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Environmental impact of antifouling technologies: state of the art and perspectives

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ABSTRACT

1. Marine fouling affects most man-made surfaces temporarily or permanently immersed in the sea, resulting in significant (or substantial) economic costs. Intense research is aimed at preventing or reducing fouling.
2. The most widespread solution to avoid fouling formation is to make surfaces unsuitable for settlers, coating them with antifouling (AF) paints containing toxic compounds. Most AF agents (e.g. tributyltin, (TBT)) have undesirable effects on non-target species, including commercially important organisms.
3. To date, the use of TBT in AF paints has been restricted (but not prohibited) in a number of countries and new biocides are in use.
4. The environmental problems posed to marine systems by AF technologies are here briefly reviewed.
5. New approaches focusing on alternatives to the use of biocidal AF paints are also considered and discussed.

KEY WORDS: antifouling (AF); ablative copper AF; biomonitoring; fouling; foul-release coatings; imposex; TBT-based AF

THE PROBLEM OF FOULING AND ITS PREVENTION

The organisms that settle on man-made surfaces are known as *fouling*. They come from the water column as propagules searching for a hard substrate to complete their life-cycle. The development of fouling begins as soon as a suitable substrate is immersed in the sea. Surfaces are immediately conditioned by organic molecules, a prerequisite for the settlement of microfouling, including bacteria, fungi and protozoans. The development of fouling communities proceeds with the establishment of macrofoulers such as macroalgae, sponges, cnidarians, polychaetes, molluscs, barnacles, bryozoans and tunicates (Woods Hole Oceanographic Institution, 1952).

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Fouling affects the hulls of ships, oil rigs, mariculture cages, pipelines, heat exchangers, and seawater intakes in general. Moreover, it accelerates surface corrosion, increasingly damaging protective coatings (Haderlie, 1984). Fouling greatly increases the frictional resistance of ships, reducing their speed and increasing fuel consumption. Ship hulls, thus, need to be periodically cleaned and restored. The US Office of Naval Research estimated a total of US$700 million was spent by the US Navy in 1981 for ship maintenance due to fouling removal and prevention (Alberte *et al*., 1992).

A common solution to avoid fouling is to make surfaces unsuitable for settlers. Surfaces are thus coated with antifouling (AF) paints containing toxic compounds. These biocides are present at the paint–water interface and affect settling organisms (Costlow and Tipper, 1984). Fouling prevention requires a constant threshold concentration (the 'effective concentration') of biocides on the painted surface. The toxicant should be released from the paint matrix for sufficiently long periods, possibly years.

AF paints can be classified into three categories, based on the chemical properties of the paint matrix and the mechanisms involved in releasing toxic compounds:

Conventional AF paints

The matrix is usually a water-soluble resin, and the toxic compound is available at the coating surface. The biocides are oxides of lead, arsenic, mercury or copper. A thin layer of paint is active, the rate of leaching is high and the concentration of biocides quickly drops below the effective level. Paint life is short (6–12 months).

Long-life AF paints

The matrix is insoluble in water. Toxicants (cuprous oxide or organotin compounds) diffuse at the paint–water interface through channels in the polymer matrix. After 18–24 months, due to channel alteration, the leaching rate decreases and the diffusion rate is sharply reduced. High quantities of toxicants remain in the paint, but the concentration at the surface falls below the effective level, and coatings have to be replaced.

Self-polishing AF paints (SPC)

The biocide, mostly tributyltin (TBT), is bound to the polymeric matrix and is released by hydrolysis at the paint surface. The rate of release is controlled and constant, depending on water movement. Microscopic matrix layers are continuously washed away when the ship is moving, and new active layers become available, with a smoothing effect. The life of SPC usually ranges between 4 and 5 years.

THE IMPACT OF TBT ON THE MARINE ENVIRONMENT

SPC AF paints incorporating TBT are the most effective ones on boat hulls (Bosselmann, 1996). Not surprisingly, since their introduction on the market, in the mid-1960s, they gained popularity, especially for the treatment of recreational boats. In the 1970s, many semi-enclosed water bodies with intensive shipping became contaminated. High TBT concentrations in sediments, for instance, were reported in harbours, shipyards, marinas and bays (Gabrielides *et al*., 1990; Cardellicchio *et al*., 1992). TBT has a residence time of days in seawater, but tends to adsorb on to particles and aggregates in sediments, where degradation processes are considerably slower (Stang *et al*., 1992). High TBT concentrations were also detected in many organisms, mostly bivalves, from highly polluted areas (Alzieu *et al*., 1986). TBT was also found to bioaccumulate in salmon held in net pens, and thus to enter the human food chain (Ellis, 1991).

