIO, have benefitted from the transfer of expertise, knowledge and results from the academic partners in the project: for example, results from Partners performing the biological evaluations have featured in several patent applications.

Another aspect of technology transfer involves the End-Users Reference Group (EURG), a collection of Partners with specific expertise in using antifouling technologies or advising others on their application. Through specific Workshops associated with project meetings, this group of Partners was exposed to modern trends in the development of new nano-inspired coating solutions, and was directly involved in their evaluation. This experience will influence the direction of any future advice they mish wish to give to customers on novel solutions to fouling problems.

3.4.3 Training

Specific Training Events

During the 5 years the project organized 4 Training Workshops:

Training Workshop 1. The SP1 Nanostructured Surfaces Workshop

This workshop was organised in month 1 by Partner 4 (UniPi). Its main aim was to review the strategies for nanostructuring technologies offered by the various Partners to explore how they may be most effectively applied to the solution of biological fouling problems contained within AMBIO.

Training Workshop 2. The Annual End-Users Workshop

This was a series of annual workshops for the End-User Group, organized by Partners 2,5 and 14 (TNO, AKZO, KIMAB). Its initial aim was to consider the requirements of practical coatings for diverse end-uses that can be used to advise the designers and producers of surfaces in Sub-Project. Later workshops involved participation in the selection of the most appropriate coatings and the detailed planning of field tests.

Training Workshop 3. The SP3 Biological Evaluation Workshop

This workshop was organised by Partners 1 (UoB), 3(TNO), 6 (UNIVDUN) and 11 (UNEW) to familiarise scientists engaged in development of coatings, with the methods that were to be used to evaluate performance in the bioassays, the requirements of evaluators and issues that may affect the quality of the evaluation.

Training Workshop 4. The SP2 Surface Characterisation Workshop

This workshop was organised by Partners 10 (LIU) and 15 (UHEI) in month 4 to share best practice on the most modern surface analytical technologies available within the AMBIO consortium.

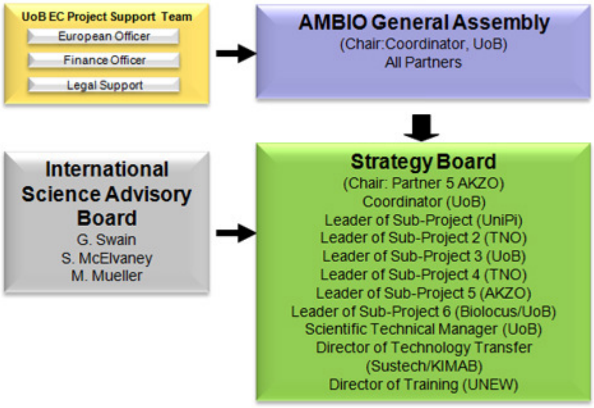
Postgraduate Training

A key training element of the AMBIO project was the appointment of 5 Training Associates (TAs) who registered for research degrees. The TAs were based in a primary host University Partner (Linkoping, Heidelberg, Dundee, Newcastle and Dresden) but a requirement of each position was that they spent time in the laboratories of other Partners, in a different countries and disciplines. Four of the TAs completed their studies for a PhD, and one submitted for a research Masters.

3.5 Sub-Project 7 Integrated Project Management

Project level management was organized through a specific Sub-Project (7). The overall aim was to link the strategic and core activity levels of the project into an **integrated whole**, to make sure that defined objectives of the IP were realised on time, within budget, and with regard to quality of output.

Strategic management and the monitoring of outputs and resources was a specific function of the Strategy Board which met at approx. 3-monthly intervals. The International Science Advisory Board provided an annual review of progress and international competitiveness.



Project coordination was provided by the Coordinator, Prof. JA Callow and the support team at the University of Birmingham. Specific functions included the preparation of rolling 18 month Implementation Plans, organisation of 10 biannual project meetings, liaison with the International Advisory Board, monitoring of project budgets and expenditure, distribution of project finances to Partners, scientific and financial reporting to EC, linkages with other research programmes (esp. USA). The Coordinator was also responsible for implementation of agreed project strategies, the preparation of annual reports and deliverables of on a day-to-day basis, an implementation of strategic decision of Strategy Board. Detailed monitoring of scientific progress and particularly the coordination of activity and the extensive exchange of samples and data between Partner organizations, was performed by the Technical Project Manager, Dr Maureen Callow.

