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Understanding Marine Fouling and Assessing Antifouling Approaches

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Understanding Marine Fouling

"**MARINE FOULING**" is a blanket term that describes a **wide range of organisms** attached to surfaces immersed in the ocean. These organisms range in size from bacteria to seaweed to molluscs, and all occupy specialised environmental niches.

Biofouling negatively affects the **hydrodynamics** of a ship's hull by increasing drag and the required propulsive power. This leads to increased fuel consumption with its attendant cost and emissions penalties. **Even minor biofilms can have a significant effect.**

Understanding and controlling marine fouling is **multidisciplinary**. Developing new antifouling technologies will require the collaboration of diverse specialists including biologists, chemists, and engineers.

Zones of Fouling on a Pier

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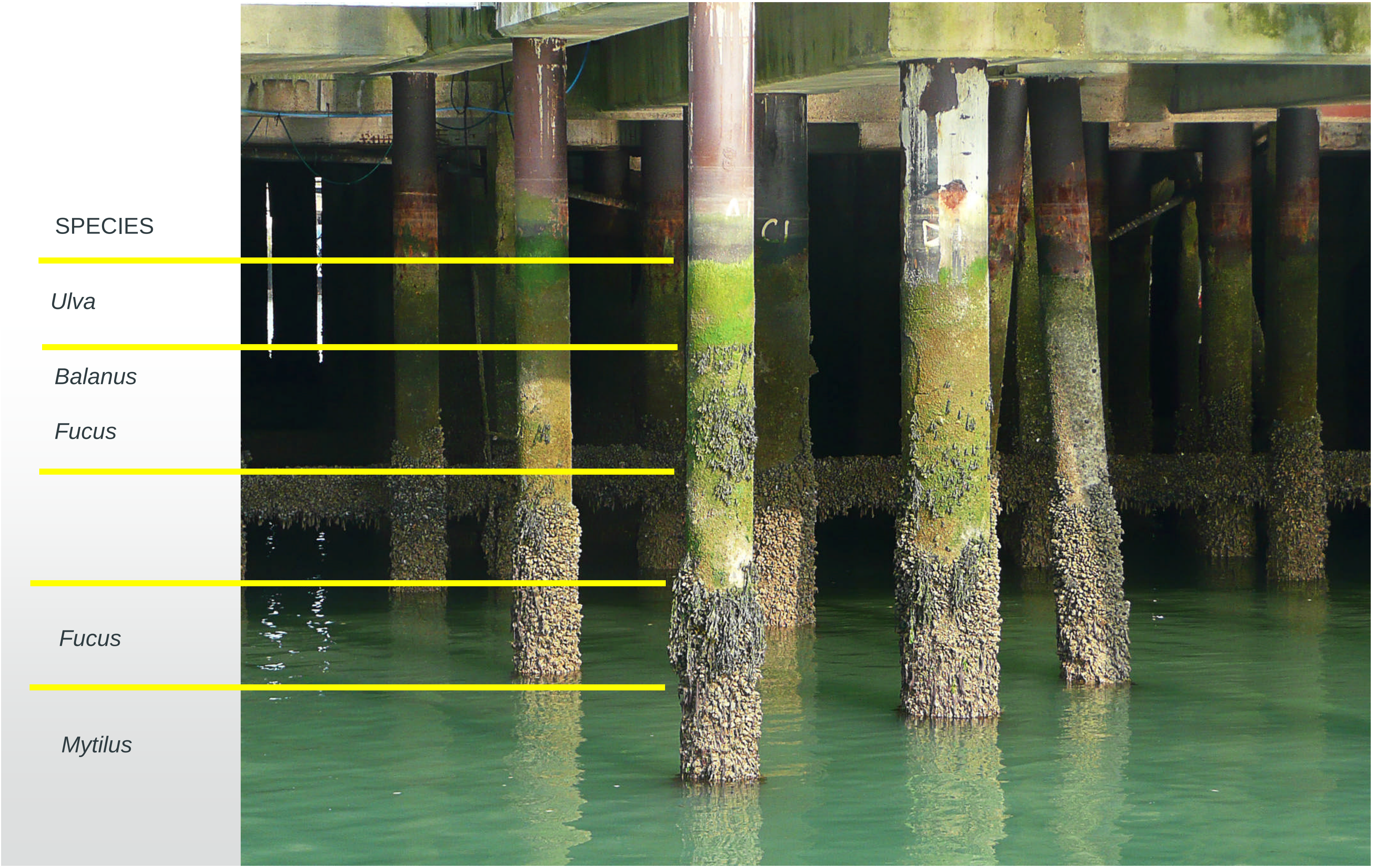