The effects of TBT on non-target organisms became apparent in the late 1970s. One of the best-documented cases is from Arcachon Bay (France), a centre for both oyster farming and yachting. High TBT concentrations caused abnormal shell growth and recruitment failure in the oyster *Crassostrea gigas* (His and Robert, 1982–1985). From 1975 to 1982, oyster production was severely disrupted, reaching only 30% of the normal harvest of 10000–12000 tons per year (Alzieu, 1991).

The desired effect of impairing larval settlement, the main reason for the success of organotin compounds, rapidly spread from ship hulls to other environments. Toxic effects were demonstrated in non-target invertebrates (Laughlin and French, 1980; Kelly *et al*., 1990; Scammell *et al*., 1991) and in both micro- and macroalgae (Wong *et al*., 1982; Beaumont and Newman, 1986). More recently, TBT has been found in some marine vertebrates, including fish (Kannan and Falandysz, 1997), seabirds (Guruge *et al*., 1996) and marine mammals (Iwata *et al*., 1994). Some authors (e.g. Kannan *et al*., 1996) argued that the accumulation of butyltins may cause mortality of the dolphin *Tursiops truncatus* by suppression of the immune system. However, the hypothesis is controversial (Evans, 1999) and calls for further studies on the putative risks that TBT accumulation may pose to marine mammals (Law *et al*., 1998).

Marine organisms are affected by low environmental concentrations of TBT, due to accumulation, and can therefore be effective biomarkers for this compound. In terms of sensitivity, however, there are no effects that rival the 'imposex' of gastropod molluscs. *Imposex* (Smith, 1971), or *pseudohermaphoditism* (Jenner, 1979), is a genital disorder caused by a hormonal imbalance of gastropod females inducing development of male sex organs (Smith, 1981a,b; Spooner *et al*., 1991). TBT and its derivatives induce imposex at ambient concentrations of just a few nanograms per litre (Gibbs *et al*., 1991). To date, abnormal penis-bearing females have been recorded in 118 species world-wide, chiefly stenoglossans (Fioroni *et al*., 1991). In some species the appearance of male characters does not impair reproduction (Gibbs *et al*., 1991); in many other species, however, advanced imposex may lead to reproductive failure (Gibbs, 1996; Terlizzi *et al*., 1999) and to population decline (Bryan *et al*., 1986). This can be due both to damage of the capsule gland (inhibition of breeding) or to vulva occlusion by vas deferens tissue (a barrier to copulation). Moreover, in highly polluted areas, the decline can also occur due to premature female mortality (Bryan *et al*., 1986). Gastropod population declines attributed to TBT contamination were reported from UK (Bryan *et al*., 1986), Ireland (Minchin *et al*., 1995), Netherlands (Ritsema *et al*., 1991), Canada (Alvarez and Ellis, 1990), New Zealand (Stewart and de Mora, 1992) and France (Oehlmann *et al*., 1996). The red-mouth purpura *Stramonita* (*Thais*) *haemastoma*, a widely distributed gastropod sensitive to TBT (Spence *et al*., 1990), almost disappeared along Italian coasts from the late 1980s to the mid-1990s (Terlizzi, 2001).

Imposex is a graded response and, since no other xenobiotic is known to induce it (but see Nias *et al*., 1993 for a different opinion), its degree of development depends on the level of TBT exposure. Since the visible stage of the syndrome appears (in most cases) at a TBT concentration of less than 0.5 ng Sn litre^{-1}, imposex is a very sensitive bioindicator and was widely used in many biomonitoring programmes (Ellis and Pattisina, 1990). Studies on imposex as a biomonitor of TBT contamination involved coastlines of the British Isles (Gibbs *et al*., 1987), France (Huet *et al*., 1996), Spain (Sole *et al*., 1998), Malta (Axiak *et al*., 1995), Italy (Terlizzi *et al*., 1998), North America (Bright and Ellis, 1989), Japan (Horiguchi *et al*., 1995), Australia (Nias *et al*., 1993) and Southeast Asia (Ellis and Pattisina, 1990).

