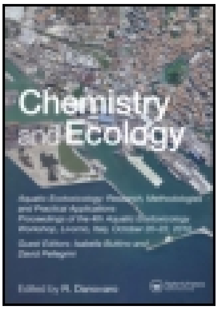

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The management of the effects of navigation on the marine environment: the case of tributyltin (TBT)

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The management of the effects of navigation on the marine environment: the case of tributyltin (TBT)

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The aim of this study is to review the fact-finding and decision-making process of the international community which, via the International Maritime Organization, has led to a ban on the use of antifouling paints containing organotin compounds. This review focuses on the importance of scientific knowledge supporting the sustainable management of the environment and on the centrality of ecotoxicological studies on the effects of human activities on the enviroment. The Italian Coast Guard Corps guarantees compliance with the regulations, through the action of Port State Control carried out in ports and onboard vessels.

Keywords: antifouling; TBT; ecotoxicology; legislation; Port State Control

1. Introduction

The English term 'fouling' indicates the accumulation of marine organisms deriving from the water column which are in search of hard sublayers in order to complete their life cycle [1]. Accumulation of these organisms on hard surfaces leads to major problems for vessel hulls, pipelines, drilling rigs and all materials/equipment submerged in seawater, such as beacons, mooring posts and piers. Fouling generally causes erosion and damage to surfaces, and increases both hull resistance during navigation and the weight of vessels. The consequences are a reduction in speed, an increase in fuel consumption and frequent careening operations in shipyards.

Biofouling starts with the deposition of macromolecules on the surface [2] forming a thin layer that facilitates the development of microorganisms (bacteria, diatoms, fungus and protozoa) which provide an appropriate sublayer for macroorganisms such as macroalgae, sponges, cnidaria, polychaetes, mussels, barnacles, bryozoans and tunicates [3].

To date, the methods employed to avoid the formation of biofouling on surfaces exposed to the marine environment have included paints containing toxic substances (the so-called antifouling paints).

These paints can be classified into three categories:

(1) Conventional paints whose matrix is resin soluble in water with the toxic compound (usually lead oxide, arsenic, mercury or copper) active on the surface of the coating. These paints have a limited life (6–12 months).

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(2) Long-life paints whose matrix is soluble in water, the toxic compound (usually copper oxide or organotin compounds) spreads towards the paint–water interface through ducts present in the paint. These paints last 18–24 months.
(3) Self-polishing paints. The biocide, usually tributyltin (TBT), is bound to the polymeric matrix and is released through hydrolysis at the water interface. The movement of water causes controlled and constant detachment of a paint microfilm, without biocide, resulting in new active layers (ablative polymerics). These paints, which are the most effective, last 4–5 years.

Following the ban on TBT and evidence of toxicity in the most recent paints containing heavy metals, many studies are underway to identify new analytical methods aimed at quickly discovering organotin compounds (Appendix 1 in Supplementary material, available online only) and identifying new antifouling substances and methods that considerably reduce the environmental impact. A brief review of these studies is given in Appendix 2 (Supplementary material, available online only).

2. Characteristics of TBT

TBTs are organic compounds characterized by the presence of covalent bonds between an atom of Sn(IV) and three atoms of carbon of butyl groups, the positive charge residue of tin forming ionic bonds with various anions (OH^-, Cl^-, ...).

The first large-scale industrial applications of byproducts of organotin compounds date back to the 1950s when their stabilizing quality for PVC was discovered; these byproducts are still in use today. The chemical characteristics of these products make them powerful biocides and they are widely used in antifouling paints applied to vessel hulls and in the cooling ducts of industrial plants.

In the marine environment, TBT soon abandoned the water column for sediment, the water distribution coefficient sediment ($\log_{10}\ K_{oc}$) is in the range 4.2–5.0 [4] given that the TBT molecule has a high specific mass, $\sim$ kg·L^{-1} at 20 °C [5], low solubility, <10 mg·L^{-1} at 20 °C and pH 7.0 [6] and the octanol/water distribution coefficient ($\log K_{ow}$) is of ∼4.4 at pH 8 [7]. The result of this is that TBT's presence in water is extremely variable and is linked to the existence of active sources of contamination, whereas its duration in sediments is remarkably long. In fact, in contaminated areas monitored before and after the ban on TBT, concentrations decreased in water flow compared with relatively steady concentrations in sediments [8].

3. Evidence of TBT contamination in waters, sediments and biota

At first, TBT was to be used on the hulls of large merchant vessels, to reduce fouling and increase ship speed and economic efficiency. Despite this, in the 1960s, a pressing marketing campaign led to the massive use of antifouling paints based on TBT also for recreational boats, and led to a large diffusion of organotin contamination [9]. The worldwide production of organotin compounds was evaluated as 40,000 t·year^{-1} in 1985 [10] and 50,000 t·year^{-1} in 1992 [11].

