Bioinspiration—the solution for biofouling control?

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Abstract
Most surfaces in the marine environment, both biotic and abiotic, are subject to biofouling. This has significant consequences for the safe and efficient conduct of marine activities. There is a pressing need to develop environmentally and economically acceptable methods to control the problem. In nature most plants and animals have evolved techniques that prevent or limit the process of fouling. These include chemical, physical, mechanical and behavioral responses. This paper reviews the knowledge with respect to natural antifouling methods, discusses similarities between natural mechanisms and existing antifouling technology and identifies potential future bioinspired approaches for the prevention of hull fouling specifically as they apply to US Navy requirements.

Introduction
Marine antifouling technology is at a crossroads. The IMO treaty to ban the use of the self-polishing tributyltin coatings went into effect in September 2008 and there is increasing opposition to the use of copper. Newer silicone-based fouling release technologies are providing solutions for constant service ships; however, they are relatively expensive, easily damaged and may become fouled (Swain et al 2007). A fouled ship has higher fuel consumption, increased costs and can aid in the dispersal of invasive species. Recently there has been increased attention to biofilms formed on silicone coatings due to their increase in drag penalty (Holm et al 2004, Swain et al 2007). Preventing the settlement of fouling organisms in a non-toxic manner is the ideal solution. It is therefore opportune to investigate new avenues which may inspire through a biomimetic approach.

Biomimetics refers to the study of the structure and function of biological systems as models for the design of engineering solutions (dictionary.com). Biomimicry is limited to copying or imitating natural solutions, which work but may not be the easiest or most ideal answers. Bioinspiration, on the other hand, expands upon biomimicry, not only copying biological concepts but also attempting to improve on them for the ideal engineering solution. In other words, bioinspiration adapts ideas from nature in a novel way to create feasible solutions to human problems; often the end use is different than the original biological one.

This paper reviews natural strategies for biofouling control and their possible application to the requirements of the US Navy. The Navy’s antifouling needs are unique and extremely challenging (table 1). In contrast to commercial shipping, where the vessels are underway for the majority of time, the Navy spends a large amount of time in port where ships are exposed to heavier fouling pressure (Ketchum 1952). A list of the desired characteristics of an antifouling coating as presented by Naval Sea Systems Command may be summarized as a 12 year design life, durable, repairable, compatible with existing cathodic protection systems, easy to apply and maintain, cost effective, smooth and effective both in port and at sea. Additionally, the product must be commercially available and registered with the Environmental Protection Agency, compliant with current and future air emission regulations and eliminate or significantly reduce copper emissions (Ingle 2007). The Navy’s requirements represent a ‘worst case scenario’ for antifouling; most of the solutions that would fulfill these requirements would surpass the requirements of other users and could easily be adapted to their needs.

All inert surfaces in the marine environment foul (Wahl 1989). Within seconds of immersion, a surface attracts and adsorbs chemicals. Next microorganisms settle and form a
Table 1. Natural antifouling mechanisms, their human equivalents and how they relate to Navy Ship requirements. + = positive, X = negative, n/a = not applicable, ? = unclear or dependent on specifics. Despite experience with many of these methods, there are still many questions. The answers depend on which specific human surrogate is used for comparison. For example the durability, smoothness and cost of a natural biocide based system will depend on the coating into which it is incorporated and the biocide itself.

<table>
<thead>
<tr>
<th>Equivalent</th>
<th>Biocides</th>
<th>Foul release</th>
<th>Self-polishing</th>
<th>Hull cleaning</th>
<th>Dry storage</th>
<th>Biocide containing self-polishing</th>
<th>Compliant silicone with oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Life span</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>+</td>
<td>+</td>
<td>?</td>
<td>X</td>
</tr>
<tr>
<td>Durability</td>
<td>?</td>
<td>?</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Repairable</td>
<td>+</td>
<td>?</td>
<td>+</td>
<td>?</td>
<td>+</td>
<td>+</td>
<td>?</td>
</tr>
<tr>
<td>Maintenance</td>
<td>+</td>
<td>?</td>
<td>+</td>
<td>X</td>
<td>+</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Smooth</td>
<td>?</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Compatible</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Cost</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>X</td>
<td>+</td>
<td>X</td>
<td>?</td>
</tr>
<tr>
<td>Environment</td>
<td>?</td>
<td>+</td>
<td>+</td>
<td>?</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>In port</td>
<td>+</td>
<td>?</td>
<td>X</td>
<td>+</td>
<td>+</td>
<td>?</td>
<td>X</td>
</tr>
<tr>
<td>Underway</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>X</td>
<td>X</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Table 2. A list of marine taxa and their antifouling strategies. Y = yes, it is used; N = not used or not reported used; ? = unclear if used.