4. Impacts of the Project

Detained analyses of the impacts of individual achievements have been identified in Section 3 above. The following analysis presents a more holistic overview.

Impact on Industry

AMBIO aimed to provide a source of innovation for relevant EU industries. EU companies are world-leaders in anti-biofouling coating technology with 70% of the global market share. However innovation is vital to coatings manufacturers who constantly reformulate their products to differentiate themselves from the competition. Innovation is especially important in the current legislative climate in which environmentally-benign products are increasingly sought. Emerging technologies, such as nanostructuring of coatings, will provide such a source of innovation. It has been estimated that in 10 years from now, 30% of paint industry sales in Europe will rely on nanotechnology applications in so-called 'smart' coatings, including those destined for marine and freshwater applications.

The actual impact of the AMBIO project on industrial Partners can be judged by the patent applications filed by AKZO, Teer Ltd., Nanocyl, TNO and BASF. In addition, at least three successful, patented coating technologies are immediately available for commercial exploitation, a) the CNT-siloxane dispersions marketed as Biocyl™ by Nanocyl, b) the SiOx-like coatings which can be deposited on optical windows by Teer, c) the sol-gel technology introduced by TNO which is available for direct application to propellers by Original Equipment Manufacturers. Other coatings that have shown good results in the project will be commercialized after further R&D. For example, the patented amphiphilic coating technology introduced to the project by the University of Pisa has been included in AKZO's portfolio of technologies for industrial exploitation.

Some Partners perceive new business opportunities to enter new markets previously unknown to them e.g. Teer Ltd has the opportunity to provide commercial coating services to the marine instruments market, and Nanocyl is now able to provide dispersions of CNTs for use in the manufacture of marine antifouling coatings. AKZO anticipates benefits in the area of protective coatings for power inlets and aquaculture through their exposure to these markets resulting from the joint work they did in the project with KEMA and VAL respectively.

Some industrial Partners have also benefitted from the project through the introduction of new evaluation tools, such as the stereological analysis of fouling communities or the introduction of the accelerated test patching procedures (AKZO).

Finally, several companies in the project (OCN, VAL, KIMAB, KEMA, TNO) anticipate that they will be able to obtain commercial benefits, e.g. in consultancy services, through their improved knowledge base and competencies.

Impact on the Research Sector

For University partners, the most significant returns on their investment in the project arise from the advancement of understanding of important scientific issues posed by the project, the publication of papers, the acquisition of new competencies, the access to new collaborative networks and the leveraging of additional support for research.

> Most Partners in AMBIO had not been involved in aquatic biofouling research before and thus their involvement in a new field of research has opened new doors where they can apply their expertise in areas such as chemistry and materials science.
>
> A sub-group of AMBIO Partners successfully applied for a Framework 7 Marie-Curie Initial Training Network (SEACOAT), starting in 2010. This will enable the continued collaboration of this group of

Partners and will provide training for 17 early research career scientists in interdisciplinary research methods relevant to biofouling.

UHEI's participation in AMBIO has facilitated new research funding from the US Office of Naval Research.