A Closer Look at Fouling…

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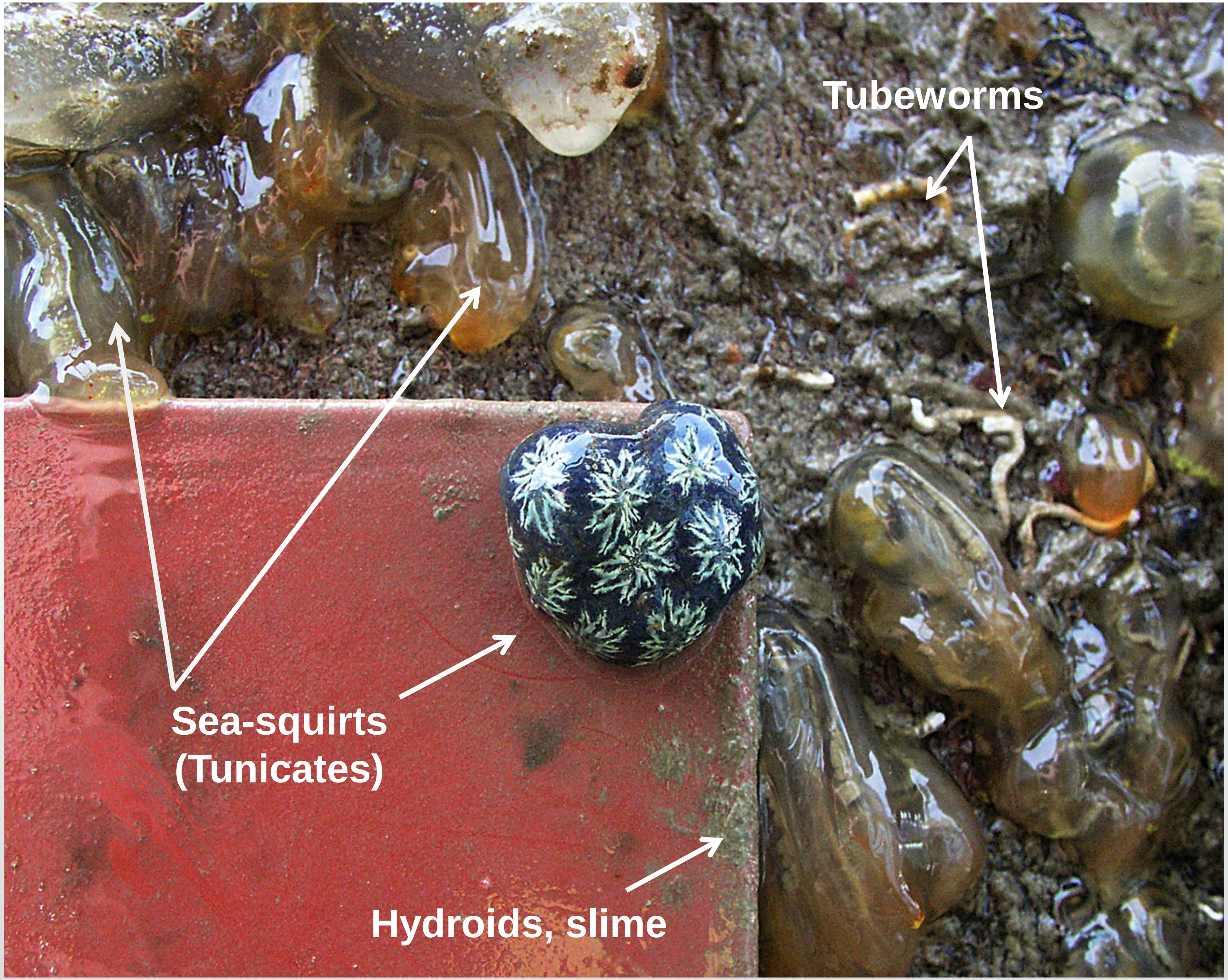
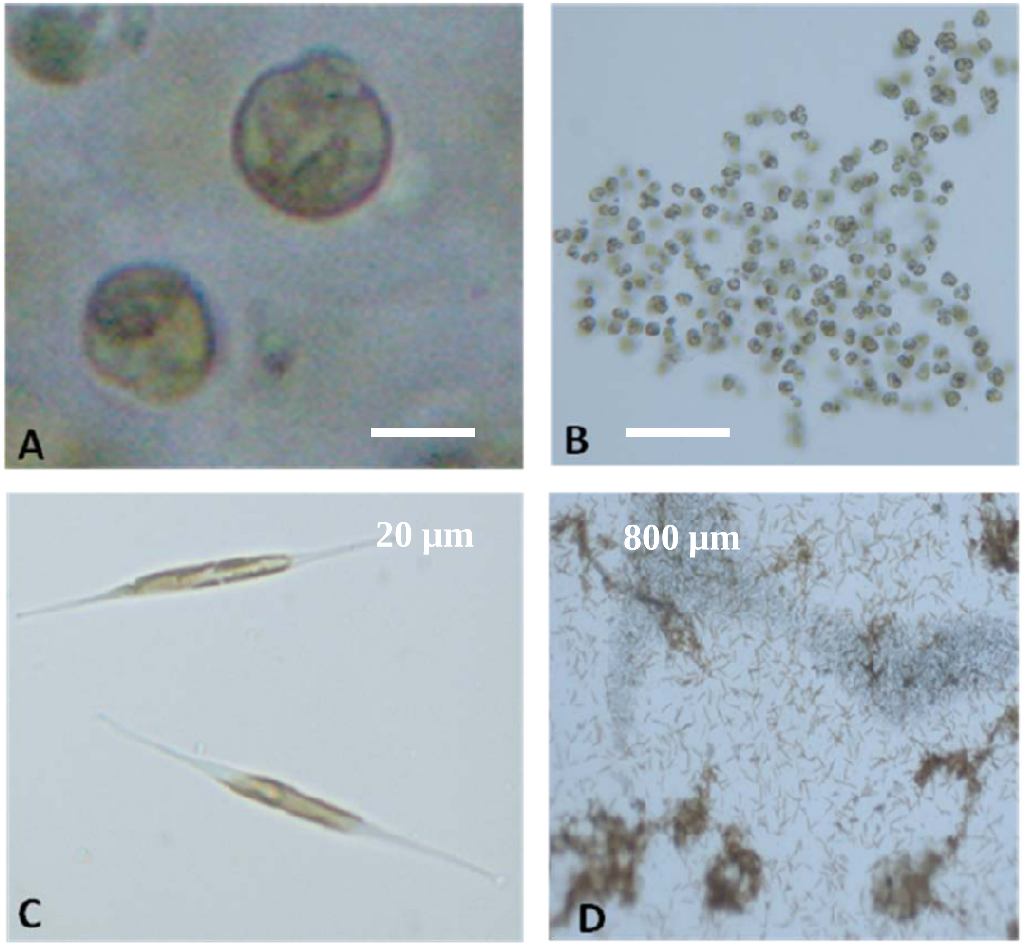
Corner of a copper oxide-based AF paint test panel after 8 months exposure Aug 09 – April10 facing NE at Southampton docks

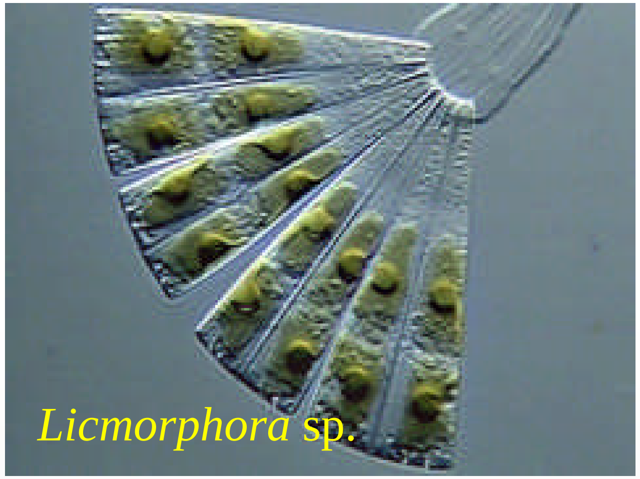


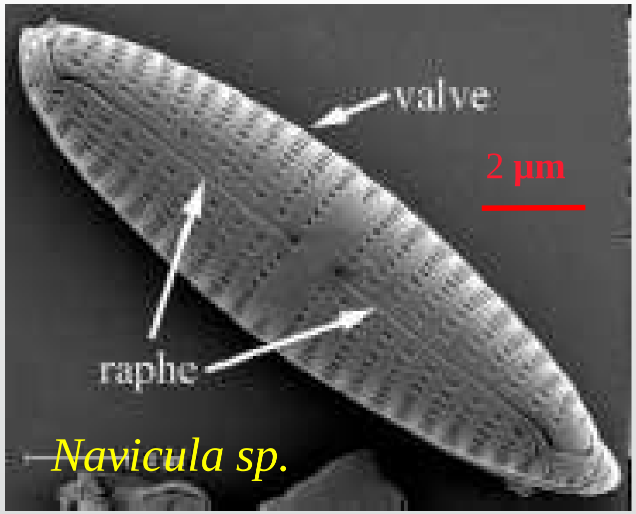
Fouling Micro-organisms: Slime

***Microalga**: Exanthemachrysis gayraliae*



***Diatom**: Cylindrotheca cloisterium*





Non-Native (Invasive) Species

Japanese oysters at the port of Den Helder, Netherlands have out-competed the local species

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Factors Affecting Fouling Growth

ENVIRONMENTAL

Temperature
Illumination
Salinity
Alkalinity, etc

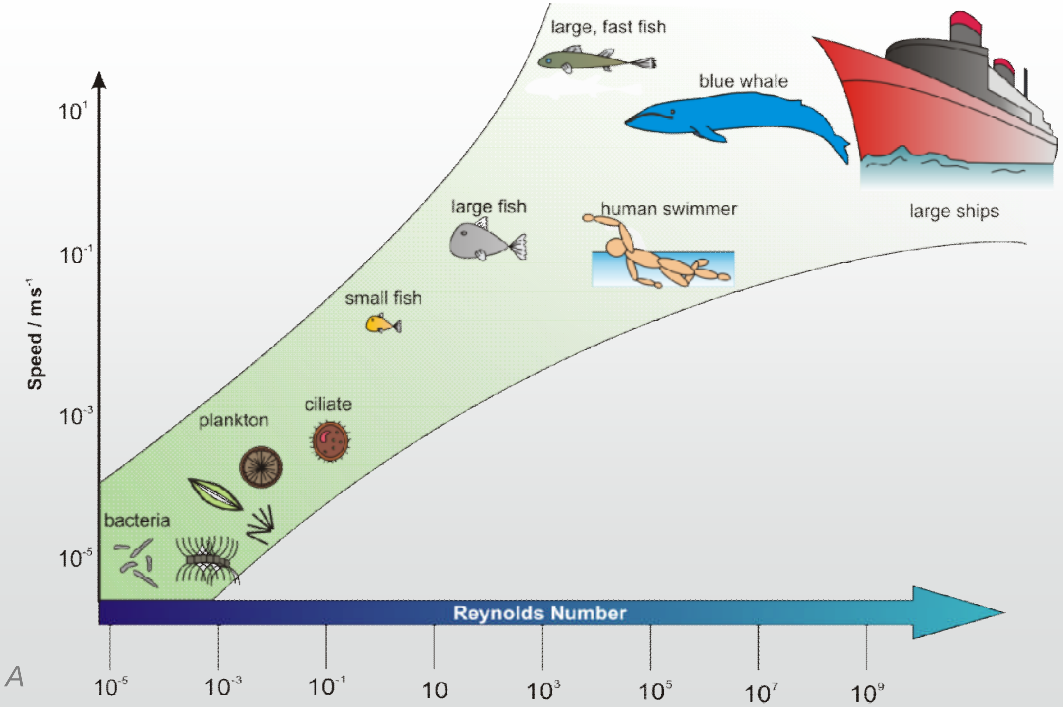
→

HYDRODYNAMIC

Flow, Turbulence,
Acceleration,
Reynolds Number

Reynolds number is a measure of **the ratio of inertial forces to viscous forces** and quantifies the relative importance of these forces for given flow conditions.