<table>
<thead>
<tr>
<th>Taxon</th>
<th>Chemical</th>
<th>Physical</th>
<th>Mechanical surface renewal</th>
<th>Mechanical grooming</th>
<th>Behavioral</th>
<th>Combination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Echinoderm</td>
<td>Y</td>
<td>?</td>
<td>N</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>Bryozoan</td>
<td>?</td>
<td>N</td>
<td>N</td>
<td>Y</td>
<td>N</td>
<td>?</td>
</tr>
<tr>
<td>Sponge</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>Soft coral</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>Stony coral</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>?</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>Crustacean</td>
<td>N</td>
<td>?</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Bony fish</td>
<td>Y</td>
<td>?</td>
<td>?</td>
<td>N</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Dolphin</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
<td>Y</td>
</tr>
</tbody>
</table>

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E Ralston and G Swain

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E Ralston and G Swain

biofilm of extracellular polymers. Diatoms move in on a time frame of days to weeks followed by macrofouling like barnacles and tubeworms (Wahl 1989). This is not strictly succession, as previously thought. The timing of these events depends on the concentrations or densities of the foulers and the characteristics of the substrate (Clare et al 1992). However, adsorbed chemicals and biofilm components can change the chemistry, energy and wettability of the surface and make it more or less attractive or more easily adhered to (Baier 1972, Meyer et al 1988). Despite this surface conditioning, it is important to note that many macrofoulers are not obligate settlers to biofilmed surfaces, some prefer clean surfaces and invertebrate larvae can settle very quickly after immersion if they are present at the surface and competent to settle (Roberts et al 1991, Clare et al 1992). Those plants and animals that do not experience epibiosis are, therefore, remarkable. The antifouling mechanisms employed by organisms include chemical, physical, mechanical, behavioral or a combination of methods (table 2; Bers and Wahl 2004, Pawlik 1992, Wahl 1989). Before a bioinspired approach can be investigated, however, a full understanding of the biology and ecology of the structure is necessary. It is this holistic approach and how it may apply to the US Navy that will be the focus of this review.

Chemical

Much effort has been directed to identifying natural chemistries that may act as antifoulants. By the early 1990s, over 2000 natural chemistries had been described from marine organisms (Pawlik 1992). Coatings that incorporate biocides or deterrents that leach into solution mimic this approach. The activity of natural chemistries includes low pH, deterrents, anesthetics, attachment and/or metamorphosis inhibitors or toxic chemicals. The specific chemicals that have been isolated have been discussed in several reviews (Pawlik 1992, Fusetani 2004, Clare 1996, Rittschof 2000) so only select examples will be included here. For most natural chemicals, the mechanism by which antifouling is achieved has not been elucidated; however, in the algae Delisea pulchra, furanones were found to inhibit bacterial colonization by interfering with a specific class of regulatory pathways (Steinberg et al 1998). The natural chemical may be surface bound or water soluble (Wahl 1989, Rittschof 2000). Unfortunately, most of the investigations have used crude whole plant and animal extracts at unnatural concentrations, which does not mimic the holistic aspect of natural antifouling. Primarily, antifouling by these means has been inferred from clean surfaces and the presence of chemicals in macerated samples or from laboratory tests where larvae either died or avoided certain substrates.
Field data have rarely been collected in any of these instances (Pawlik 1992, Walters et al 2003). However, chemicals with antifouling activity have been isolated from sponges, soft corals, a limpet and algae that are either available at the surface or released when the organism is disturbed (de Nys and Steinberg 2002, Hellio et al 2002, Fusetani 2004). There are anti-attachment chemistries found in the mucus of certain echinoderm species (Bavington et al 2004). Fish mucus contains substances shown to lyse cells for an antimicrobial effect (Shephard 1994, Videler et al 1999, Ebran et al 2000). Many tunicate species have extremely low (acidic) pH body fluids available at or near the body surface. These species showed little epibiosis (Stoecker 1980) especially in areas of the body with the highest density of acidic vacuoles (Hirose et al 2001). Some unfouled tunicates also contain chemicals that are cytotoxic, antimicrobial and antiviral when whole body extracts are prepared (Davis and Wright 1989). The red algae Delisea pulchra prevents fouling by surface available chemicals that interfere with cell signaling in bacteria and algae and prevent attachment in barnacles (Steinberg et al 1998). The barnacles Balanus glandula and Semibalanus balanoides have been found to avoid settling in areas where predatory whelks had crawled. This was attributed to predatory kairomones in the mucus trails of the snails (Johnson and Strathman 1989, Davies and Hawkins 1998). The eggs of many organisms, including corals and fish, are highly protected by antimicrobial chemistries. In the case of corals, it is the eggs that contain zooxanthellae that are protected (Marquis et al 2005, Ramasamy and Murugan 2007). Frequently, chemistries that were attributed to sponges, algae and other organisms are, on closer examination, produced by surface-associated microorganisms (Clare 1996, Krug 2006).