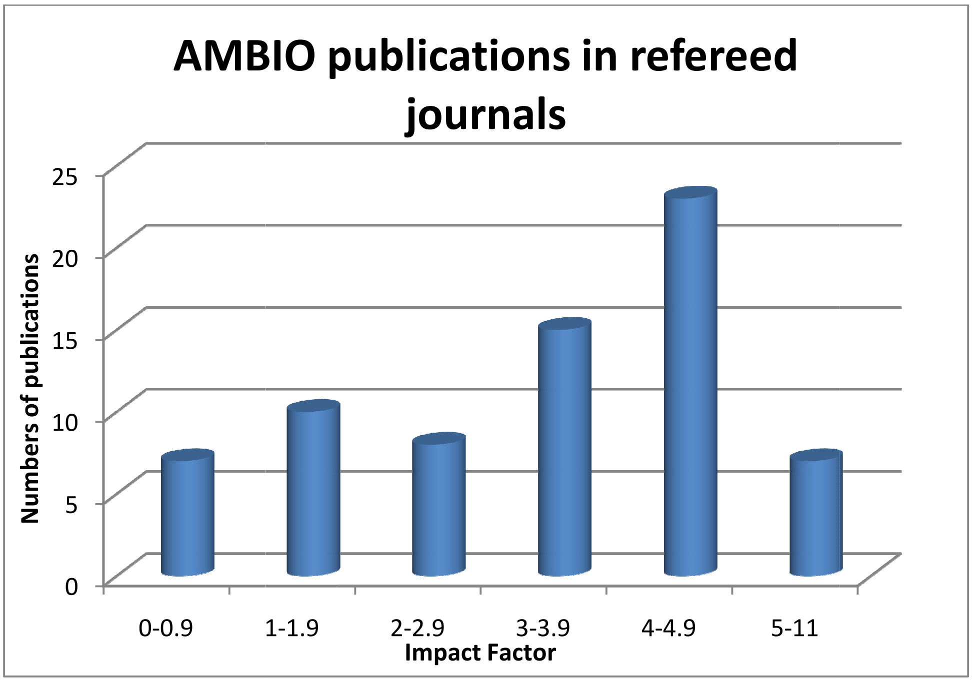
Some Partners have been able to consolidate their collaborations with industry through direct financial support from the companies themselves, e.g. UoB, UNEW.

New skills in nanotechnology have been acquired by Partners such as Linkoping University (soft patterning technologies such as UV-free radical polymerization, microcontact printing and nano-imprinting). These can now be applied to work in new projects.

AMBIO partners published extensively in international refereed journals (Appendix 1). The papers have been subjected to a simple bibliometric analysis as a measure of impact. The analysis took account of 70 publications in which AMBIO has been acknowledged. Several articles in new scientific journals do not yet have an impact factor and they have been excluded from the analysis. The table below shows that the average (weighted) impact factor of all publications (excluding those that do not yet have an impact factor) is 3.789. The graph below shows that the top 75% of articles were published in journals with an impact factor >2.0.

Scientific Journal	Number of publications to 1/04/10 (A)	Impact Factor 2008 (B)	weighted impact factor (AxB)
Angewandte Chemie: International Edition	2	10.879	21.758
Advanced Materials	2	8.191	16.382
Advanced Functional Materials	1	6.808	6.808
Small	2	6.525	13.05
Soft Matter	1	4.586	4.586
Journal of Physical Chemistry: B	1	4.189	4.189
Biomacromolecules	3	4.146	12.438
Langmuir	16	4.097	65.552
Physical Chemistry Chemical Physics	2	4.064	8.128
J. Polymer Science Part A: Polymer Chemistry	1	3.821	3.821
Acta Biomaterialia	1	3.727	3.727
Biofouling	10	3.707	37.07
J. Royal Soc. Interface	1	3.621	3.621
New Journal of Physics	1	3.44	3.44
Macromolecular Bioscience	1	3.298	3.298
Journal of Biomedical Materials Research Part A	1	2.706	2.706
Journal of Colloid and Interface Science	1	2.443	2.443
Biointerphases	4	2.347	9.388
Macromol. Che. Phys.	1	2.202	2.202
Biotechnology Progress	1	2.108	2.108
European Physical Journal	1	1.943	1.943
J. Nanoscience & Nanotechnology	2	1.929	3.858
Journal of Industrial Microbiology & Biotechnology	1	1.919	1.919
Surface & Coating Technology	2	1.86	3.72
International Journal of Adhesion & Adhesives	1	1.678	1.678
Applied Surface Science	1	1.576	1.576
Biotechnology Letters	1	1.595	1.595
Progress in Organic Coatings	1	1.375	1.375