"A challenge to biomimicry is to adapt natural systems that are effective at relatively low Reynolds numbers to man-made systems which operate under parameters orders of magnitude greater".



Salta, M., et al – *submitted to Roy. Soc Phil. Trans. A*

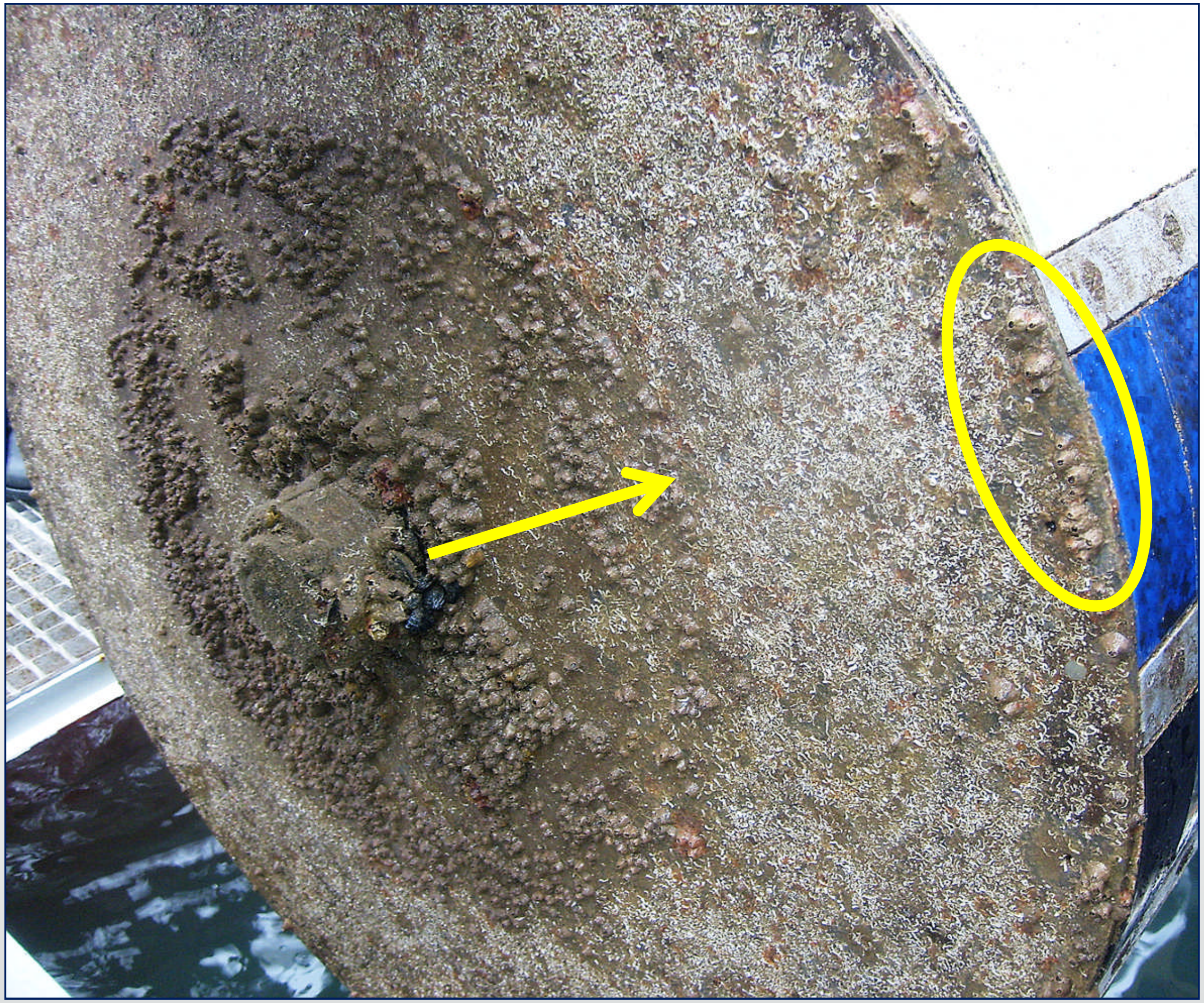
The Effect of Flow

An experimental rotor operated continuously in the Mediterranean Sea

The surface is colonised by barnacles up to a definite radius

The faster outer area of the rotor is covered in tubeworms..

..but note barnacles at the periphery!



Photograph used with permission

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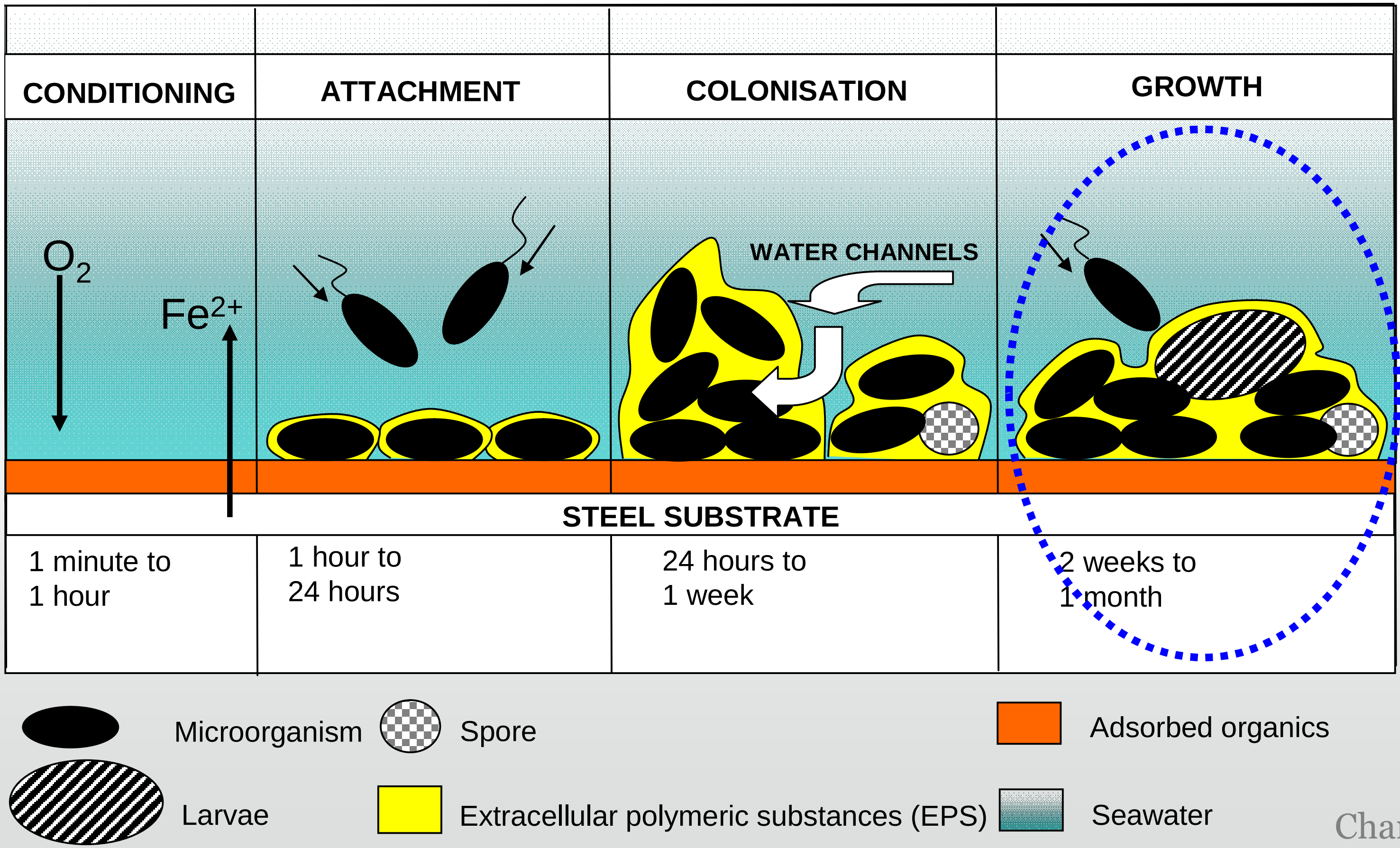
MICROFOULING - Biofilms