As coatings have become more effective at preventing or ameliorating the effects of macrofouling, attention has shifted to both the positive and negative effects of biofilms. Some organisms, like the tubeworm Hydroiades elegans, need a biofilm to induce settlement while others, like most barnacles and some bryozoans, may settle with or without a biofilm (Brancauto and Woollacott 1982, Burke 1983, Clare et al 1992, Keough and Raimondi 1995, Rittschof 2000, Faimali et al 2004). Some biofilms are detrimental to settling larvae due to toxic or deterrent chemicals from the microfoulers making up the biofilm (Pawlik 1992, Dobretsov et al 2006). Holmstrom and colleagues (1992) found that 5 out of 40 bacterial strains produced deterrent or toxic compounds into the water column above the biofilm that prevented settlement of barnacle and tunicate larvae. Many of these bacterial compounds are associated with specific pigments and are dependent on the age of the biofilm (Holmstrom et al 1992, Faimali et al 2004). Sponges have a higher density and diversity of bacteria at their surface than the surrounding water and substrate and their surfaces are frequently unfouled by diatoms or macrofoulers. This has been attributed to secondary metabolites from the sponge or from the biofilm or possibly from a combination sequestered at the surface (Dobretsov et al 2005). The algae Ulva australis contains two bacterial strains on its surface that inhibit fouling at realistic low concentrations (Rao et al 2007). Greater than 50% of the bacterial strains from the soft coral, Dendronephthya, have been found to range from non-inductive to inhibitive for larvae of the tubeworm Hydroiades elegans in laboratory assays (Dobretsov and Qian 2004).

There are benefits and drawbacks to searching for a bioinspired or biomimetic chemical antifoulant. Chemicals have been in use since the earliest ship paints and so there are well-developed binder chemistries that can be employed to make a coating (Laidlaw 1952, Omae 2003). They can be easy to apply and maintain and will most likely be compatible with present technology. Chemical antifoulants are effective both in port and underway when incorporated into appropriate paints. The main negative of antifouling based on natural chemistries is the lifespan with most lasting days to months, not the years required (de Nys and Steinberg 2002). This is not surprising as chemical deterrents used by nature cannot create toxicity to the organism, and therefore, typically have lower toxicities and shorter half-lives than the presently favored biocides such as copper, zinc pyrithione, isothiazolone (Sea-Nine), etc (Clare 1996, Evans and Clarkson 1993, Rittschof 2000, de Nys and Steinberg 2002). Additionally, chemical licensing has become more rigorous and expensive, costing millions of dollars to get a novel chemistry approved for use (Rittschof 2000). Finally, there are many unknowns associated with the use of chemicals to prevent fouling. Even the most studied natural chemistries are not yet to the stage of incorporation into paint, so questions of cost, durability, repairability and coating smoothness remain. Furthermore, the molecular structure of most natural chemical compounds is large and complex and will be expensive to produce or obtain (Rittschof 2000). The environmental friendliness of most of these chemistries is still untested and unknown. The ideal natural product would be non-toxic, have a high activity against a range of fouling organisms and must be from an organism that can be mass cultured or, more preferably, be a chemistry that can be synthesized in a laboratory (Hellio et al 2002, Rittschof 2000).