THE TBT BAN

The impact of TBT on marine organisms induced many governments to restrict its use. France was the first to ban the application of TBT-based AF paints on vessels less than 25 m long in 1982. Similar restrictions were adopted in other European countries, Australia and North America (Evans, 1999). Such regulations were effective in reducing TBT contamination: monitoring programmes reported a decrease of organotins in water, sediments, and mollusc tissues (Dowson *et al*., 1993). Moreover, decreasing levels of imposex and recovery of gastropod populations were recorded (Evans, 1999). Along the Italian coast, *S. haemastoma* recovered at sites from where it almost disappeared prior to 1998 (Terlizzi, unpublished data).

The restriction on the use of TBT is leading to a renewed use of old-fashioned copper-based paints and/or to the use of new paints incorporating high booster levels of copper. Copper (and other metals) may also pose problems to the environment (Young *et al*., 1979) and the possible impact linked to a renewed use of copper-based paints was hypothesized by several authors (e.g. Evans, 1999). Claisse and Alzieu (1993) found that the copper content of oysters increased at Arcachon Bay following the ban on TBT-based antifoulants on small vessels.

Besides the increasing use of copper-based AF paints, several alternatives to TBT have been developed. The effects of new biocides as AF agents, however, are poorly known and concerns have been expressed about their putative impact on non-target organisms. Dahl and Blanck (1996), for instance, found that low concentrations of the algicide Irgarol 1051 were sufficient to change the structure of periphyton communities off the west coast of Sweden.

The opportunity to negotiate a global ban on the use of TBT is under debate. The complete ban of TBT is probably premature until alternative products performing at least as well as TBT in environmental and cost–benefit analyses become available. Bennet (1996) estimated that the use of TBT in AF paints led to an annual saving of about 7 million tons of fuel. Evans (1999) argued that, as a consequence of fuel savings due to TBT use on large ships, 22 million tons less CO_2 and 0.6 million tonnes less SO_2 are emitted annually.

NEW APPROACHES FOR AF RESEARCH

Environmentally-safe biocidal additives which will perform as well as, or better than TBT in AF paints are currently being searched for. This search led investigators to study natural products. Larvae, in fact, respond to biochemical stimuli during settlement (Morse, 1984) and some natural products may provide negative cues, inducing them to search elsewhere for suitable substrata. One source of potential products is a number of animals that are resistant to epibiosis (Clare, 1996). Davis *et al*. (1991) demonstrated that ascidian larvae are selective for settling substrata, consistently refusing different sponge species.

Laboratory-assessed performances and related impact of newly developed toxic agents (both natural and synthetic) are particularly useful. To date, no bioassay allows extrapolating the possible impact of a biocide on marine communities. However, the impact of a toxicant on test organisms might suggest its potential environmental effect (Geraci and Faimali, 1999).

Other methods to control fouling development include ultrasonic, electrical and radiochemical technologies (Kohn, 1998; Matsunaga *et al*., 1998), low frequency sound waves (Branscomb and Rittschof, 1984), and proteolytic enzymes inhibiting larval adhesion. However, none of these approaches proved to be very effective and such technologies are still far from being widely marketed. The isolation of AF compounds from bacteria constitutes a novel and promising approach. Naturally-produced compounds have been isolated from marine cnidarians (Standing *et al*., 1984), sponges (Tsukamoto *et al*., 1996), algae (de Nys *et al*., 1995) and seagrasses (Todd *et al*., 1993). Unless an identified biocide is chemically synthesized, it is difficult to obtain large amounts of the active substance. Conversely, the use of bacteria as a source of antifoulants benefits from the ease of obtaining large amounts of the required compound (Holmström and Kjelleberg, 1994).

Silicon technology is receiving increasing attention. The new approach is not to avoid settlement, but to utilize non-polluting and long-lasting foul-release silicone elastomers, from which settled organisms could be easily removed by periodic cleaning operations. Preliminary results (Rittschof *et al*., 1992; Swain *et al*., 1992) suggested silicone technologies as acceptable, environmentally safe AF systems that could offer an alternative to the toxic approach. Terlizzi *et al*. (2000) observed that silicon-treated surfaces modify the pattern of evolution of fouling communities, concluding that, with improvements with respect to technical aspects such as delamination, abrasion and costs in painting surfaces, silicon technologies could represent an alternative to the use of biocides in AF paints.

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