- **Micro**fouling precedes **macro**fouling
- It attracts macro-organisms via chemical cues
- Biofilms are complex dynamic systems that contribute to biofouling



Complex Community

BIOFOULING

Chambers *et al.*, 2006

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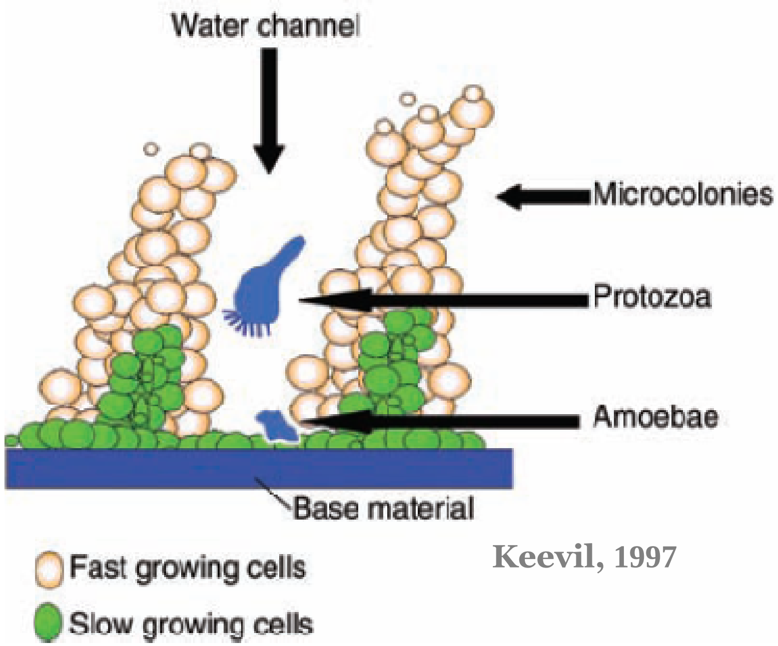
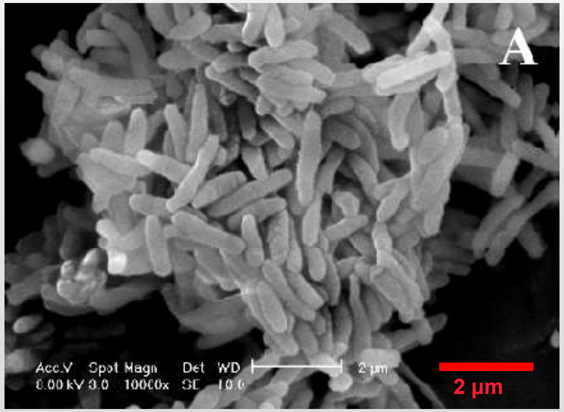
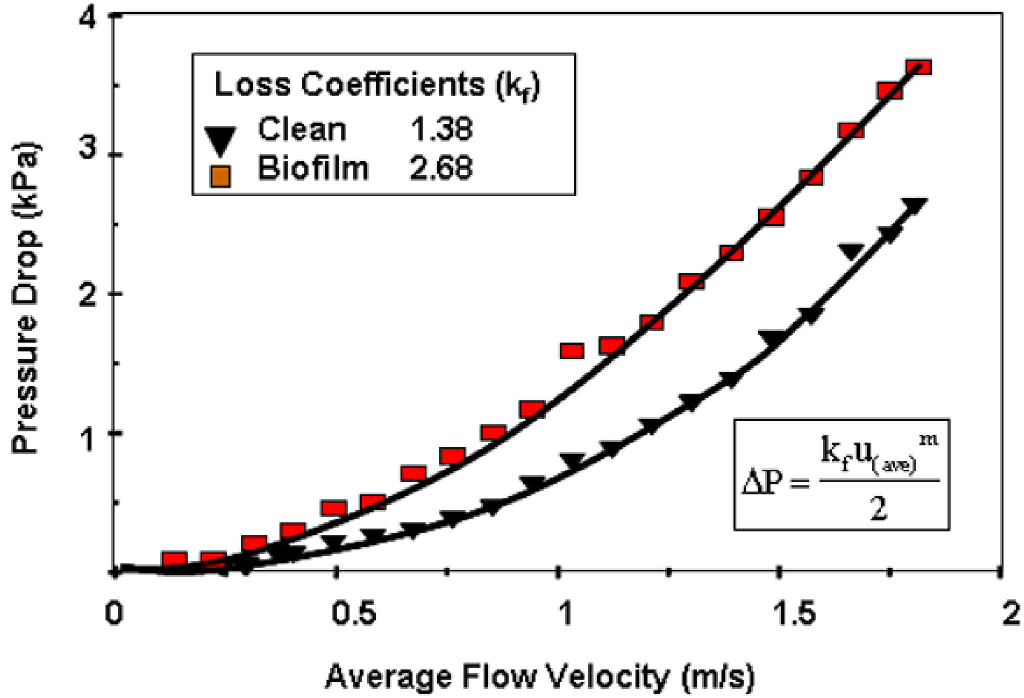
Bacterial Biofilms are 3-Dimensional



Keevil, 1997



Mimura et al., 2008



Pressure drop (ΔP) vs. velocity (u_{ave}) measured in a clean smooth glass tube with and without bacterial biofilm.

Stoodley, P., UoS, Unpublished data

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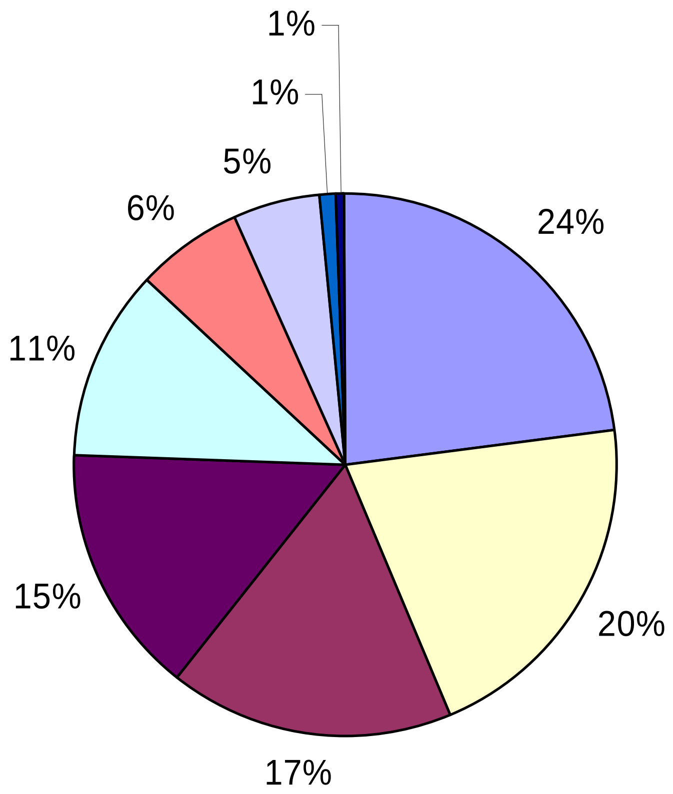
Fouling Communities on Ships