Physical

Physical properties that may be used for fouling prevention include surface energy and topography. These have been extensively investigated as engineered antifouling solutions. It has been proposed that adhesion is reduced to the point that epibionts are easily removed at an ideal surface energy range of 20–30 dyn cm⁻¹ (Baier 1972, Dexter 1979). This range has been found on the surface of killer whales (Baier 1986), gorgonians (Vrolijk et al 1990) and on the surface of healthy teeth (Glantz et al 1991, Baier 1986). Surface energy can also affect initial settlement and colonization of surfaces in a species-specific manner. Avoidance of low surface energy surfaces is found in bacterial biofilms from salt, brackish and freshwater (Meyer et al 1988) and barnacles (Rittschof and Costlow 1989) with barnacles showing further preference for substrates with intermediate wettability (Dahlstrom et al 2004). Bryozoans showed an opposite settlement pattern, preferring substrates with lower initial surface wettability in laboratory and field assays (Rittschof and Costlow 1989). Recent observations on diatoms suggest that these organisms...
may favor low energy surfaces (Molino and Wetherbee 2008, Anderson et al. 2003).

Fouling release surfaces in nature have also been associated with the presence of waxes (the best known is the lotus leaf), surfactants, oils, mucuses or fluorinated and methylated compounds (Wahl 1989, Shephard 1994, Baum et al. 2003, Krug 2006). Certain plants and animals have surfaces that release fouling (Wahl et al. 1998, Vrolijk et al. 1990). This, along with compliance (Gray et al. 2002), is the technology that is frequently cited to explain the effectiveness of silicone foul release coatings. Some organisms, such as algae, remove settled epibionts by bending and having greater ability to flex than heavily calcified epibionts such as barnacles and tubeworms (Walters et al. 2003).

Surface topography has been shown to provide cues for settling larvae (Crisp 1984). Larval animals and plants seek refuges of approximately their size as ideal settlement sites. A surface that is exceptionally smooth would prove unattractive as it offers no refuge from predation or shear stress (Walters and Wethey 1996, Kohler et al. 1999). Additionally, surfaces with certain scales of topography may deter settlement or reduce adhesion of specific organisms. The scale and shape of the texture affects the area available for attachment of settling larvae. A sharp small texture, in reference to the size of the settler, would cause the organism to attach more strongly due to multiple attachment points. A texture of the same size or larger would provide a large area for adherence and a refuge (Callow et al. 2002, Scardino et al. 2006). In laboratory assays with barnacle cyprid larvae, it has been shown that surface texture on the micro-scale increases the amount of time spent searching and the likelihood for rejection (Bermisson et al. 2000). Conversely, barnacles are found to recruit preferentially to pits that are of the same size or slightly larger than the juveniles (Crisp 1984, Hills and Thomason 1998, Herbert and Hawkins 2006). Spines are hypothesized to prevent settlement and overgrowth of fouling organisms (Dyrynda 1986, Wahl 1989) and the hairy spat of the mussel Mytilus is purported to prevent fouling by conspecifics (Dixon et al. 1995). The crab Cancer pagurus has two scales of texture while dogfish egg cases and the brittle star Ophiura texturata have one scale of texture spread heterogeneously across their surfaces (Bers and Wahl 2004). In mussels, the homogeneous structured surface ridges have been reported to prevent fouling (Scardino and de Nys 2004). The effect of topography on settlement generally only lasts a few months or less, is size dependent and is effective against only specific fouling organisms, primarily those with searching behavior (Bers and Wahl 2004).

Physical methods of natural fouling defense have often been inferred but seldom proved. Testing the wettability of cells and living tissue is challenging. The validity of testing wettability in air when concerned with aquatic systems has been called into question. The importance of topography has been tested in laboratory assays using artificial surfaces; however, the long-term efficacy, biological appropriateness and validity in the field have yet to be shown. Surface wettability may elicit a different response from different organisms, with some responding favorably to hydrophobic surfaces and others preferring hydrophilic surfaces (Callow et al. 2002, Dahlstrom et al. 2004). Surface topography is scale dependent where both the size of the texture and the size of the organism are important (Scardino et al. 2006, Schumacher et al. 2007). Therefore, finding a topography that provides universal deterrence may be difficult. The antifouling attributed to physical methods is short-lived, often a month or less. On the positive side, these methods are likely to be compatible with existing technologies and environmentally friendly.