Journal of Adhesion	2	0.685	1.37
Molecular Crystals & Liquid Crystals	1	0.537	0.537
eXPRESS Polymer Letters	1	0	0
J. Nanostruct. Polymers and Nanocomp.	1	0	0
ePOLYMERS	1	0	0
Macromolecualr Symposia	1	0	0
Total Papers	**70**		**246.286**
Average weighted impact factor (excluding journals without an impact factor)			**3.789**



Impact on Sustainability and the Environment

All AMBIO technologies are designed to be environmentally benign since none contain biocides that would require registration under the Biocidal Products Directive. Coatings containing nanoparticles (such as carbon nanotubes) will be 'environmentally friendly' since the nanoparticles are tightly bound.

Cleaner, renewable technologies are at the heart of the European Union's objective of becoming the most competitive and dynamic knowledge-based economy in the world, whilst safeguarding natural resources and the environment. Consistent with this objective, the AMBIO project aimed to inspire a new generation of coatings for ship hulls, power plants, aquaculture etc. that do not rely upon biocides for their effectiveness thus reducing the environmental load of polluting and costly chemicals and toxic metallic ions.

The replacement of biocide-containing coatings by their environmentally friendly equivalents will also encourage the introduction of a tighter regulatory regime on releases of pollutants into the environment and the health and safety of workers. Effective solutions will also have an indirect consequence of minimizing energy losses, thus reducing the consumption of fossil fuels and the concomitant release of greenhouse gases (if the world fleet was totally fouled, an extra 70.6M tonnes of fossil fuel would be burned per annum, liberating >210M tonnes CO_2 and >5.6 M tonnes SO_2).[6]

Broader Socio-Economic Impacts

AMBIO provided a significant source of employment for early career researchers with some 47 positions being identified, some of which resulted in permanent employment. In addition, the Training Associate scheme created a small pool of 5 students with interdisciplinary skills that should fit them well for future careers.

Impact on the European Research Area

The mix of Partners from 'established', 'new', 'associated' and 'candidate' states directly contributes to the FP6 objective of a more integrated, focussed, interdisciplinary ERA.

New networks of collaborators were formed, promoting knowledge transfer (for examples see p35)

Some organisations were exposed to EC funding and associated policies for the first time. This familiarity should encourage future applications for EC funding from new states such as Slovenia and Poland

The trans-sectoral Partner base will encourage new/improved links between academia and industry

Over 500 items of Dissemination have publicised the contribution of the indirect funding instruments of the EC to the promotion of the aspirations of the ERA (see Section 5)

The AMBIO Training Associate scheme was specifically aimed at producing individuals who are more familiar with interdisciplinary research and national research cultures other than their own