	EXAMPLES
Algae	Seaweed
Coelenterata	Hydroids
Arthropoda	Barnacles
Bryozoa	Sea-mats
Mollusca	Mussels
Tunicates	Sea-squirts
Annelida	Tubeworms
Protozoa	Ciliates
Echinodermata	Sea stars

Total species on 73 ships (including yachts and barges)
Woods Hole, 1952

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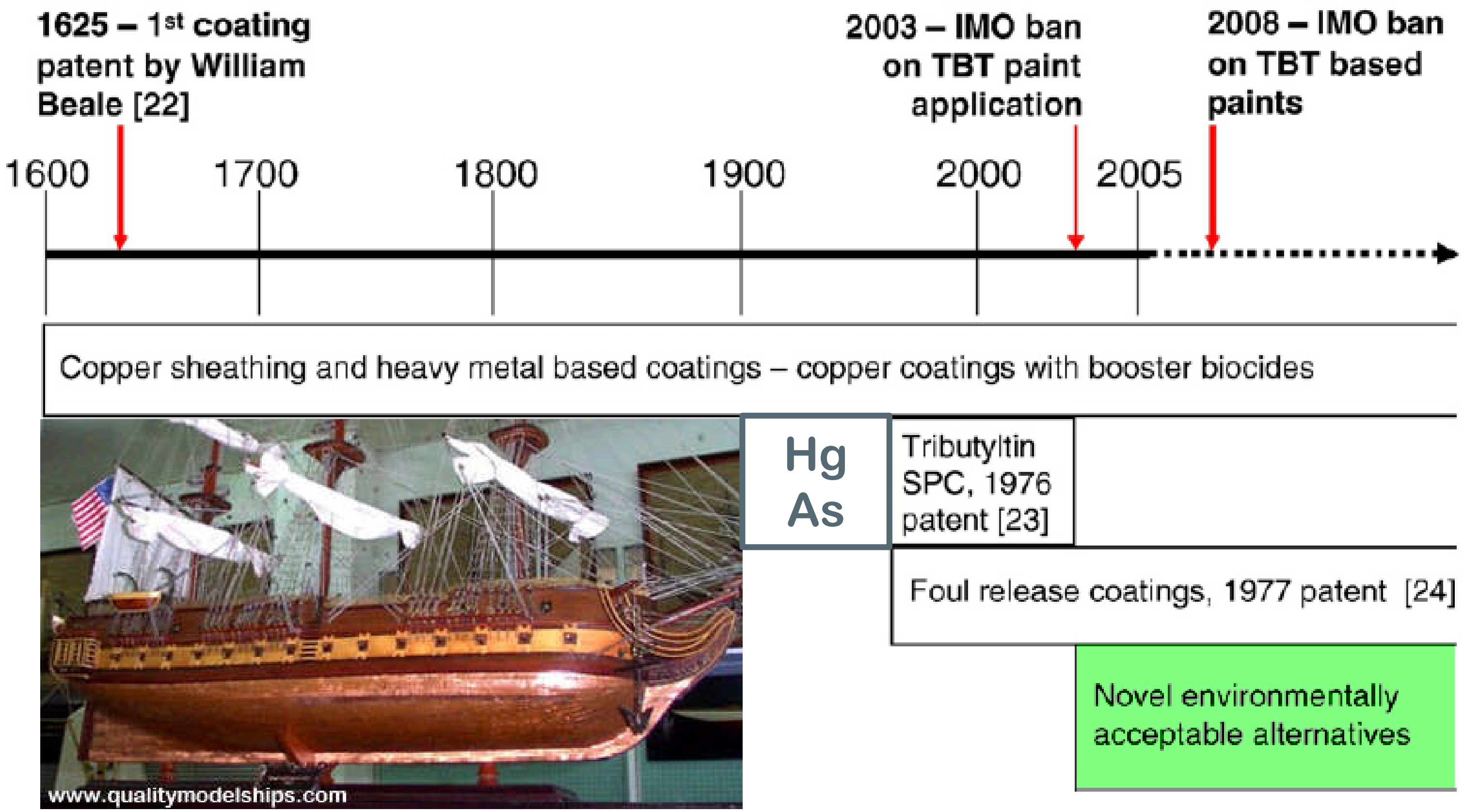
Solutions for Controlling Biofouling



Timeline for key antifouling generations

After Chambers, L.D., F.C. Walsh, R.J.K. Wood, K.R. Stokes, World Maritime Technology Conference, ICMES Proceedings, The Institute of Marine Engineering, Science and Technology, March 2006.

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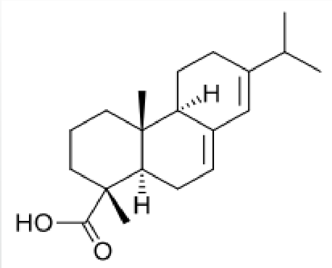
Traditional Antifouling Paint Binders

ROSIN has been used in antifouling paint binders for more than 100 years

Rosin

It is a natural product derived from pine tree resin. It consists mainly of **abietic acid** which is slightly soluble as the sodium salt in seawater (pH 8,0 ± 0,2)

Rosin allows seawater to penetrate the binder enabling the release of biocides (e.g. **Cuprous oxide**)



Abietic acid

A **LOW** rosin content leaves the binder system hard and insoluble → **"Contact Leaching" AF**

A **HIGH** rosin content means that the binder system is more soluble in seawater → **"Soluble Matrix" AF**

Soluble Matrix Paint Nomenclature

"All marine paint companies now market modern versions of the traditional Soluble Matrix antifoulings, with a wide variety of confusing nomenclatures to describe them:

Controlled Depletion Polymer antifoulings,
Eroding antifoulings,
Ablative antifoulings
Polishing antifoulings
Hydration antifoulings
Ref: E. Bie Kjaer, Prog. Org. Coatings 20, 339 (1999).

These all refer to the physical dissolution of the rosin-based antifoulings"

Ref: Andersen, C., in "Antifoulings", Kirk-Othmer Encyclopedia, 3rd ed.

Self-Polishing Copolymer (SPC) Paints

Self-polishing antifouling paint systems have enjoyed great success over the past 30 years. In these paints the biocide is **chemically linked** to the polymer binder, and is slowly released by hydrolysis in seawater. The hydrolysed polymer is also made soluble and is washed away leading to a smooth, self-renewing paint surface.

In the original SPCs the linked biocide was tributyl tin (TBT). This highly toxic chemical is now banned and new generation SPCs are being marketed which do not incorporate TBT.