Mechanical

Mechanical cleaning is employed as a fouling control strategy for ships and structures that do not use antifouling coatings or for when a coating has become fouled. In nature, however, cleaning is typically gentler and may be described as grooming. Grooming primarily involves specialized structures that either pick or sweep the animal’s surface (Wahl 1989). Decapod crustaceans have specialized brush structures for grooming, each tailored to remove epibiosis from specific areas of the animal including the gills and swimming appendages (Acosta and Poirrier 1992, Bauer 1981, Batang and Suzuki 2003). In addition to crustacean brush grooming, echinoderms and bryozoans have been shown to pick macroepibionts off of their surfaces using specialized structures such as pedicellaria (echinoid echinoderms; Campbell and Rainbow 1977) or avicularia and vibracularia (bryozoans; Dyrynda 1986). Ciliary cleaning in conjunction with mucus may help molluscs, corals, worms and many others prevent surface fouling (Wahl et al. 1998). Some animals form symbiotic relationships with one organism gaining protection and/or food in return for cleaning. For example, crayfish have branchiobdellid annelids in their gill chambers which may feed on epibionts (Brown et al. 2002) and fish are known to frequent ‘Cleaning Stations’ where other marine organisms will remove unwanted fouling (Poulin and Grutter 1996). Grazing is another way in which mutual grooming can keep surfaces clear of fouling. Certain snail populations are clean at high densities and fouled at lower densities. When snails from the high-density populations are caged to prevent sympatric grazing, they foul heavily (Wahl and Sonnichsen 1992, Wahl et al. 1998). In natural environments, however, cleaning may be insufficient to prevent fouling. In experiments performed on the crayfish Procambarus clarkia, it was found that there was no difference in fouling coverage between crayfish with cleaning apparatus removed and those that were intact (Bauer 2002). Additionally, in the asteroid starfish Acanthaster planci, the pedicellaria were found to be too widely spaced and unresponsive to tactile cues from both bryozoan and algal stimuli to prevent fouling despite having a clean surface (Guenther et al. 2007).

For man-made structures, cleaning is an effective mechanism for removing fouling especially when paired with a hard durable coating. This method is effective in port and is compatible with existing technologies. However, cleaning does require the deployment of machinery and usually divers, may damage the coating, and if applied to antifouling coatings, may release undesirable amounts of biocide. Furthermore,
cleaning may enhance the recruitment of organisms to a surface that has been cleaned or that contains cues from previously removed conspecifics (Floerl et al 2005).

The other mechanical method to remove fouling is renewal of surface layers. The best known is ec dysis, or molting as used by crustaceans (Wahl 1989). The stonefish Synanceja horribilis has also been shown to undergo periodic skin molting to remove fouling (Bakus et al 1986) and seaweeds often slough their surface layer. They can either shed a large area of cells simultaneously or the cells may degenerate individually (Keats et al 1997). Most marine organisms use mucus as a membrane that separates them from the environment (Davies and Hawkins 1998, Denny 1989, Shephard 1994). Corals which produce copious amounts of mucus are perhaps the best known (Dyrynda 1986, Brown and Bythell 2005). The sheeting action of the mucus makes adhesion difficult, fouls cilia and sensory apparatus of settling organisms and removes organisms that have managed to attach (Dyrynda 1986, Wahl 1989, Shephard 1994, Wahl et al 1998).

Mechanical methods of defense against fouling are imperfect. Grooming is only effective on parts of the body the animal can reach and has the apparatus to clean. The period of time between molts and sloughs may be too long to prevent fouling completely. Mucus production can be very effective but tends to be energetically demanding (Davies and Hawkins 1998).

Surface renewal as a biomimetic solution in modern day antifouling coatings is seen in self-polishing paints. In these systems, polymers have been developed where the surface hydrolyzes and dissolves in seawater leaving a renewed surface (Candries 2000). To date, this technology has only proven commercially viable when combined with biocides and they provide durable and repairable coatings that require little maintenance, are easy to use, compatible with existing technologies and are usually hydrodynamically smooth. The polishing or ablation rates required for a biocide-free coating are too high for practical purposes. A better understanding of systems may lead to the development of a biocide-free renewable surface that will not require biocides to work as an effective antifouling solution.