[6] http://www.limnomar.de/download/18_Hunter.pdf

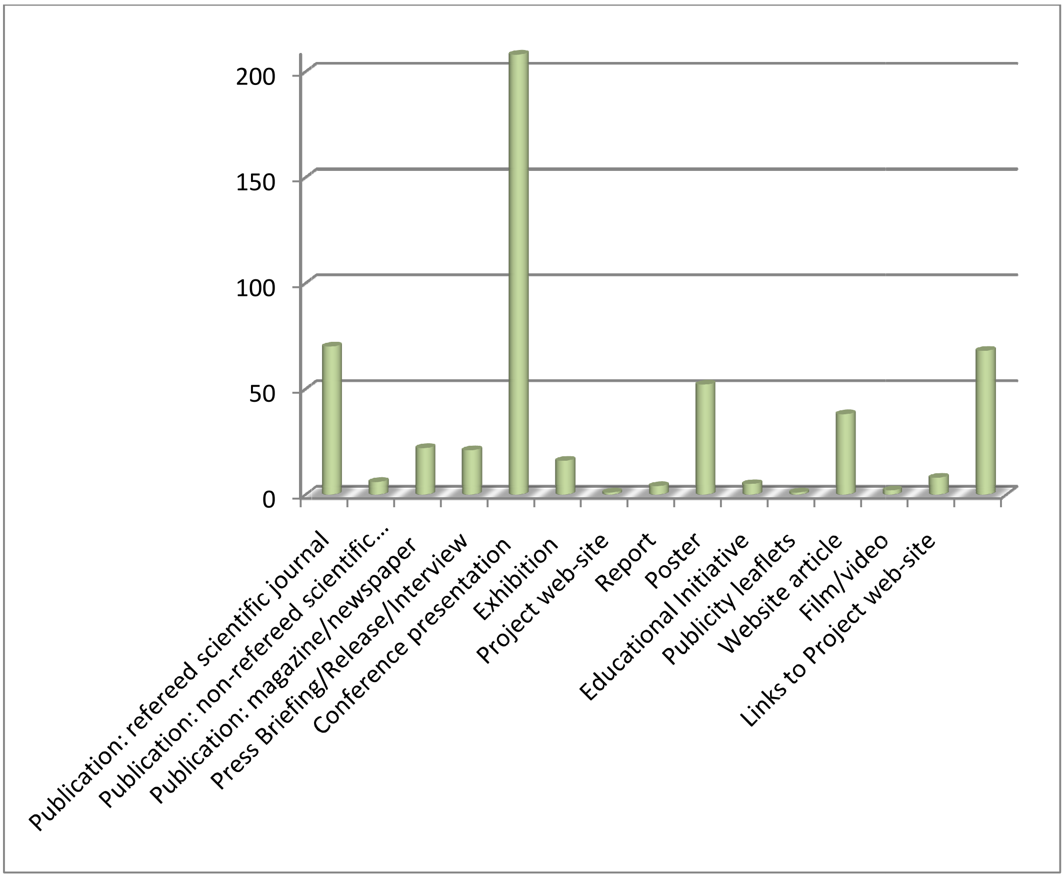
5. Dissemination and Use

Dissemination Activities:

At the start of the project AMBIO developed a Plan for Use and Dissemination of Knowledge (PUDIK) to encourage and assist Partners to maximise disseminatable and exploitable outputs: the plan was updated annually. While each Partner was individually responsible for publications, conferences, etc. the project also organized some specific activities to enhance dissemination, involving:

- Production of posters and leaflets by the Coordinator and made available to the Partners for their own use.
- Project web-site with updated results
- Specific dissemination activities were organized through the project:
    - 4 Joint Workshops were held with the 'Marine Coatings' programme of the US Office of Naval Research
    - An international symposium "Progress and Perspectives in Nanostructured Coatings for Biofouling" was organised in September 2007. The symposium included 5 external speakers in addition to members of AMBIO. Invitations were issued to selected external attendees (e.g. members of the AAG, trade organisations and the media).
    - AMBIO was invited to present organized sessions at several conferences, including: EuroNanoForum2009, and the European Coatings Congress (2009)

In total there were 531 items of dissemination over the 5 years of the project. The distribution of items within different categories is shown below. The detailed record of publications in refereed journals is shown in Section 4 above, and in Appendix 1. The totality of dissemination activity across the whole project is shown in the accompanying document 'Final Plan for Using and Disseminating Knowledge'.



Exploitation Activities:

Exploitation Plans:

In the final Period of the project Partners completed their plans for Exploitation of the results of the project, and these were entered into the Exploitation Database (see the accompanying document 'Final Plan for Using and Disseminating Knowledge'). The plans were then analysed and are presented here within the following categories:

Type of exploitation activity	Number of items
Commercial sales through improved competitive position	2
Knowledge or tools enabling further collaborative research	12
IPR Protection/patenting	6
Wide publication in scientific or other journals on a free-to-use basis	47*
Licensing to other organisations	2
Consultancy	5
Start-up businesses	0
University spin-offs or graduate enterprise	0
Knowledge or tools for public or social good organisations	0
Input to Standards	0
Input to EU policy-making (studies, workshop results)	0
Educational initiatives	3

*This is not the same as the number of papers published in refereed journals, which was 70 (see Dissemination analysis above)