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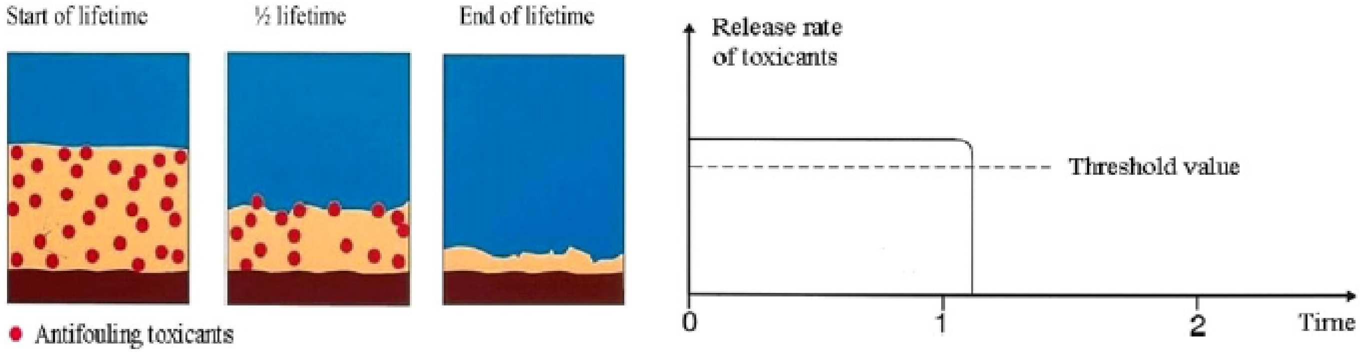
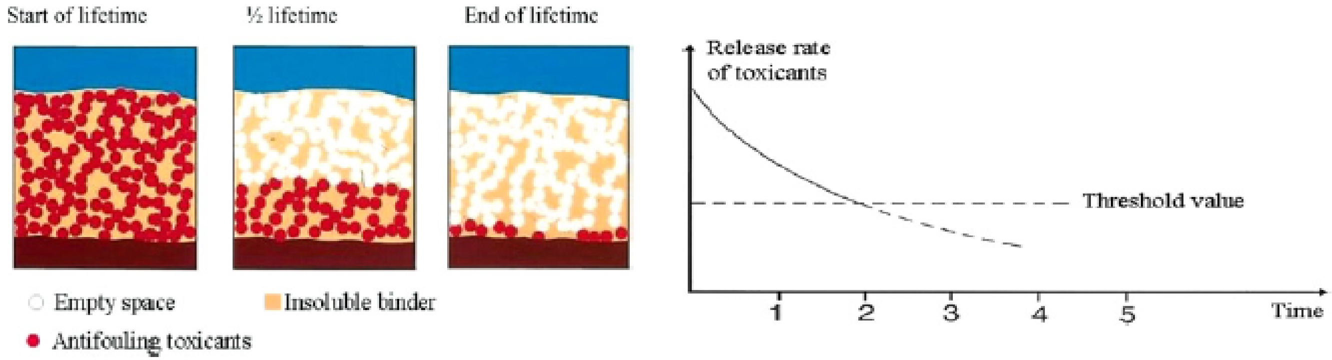
Biocide Release Mechanisms

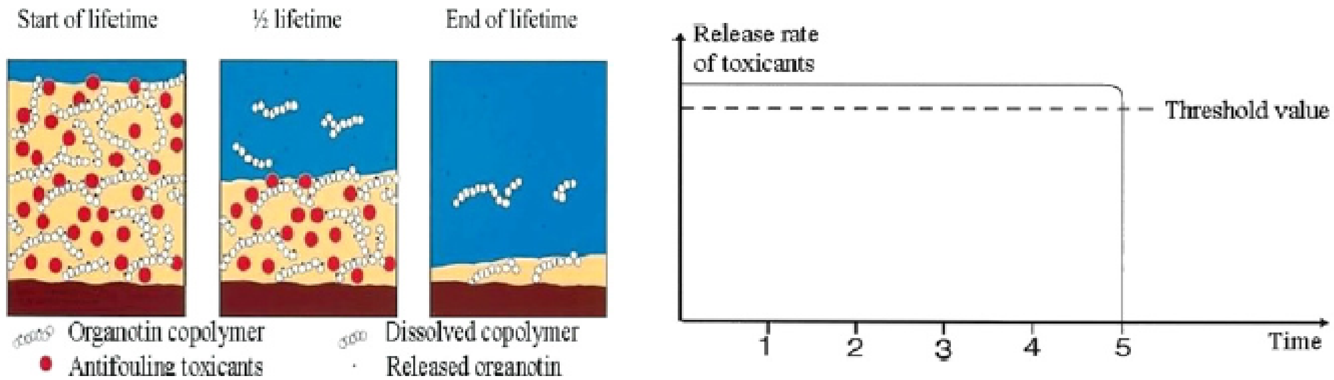
SOLUBLE MATRIX



INSOLUBLE MATRIX (contact leaching)



SPC (Self-polishing)



E. Almeida et al. / Progress in Organic Coatings 59 (2007) 2–20

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Fouling Release Coatings

Fouling Release Coatings (**FRC**) do not depend on a biocide for their antifouling effect. The coatings have low surface energy, and marine organisms cannot attach strongly to them. FRC coatings are normally based on silicones and/or fluorinated polymers (analogous to “non-stick” cookware)

Organisms can attach to the coatings when vessels are stationary, but are removed by hydrodynamic forces when the ship reaches a high enough speed to dislodge them.

On areas of the hull with low water flow, organisms may not be removed which can lead to the spread of invasive species.

Natural Products as Antifouling Agents

The surfaces of many marine organisms remain **relatively free of fouling growth** (*epibiosis*) – **natural products** that inhibit fouling have been isolated from various organisms. Some of these are being tested as potential AF paint biocides

BENEFITS:

- **Natural products** are **present in the marine environment**, so will have **low (or zero)** environmental impact.
- Natural products may be obtainable from **renewable resources**. For research purposes extraction is a simple procedure compared to synthesizing new compounds.

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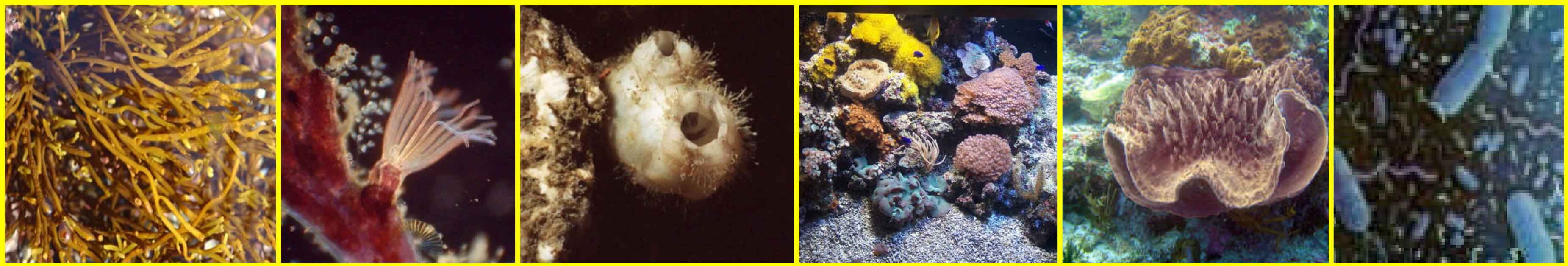
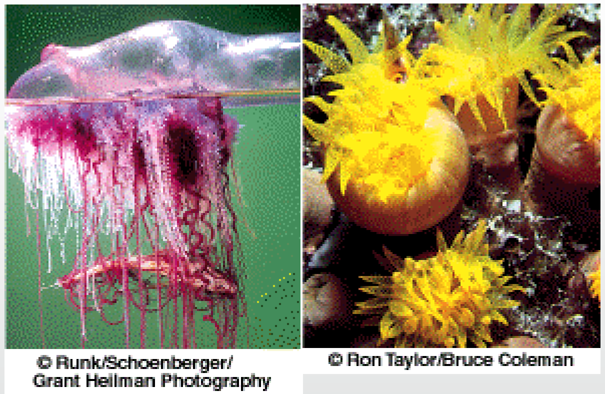
Sources of Marine Natural Products