Behavioral

Behavioral mechanisms, described as direct and indirect active avoidance of fouling and include burying, hiding or crypsis, change in salinity and emersion into air, are considered the primary mechanism of antifouling for many organisms along with periodic molting (Becker and Wahl 1996). Many animals burrow into the sediment which scrapes epibionts from their surfaces and removes them from much of the fouling pressure (Wahl 1989). For animals that have a high tolerance for changes in salinity, moving between fresh and salt water can remove less tolerant epibionts. Likewise movement between water and air or into areas with vastly different oxygen concentrations such as burrows will deter or remove most epibionts. Activity at night or hiding in dark crevices can lessen the amount of algal fouling (Wahl 1989, Becker and Wahl 1996, Wahl et al 1998). The shells of free-living crabs are much less densely fouled than empty carapaces and substrate which is attributed to burrowing, migration into air and/or burrows and grooming. Cleaning by burying and movement patterns tends to be an imperfect antifouling method as it selects for specific organisms and allows the surface to foul in the interim. Additionally, the effectiveness of movement as an antifouling method depends on the rate and level of change in salinity, the tolerances of the specific fouling organisms, the similarity of source and recipient habitat and the habitat requirements of the transported species (Brock et al 1999).

Mimicking behavioral methods of antifouling is arguably the oldest and most used fouling preventative for some vessels. For small boats, simple activities such as trailering or lifting boats out of the water between uses prevent fouling. For ships, such activities are impractical; however, moving into freshwater as in bodies of water such as the Panama Canal will remove much of the marine fouling. Brock and colleagues (1999) found that moving a heavily fouled ship from marine into freshwater for 9 days then back to salt water was effective in removal of 90% of fouling organisms from the hull.

Combination

It is unlikely that one mechanism on its own is sufficient to control fouling and research and observations show that organisms usually use a combination of methods to combat fouling. For instance, the mussel Mytilus edulis removes many settling larvae during filter feeding and it is hypothesized that the periostracal hairs create unattractive shell topography (Wahl et al 1998). Perna viridis also filter feeds removing many macrofoulers before they settle and shell grazing by co-occurring gastropods removes microfouling organisms (Becker 1995). Filtering mechanisms are likely just byproducts of feeding and probably cannot be categorized as an antifouling method. Many crustaceans groom, shed their shells and have behavioral patterns such as burying and movement among environments that contribute to their clean exteriors (Becker and Wahl 1996, Wahl et al 1998). Echinoderms groom their surfaces, slough and use anti-adhesive mucus, have secondary metabolites that either deter microfoulers or attract deterrent bacteria and may use a strong negatively charged cuticle to prevent fouling (Bakus et al 1986, Bryan et al 1996, McKenzie and Grigolava 1996, Bavington et al 2004). Sharks have been hypothesized to use a combination of the flexion of denticles over a compliant surface to prevent settlement of fouling organisms (Kesel and Liedert 2007); however, this has yet to be proven. The red algae Dilsea carnosa is relatively well studied with respect to antifouling. Its clean surface has been attributed to a combination of secondary metabolites and surface sloughing (Nyland and Pavia 2005).

This holistic approach has not been adapted to ship antifouling in an environmentally acceptable or realistic manner. The closest humans have come to a multi-pronged approach is via self-polishing biocidal coatings and frequent cleaning of biocidal, inert and foul release coatings. Although these have been relatively effective, concerns over release of chemicals, damage to coatings and the reactive nature of
cleaning once a hull is heavily fouled make these imperfect. When research is directed to studying natural antifouling mechanisms, there is a tendency to focus on one mode of action without considering the synergistic effect of the combined mechanisms. As such, there are no real answers to whether a holistic antifouling suite will fit the Navy requirements. More testing of combined ecological antifouling strategies is needed.

**Bioinspired applications**

To date, most bioinspired research has been directed to the discovery of natural chemicals, but there are many issues associated with such an approach. These include proving environmental compliance, incorporation into coatings, ecological relevance, length of activity and the inability associated with such an approach. These include proving discovery of natural chemicals, but there are many issues to date, most bioinspired research has been directed to the testing of combined ecological antifouling strategies is needed.

Bioinspired Underwater Grooming, a proactive autonomous underwater hull grooming robot that will travel over the hull to both speed the rate of re-colonization and may increase the risk of transport of non-indigenous species (Floerl et al. 2007). Enzymes can also act indirectly by converting compounds in the water to antifoulants, control the release of active ingredients from coatings or facilitate polishing of coatings (Olsen et al. 2007). In order to create a viable enzyme coating, several negative aspects must be overcome, such as the expense, instability and the specificity leading to a need for more than one enzyme to control all fouling (Abarzua and Jakubowski 1995). In addition, any enzyme will need to be approved for use which is an expensive and time-consuming process (Olsen et al. 2007, Rittschof 2000). Still, because they are biodegradable and available, though expensive, enzymes are an area of interest for continued research.