The widespread use of antifouling paints based on TBT in the maritime and industrial fields has created serious marine pollution in all environmental sectors. Numerous studies have shown high levels of TBT and its derivatives (DBT and MBT) in ports [12], with particular reference to areas close to shipyards. This evidence of contamination refers to both waters and sediments, but further research has discovered cases of bioaccumulation [13] that occur in the marine environment through biomagnification [14,15].

Contamination occurs due to the chemical characteristics of these paints. Through an hydrolysis reaction, there is controlled detachment of the active agent (TBT) from the paint, with release values of 1.6 $\mu g[Sn] \cdot cm^{-2} \cdot day^{-1}$, up to $mg[Sn] \cdot cm^{-2} \cdot day^{-1}$ for paints applied lightly [16]. Therefore, for example, a merchant ship that stays in a port for 3 days releases >200 g of TBT (the value can can reach 600 g if the ship is freshly painted). This leads to concentrations in nearby waters from 100/200 $ng[Sn] \cdot L^{-1}$ up to $\sim$600 $ng[Sn] \cdot L^{-1}$, respectively [16]. Recently, an important TBT contamination has been found in the Ross Sea in Antarctica with a maximum concentration in sediments of 2290 $\mu g\ Sn \cdot kg^{-1}$, equal to levels found in busy port areas [17]. This contamination might depend on contact between the icebreaker's hull and the ice and friction during grounding operations. The above-mentioned values become relevant if, for example, they are compared with the Italian quality standard for sediment in coastal, lagoon and coastal pond waters, established by the Ministerial Decree 14 April 2009 n. 56 [18] which fixes the acceptable TBT concentration at 5 $\mu g \cdot kg^{-1}$.

4. Evidence of the toxic effects of TBT

The toxic potential of organotin compounds on living organisms is well documented [6,19] and TBT has been defined as the most toxic substance ever deliberately released into the marine environment.

The effects of TBT on non-target organisms became evident in the 1970s when, in Plymouth (UK), Blaber discovered that numerous female *Nucella lapillus* presented a phallic growth behind their right cephalic tentacle [20]. The following year, Smith noticed that female *Ilyanassa obsoleta*, collected along the coast of Connecticut, had a growth similar to a phallus and also a deferent vase and a convolute gonoduct [21]. To describe this, Smith coined the term 'imposex' which indicates the occurrence of male characteristics in female gonochorist gasteropods.

The consequences of imposex vary according to the species. In some cases, it is not serious enough to prevent reproduction [22], whereas in others laboratory studies [23] have shown that it may cause a decline in the population. To date, imposex has been documented in at least 195 species and is considered a global phenomenon [24].

More proof of the toxicity of TBT derives from observations carried out in Arcachon Bay (France), famous for its oyster production. The bay, which is a naturally closed basin, has seen the accumulation of pollutants such as TBT, owing to its port, and is strongly influenced by the effects of recreational boat use. The high concentration of TBT has reduced reproduction and created anomalies in the calcification of the shells of *Crassostrea gigas* oysters, with a 70% decrease in production [25].

The toxicity of organotin compounds varies according to the number and type of organic groups connected to tin: it is highest for trisubstituted compounds and decreases progressively in di- and mono-substituted compounds [10]. Indeed, it seems that whereas DBT obstructs the absorption of oxygen by mitocondria, TBT directly destroys mitochondrial function [26]. Studies have demonstrated that TBT causes problems in the growth, development, reproduction and survival of many marine species [27,28]. The most obvious effects of TBT at an endocrine level were demonstrated in marine gastropods and occur at concentrations of only a few $ng \cdot L^{-1}$ of seawater [29,30].

Although there is no doubt that TBT is the direct cause of imposex in gastropods, there is also evidence that it is not the only causative agent [31,32]. Evans et al. [31] underlined how other agents with oestrogenic activity, such as nonylphenol, are able to cause imposex. In a recent study, carried out on *Hexaplex trunculus* [33], the occurrence of imposex has been reconsidered; it is no longer seen as a specific sign of TBT contamination, but rather as a more general non-specific stress indicator.

Work carried out by Berto [13] in the Venice lagoon, Italy, 3 years after the complete ban on antifouling TBT paints in Italy, confirms the presence of TBT and DBT compounds in our seas and sediments, especially in shipyards and ports. In a study on the gastropod *Nassarius nitidus*, it was demonstrated that a high concentration of organotin compounds often exists due to processes of suspension of sediments in the water column, facilitating its transference to marine species.