Details of Patents applied for:

Partner	Title	Number	Priority countries	Filing date	Current status (pending/approved/published)
Nanocyl	Marine anti-biofouling and fouling release composition	US 60/852,771	USA	18/10/2006	pending
		EP 07447043.6	Europe	11/07/2007	pending
		PCT/BE07/000114	International	18/10/2007	pending
TNO	A coating composition	EP06076473.5	international	20/07/2007	pending
		US12/374208	USA	16/01/2009	pending
BASF	Method of inhibiting biofouling on a surface in contact with water	EP08155631.8	Europe	05/05/2008	pending
TEER	Coatings to resist aquatic biofouling	PCT/GB2008/003123	International	15/09/08 with priority date 14/09/07	pending
AKZO	Amphiphilic blends of zonyl-acrylates and silicones		International	to be filed April 2010	in progress

Appendix 1. List of all Publications in Refereed Journals

1. Bowen, J., Pettitt, M.E., Kendall, K., Leggett, G.J., Preece, J.A., Callow, M.E., Callow, J.A. (2006) The Influence of Surface Lubricity on the Adhesion of *Navicula perminuta* and *Ulva linza* to Alkanethiol Self-Assembled Monolayers. Journal of the Royal Society Interface. **22**, 473-478.

2. Marmur, A., (2006) Underwater superhydrophobicity: theoretical feasibility, Langmuir **22,** 1400-1402.

3. Marmur, A. (2006) Super-hydrophobicity fundamentals: Implications to biofouling prevention, Biofouling **22**, 107-115.

4. Qiang He, Ying Ti, Küller Alexander, Grunze Michael, Gölzhäuser Armin, Junbai Li (2006) Self-assembled molecular pattern by chemical lithography and interfacial chemical reactions. Journal of Nanoscience and Nanotechnology, 6, 1838-1841.

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6. Schmelmer, U., Paul, A., Küller, A., Steenackers**, M.,** Ulman, A., Grunze, M., Gölzhäuser, A., Jordan R., (2007) Nanostructured polymer brushes. Small, 3, 459-465.

7. Steenackers, M., Küller, A., Ballav, N., Zharnikov, M., Grunze, M., Jordan, R.(2007) Morphology control of structured polymer brushes. Small, **3**, 1764-1773.

8. Heydt, M., Rosenhahn, A., Grunze, M., Pettitt, M., Callow, M.E., Callow, J.A. (2007) Digital In-Line Holography as a Three-Dimensional Tool to Study Motile Marine Organisms During Their Exploration of Surfaces. Journal of Adhesion, 83, 417-430.

9. Schilp, S., Kueller, A., Rosenhahn, A., Grunze, M., Pettitt, M.E., Callow, M.E., Callow, J.A. (2007) Settlement and adhesion of algal cells to hexa(ethylene glycol)-containing self-assembled monolayers with systematically changed wetting properties. Biointerphases, **2**, 143-150.

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11. Conlan S.L., Mutton R.J., Aldred N., Clare A.S. (2008) Evaluation of a fully automated method to measure the critical removal stress of adult barnacles. Biofouling **24**, 471-481.

12. Rosenhahn, A., Ederth, T., Pettitt, ME. (2008) Advanced nanostructures for the control of biofouling: the FP6 EU Integrated Project AMBIO. Biointerphases, **3**, IR1-IR5.

13. Dong, J., Mielczarski, J.A., Mielczarski, E., Xu, Z. (2008). In situ characterization of the adsorbed Concanavalin A on germanium at various pH. Biotechnology Progress, **24**, 972-980.

14. Mielczarski, J.A., Dong, J., Mielczarski, E. (2008) Real Time Evaluation of the Composition and Structure of Concanavalin A Adsorbed on Polystyrene Surface. Journal of Physical Chemistry, **112**, 5228-5237.

15. Marmur, A. (2008). From Hygrophilic to Superhygrophobic: Theoretical Conditions for Making High-Contact-Angle Surfaces from Low-Contact-Angle Materials. Langmuir **24**, 7573-7579

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