More recently, researchers have been revisiting other avenues of bioinspired antifouling. Mimics of the topography from crustose coralline algae, crabs, dogfish egg cases, brittle stars and mussels have been shown to reduce settlement in short-term laboratory experiments (Bers and Wahl 2004, Scardino and de Nys 2004). These are based on attachment point theory which predicts lower settlement on microtextures with a smaller size than the width of the settler and higher settlement where the texture is wider than the settler when the larvae exhibits choice during settlement (Scardino et al. 2008). The ‘Sharklet’, an example of the use of topography in an engineered surface to prevent fouling, has tested well in laboratory assays against Ulva spores and Balanus amphitrite cyprids (Carmen et al. 2006, Schumacher et al. 2007) and is being investigated in scale-up experiments for commercialization.

The Navy cleans their vessels once a certain level of fouling is reached (Cologer 1984). This is a reactive measure and caution must be exercised as cleaning has been shown to both speed the rate of re-colonization and may increase the risk of transport of non-indigenous species (Floerl et al. 2005). One new idea is to mimic more natural grooming rather than a cleaning. This is the idea behind the ‘HullBUG’ (Hull Bioinspired Underwater Grooming), a proactive autonomous underwater hull grooming robot that will travel over the hull of a ship while it is in port. Its mode of action is a gentle wiping or brushing that will be done at sufficient frequency to prevent macrofoulers from permanently attaching.

Most of the biologically based antifouling solutions that have been investigated are biomimetic rather than bioinspired. Only recently have researchers begun looking at novel uses for natural solutions. For example, the use of dopamine has been investigated for use in antifouling coatings formulations to assist in adhering the coating to any substrate. This was inspired not by a natural antifoulant but by the adhesive system in mussels, a common fouling organism (Lee et al. 2007). The dopamine-modified coatings outperformed standard silicone coatings in laboratory assays comparing both settlement and adhesion of the diatom Navicula perminuta and the algae Ulva linza (Statz et al. 2006). To our knowledge, this coating has not been tested against invertebrate fouling or field tested. With innovations like this, natural systems can be used in novel and nontraditional ways to improve engineered solutions to fouling.
Summary

This review was initiated to investigate natural mechanisms that could be identified to inspire solutions for Navy vessels. These ships can be considered to occupy two ecological niches: in port, they are more akin to corals, whereas, while they are underway they are more like dolphins. In both organisms, a combined approach is used to keep a clean surface. Corals have been found to use antibacterial compounds in mucus to select for specific surface bacterial populations that are different than bacteria in surrounding waters and substrates. These bacteria engage in chemical warfare against disease causing microorganisms and keep the corals healthy and, in conjunction with mucus sloughing, prevent macrofouling (Ritchie 2006). Corals have also been shown to sequester various secondary metabolites in their surface mucus layer (Brown and Bythell 2005) and to slough this surface mucus layer in conjunction with mucus sloughing, prevent macrofouling causing microorganisms and keep the corals healthy and, in a combined approach, prevent fouling of coral surfaces. Whales and dolphins are hypothesized to use microtopography and a heterogeneous amphiphilic surface gel in conjunction with a zymogel that contains enzymes which hydrolyze the adhesives of fouling organisms (Baum et al 2003, Meyer and Seegers 2004) although this has not been proven in situ. Additionally, the similarity of dolphin skin to oral mucosa in terms of mucus films and surface roughness is a means of self-cleaning has been noted (Fish and Rohr 1999). These have been hypothesized to help remove fouling at the earliest stages especially when dolphins jump from the water (Baum et al 2003). Based on current knowledge and technology, the most promising biodesigned solution to fulfill Navy requirements maybe grooming in combination with foul-release or toughened silicone coatings.

Marine organisms have in many instances achieved long-term protection from biofouling using short-term, renewable mechanisms. This is attributable to the use of a combination of antifouling methods including chemical defense, physical surface characteristics, grooming and shedding and behaviors that prevent or ameliorate fouling pressure. At present, our knowledge is incomplete and it is not possible to identify all relevant information to describe natural antifouling. Despite this, biomimetics may provide inspiration for an engineered solution to the fouling problem, many of which are already being investigated. The challenge lies in identifying and selecting the best natural systems that may be adapted to solve this problem. More research is required to understand the holistic ecology of natural antifouling and will necessitate increased communication among scientists and engineers. It is by better understanding how long-lived organisms, such as dolphins and corals, maintain their surfaces free from fouling that we may develop a biodesigned engineered antifouling solution.

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