Algae Bryozoans Ascidians Corals Sponges Bacteria



Cnidaria

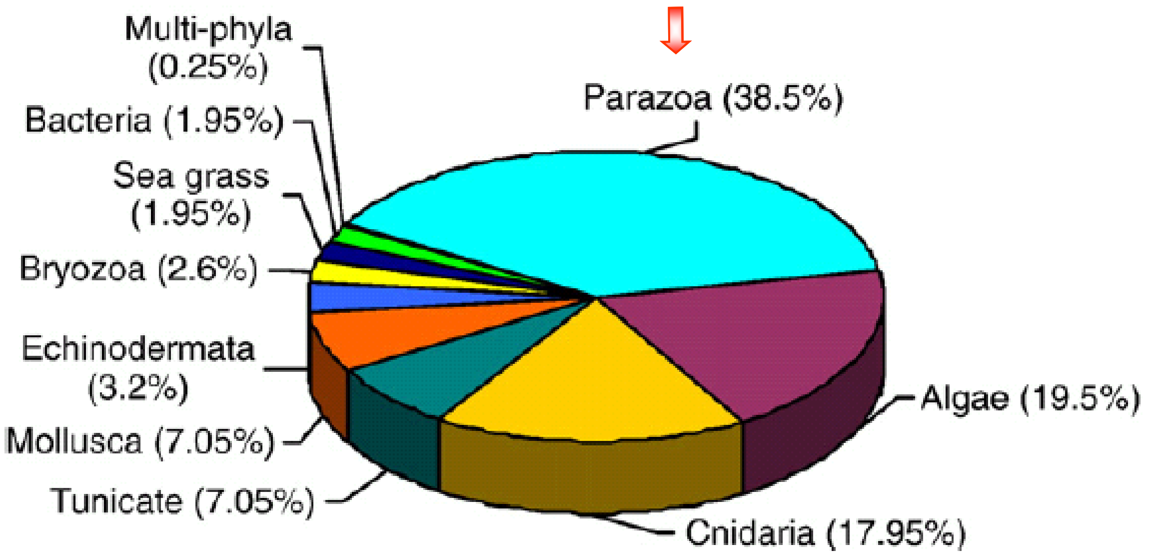


Fig. 4. Phyletic distribution of 160 reviewed marine species from which potential antifouling natural products have been extracted.

Ref: Chambers, 2006

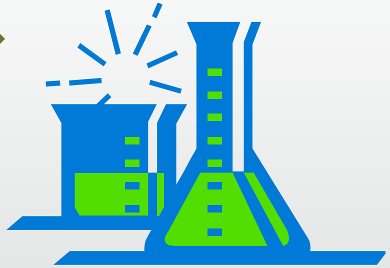
Extraction of Natural Products

1 kg fresh seaweed (*Chondrus crispus*)

Freeze-dried and crushed → 250 g powder

Extracted with solvent

Solvent removed under vacuum



YIELD: 1 g of extract

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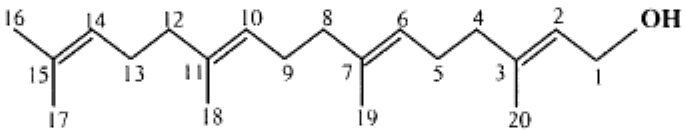
Diterpenes from *B. bifurcarta*

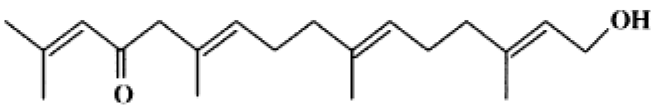


1

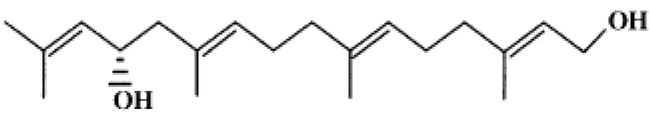
[1] Geranylgeraniol
cLog P = 6,3

cLogP is the calculated log of the partition coefficient between octanol and water – shows this compound is very **hydrophobic**

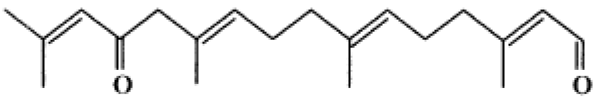
Bifurcaria bifurcata



2 Eleganolone



3 Eleganediol



4 Eleganolal

[3] is toxic to sea urchin eggs (antimitotic)
Valls et al., Phytochemistry, Vo l. 34, No. 6 pp. 1585-1588, 1993

Diterpene content and composition varies according to season and location of growth
Maréchal et al., J. Exp. Mar. Biol. Ecol., **313**, 2004, 47

Culioli et al., Biochem. Systematics and Ecology 28 , 2000, 185 -187

Issues faced by NP Antifoulants

- **Efficacy**
- **Availability**
- **Legislation**
- **Incorporation into paints**

To be successful as an antifoulant a Natural Product must exert a powerful effect, be readily available at an economic price, meet current (and future) legislation, and be capable of incorporation into paints

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Regulation of Biocides

The '**BIOCIDAL PRODUCTS DIRECTIVE**' (BPD) 98/8/EC entered into force 14 May 2000. **This regulatory scheme will ultimately require all biocidal products to be authorised before they can be placed on the EU market**.

The BPD definition of biocidal products is broad: **"Despite the name a biocide does not actually have to kill, it may instead make harmless, repel or control harmful organisms by chemical or biological means"**
http://www.hse.gov.uk/biocides/

REACH is the new European Community Regulation on chemicals and their safe use which entered into force on 1 June 2007. Non-dangerous substances **which occur in nature are exempt**. The definition applicable to these is: "*A naturally occurring substance as such, unprocessed or processed only by manual, mechanical or gravitational means, by dissolution in water, by flotation, by extraction with water, by steam distillation or by heating solely to remove water, or which is extracted from air by any means*" Ref: EC 1907/2006

Assessment of Antifouling Effects

- The antifouling (AF) effect of chemicals or coatings can be tested in the laboratory or in the ocean.
- In the laboratory bioassays are used
  - These usually measure the inhibitory effect and toxicity of chemicals against a single target species. Values such as **LC50** are obtained.
- Exposure of AF coatings in the ocean
  - Initially applied to static panels suspended from rafts and then as test patches on ships' hulls – this is the **ultimate test** of practical performance

Bioassays

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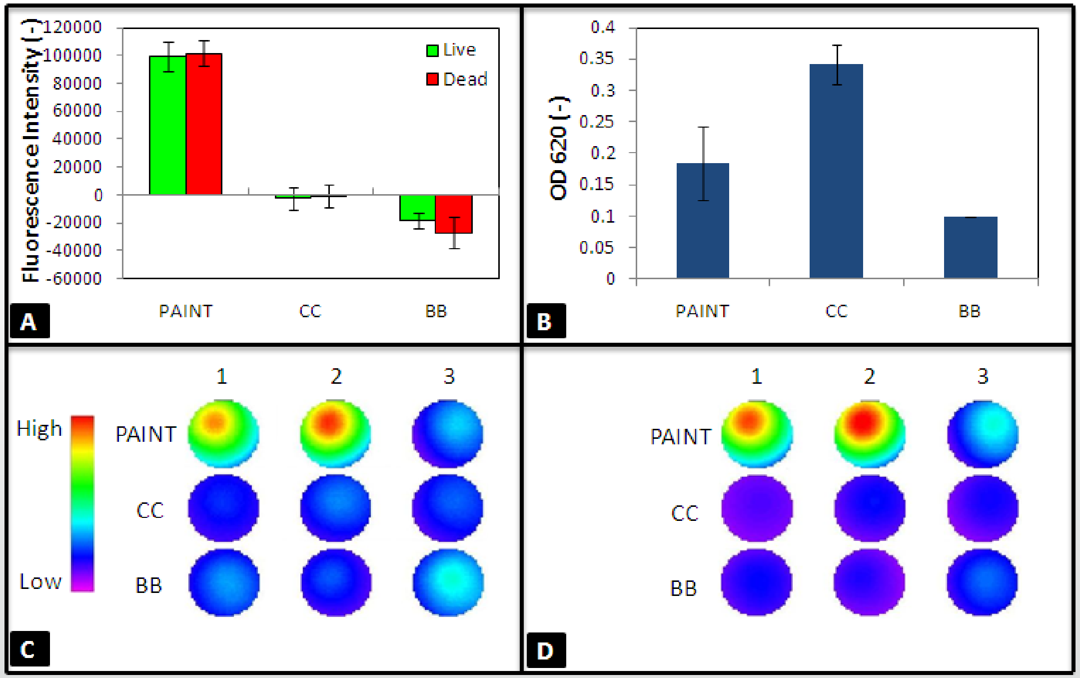
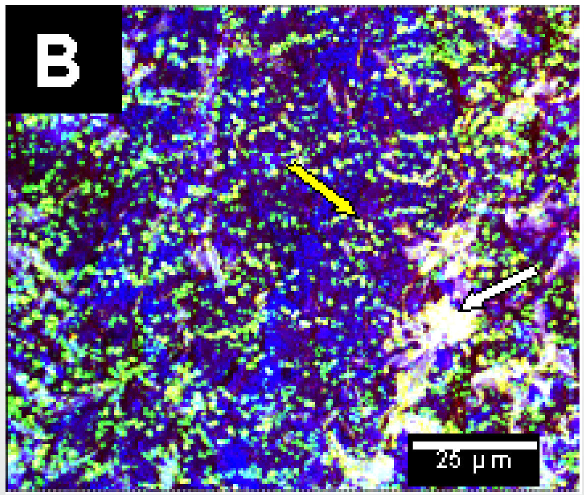
A biological assay, or **bioassay**, is a method for measuring the response of living organisms to a chemical substance.

High-throughput bioassays are being developed at UoS that measure the response of fouling organisms to AF **coatings**:



Bacterial growth (*Pseudoalteromonas sp*) on coatings with/without algal extracts visualised using a multidetection microplate reader



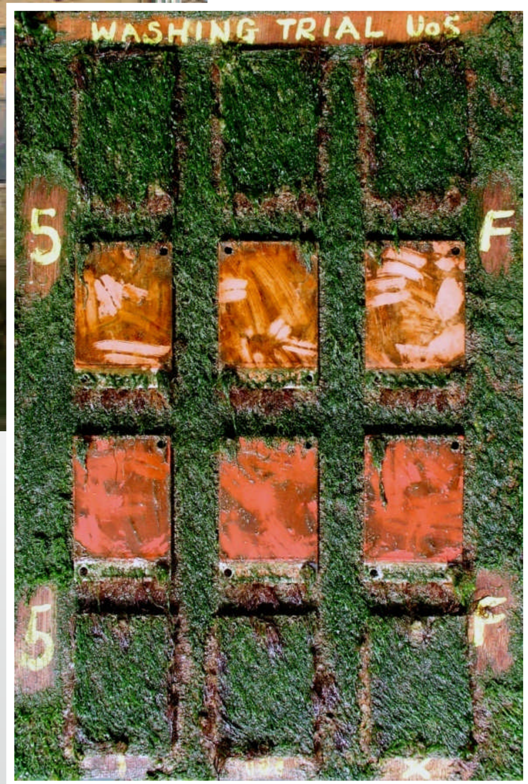
Confocal laser microscope image of bacteria on a polycarbonate coupon

Salta, M., et al – *submitted to Roy. Soc Phil. Trans. A*

Static Immersion Testing

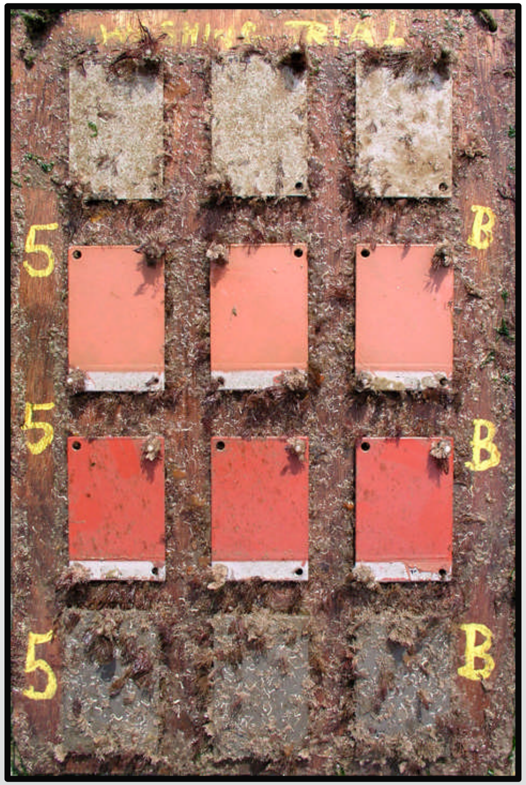
NOCS: National Oceanography Centre, Southampton (view North)

SE



Sunlit

NW



Shaded

Fouling growth on AF test panels shows the effect of illumination on fouling (exposed 1 month Aug 09)

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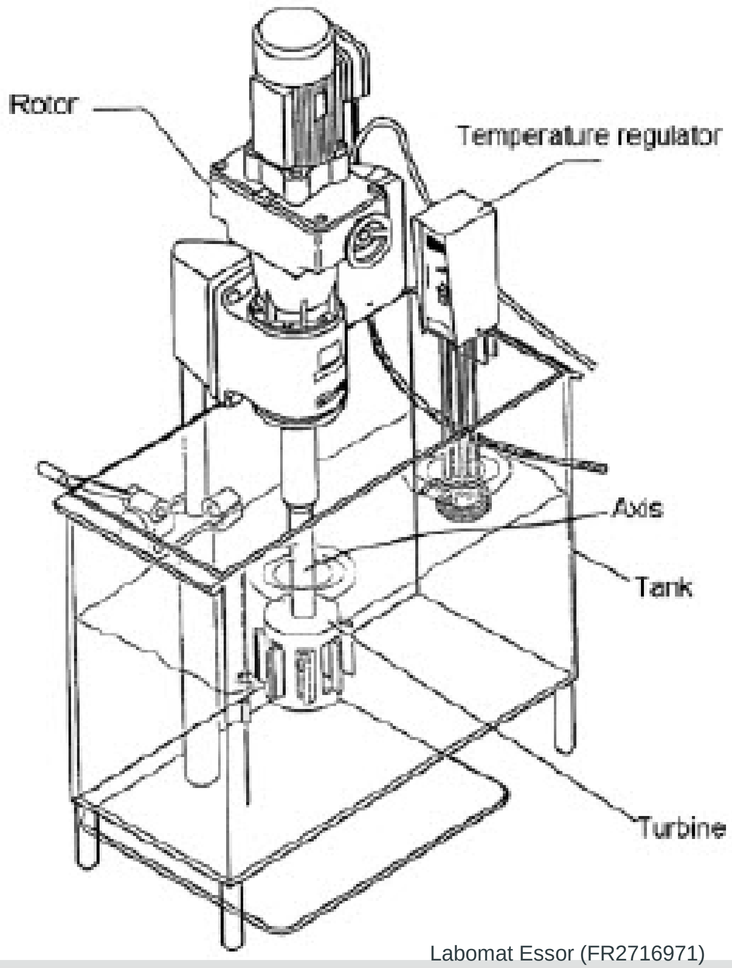
Rotor Testing of SPCs



Labomat Essor (FR2716971)

MAPIEM (Univ. du Sud, Toulon, France)

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SUMMARY

- Marine biofouling is a complex biological phenomenon
  - Displacing an organism from its niche habitat may allow another organism to take it over
- Combatting marine fouling is an on-going quest
  - Improvements are driven by legislative and operational factors
- Previous effective toxic systems will not be available
  - The recent banning of TBT has renewed the search for environment-friendly biocides
- Different surfaces will require different approaches
  - Ships and e.g. offshore rigs may require different systems
- The need for tailored approaches gives scope for much interesting research and collaborations between specialities

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Acknowledgements

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- Université du Sud, Toulon, France (MAPIEM)

- Dstl

...and Thank You for your attention!