The toxic effects of TBT have been demonstrated not only in invertebrates and micro- and macroalgae [1], but also in some marine vertebrates such as fish, birds and marine mammals. Ferraro et al. [34] confirmed the genotoxicity of TBT using genetic tests (comet test, micronucleus test and tests on chromosome aberrations) on the neo-tropical fish *Hoplias malabaricus*, and found TBT to be a potential mutagenic agent.

Mizukawa [15] demonstrated the presence of contamination by organotin compounds in cormorants (*Phalacrocorax carbo*) on Lake Biwa in Japan, while Kim et al. [14] revealed the presence of butyl tin in cetaceans off the Pacific coast of Japan.

Ema et al. [35,36] showed a direct correlation between the length of exposure to DBT and the onset of defects in developing rat embryos. Another study described toxic effects that cause anomalies in the development of testicles in mice [37]. In humans, the main source of exposure to organotin is probably the consumption of molluscs and exposure to dust in shipyards [38,39].

Penninks' study, based on experiments on the immune system in mammals, fixed safe daily limit for TBT exposure by humans at 0.25 $\mu g \cdot kg\, bw^{-1} \cdot day^{-1}$ [40].

It is possible for TBT to accumulate in human organs in nanomolar quantities and to have a potential toxic effect [41]. The action range of TBT is quite vast and includes immunosuppression and destruction of the endocrine system. The effects of TBT have been thoroughly studied in mice with the thymus gland one of the main targets. It is well-known that TBT increases the intracellular concentration of Ca^{2+} and induces apoptosis [42–44]. Yamada et al. [41] showed that TBT influences synaptogenesis and neuronal survival, especially during the first stages of development.

Carfì et al. demonstrated, in a human mononuclear bone marrow culture, that TBT induces the inhibition of lymphocyte B and the differentiation of adipocytes, through the modulation of the expression of PPARγ and RXRα genes, which leads to a decrease in neuroactive molecules produced by these cells [45].

Although many studies have been carried out on the toxic potential of organotin compounds, we still do not know their target molecules or the toxic mechanism in humans [46–48].

5. Limitations to the use of TBT: national and international legislation

In 1982, France was the first country to issue a law limiting the use of organotin compounds after an incident that occurred in Arcachon Bay; similar provisions followed in many countries such as the UK, USA, Switzerland, Germany and Japan.

In Italy, the first law dates back to 1982 when EEC Directive n. 75/769 was implemented with D.P.R. n. 904 of 10/09/82, concerning the introduction and use of certain dangerous substances and compounds. This legislation imposed restrictions on the use of organotin compounds such as biocides, which with Ministerial Decree 13/12/1999 (GU n. 67 dated 21/03/2000) became a total commercial ban on organotin compounds for antifouling purposes.

In October 2001, at the United Nations, the International Maritime Organization (IMO) [49] adopted the AFS Convention (International Convention on the Control of Harmful Antifouling Systems on Ships) which, on 1 January 2003, introduced a ban on the use of antifouling paints containing TBT and other tin components. The convention fixed 1 January 2008 as the deadline for the complete retirement of paints containing tin from the hulls of vessels. The convention entered into force on 17 September 2008, 12 months after its ratification by at least 25 states representing at least 25% of the world's tonnage. At present, 47 states have ratified the convention and the percentage of world shipping tonnage is of 74.40% (data of the Secretary General of the IMO up-dated to 31/08/2010).

Awaiting the AFS Convention, the European Community issued the Regulation (CE) n. 782/2003 [50] of the European Parliament and Council on 14/4/2003, banning the use of organotin compounds on ships.

The European regulation, promptly adopted in order to ban organotin compounds, introduced the international laws established by IMO far in advance of the community legislation. In fact, the ban on applying organotin compounds that act as biocides, began on 1 July 2003 on ships flying European flags or which operateed under the authority of an EU member state.

Beginning on 1 January 2008, the presence of organotin compounds was banned for ships flying under the flags of EU member states or which operate under their authority, and for all ships that dock in the port or off-shore facilities of a member state. To the control regime, starting 1 July 2003, ships of >400 gross tonnage are subject to inspection and certification by the state flag before entering into service for the first time or when antifouling systems are modified or substituted. However, ships over 24 m long but of <400 gross tonnage must have a certificate that demonstrates compliance with the AFS Convention.

The entry into force of the AFS Convention has solved the need to harmonize national laws [51] and implement a distributed control system. This has proved very effective through the activities of Port State Control (PSC) which are carried out in ports of call. From this perspective, and despite the introduction of Regulation (EC) 782\2003 which has anticipated the ban on TBT-based paints, it is desirable that all European states ratify the AFS Convention.

6. Duties of the Italian Coast Guard Corps

As mentioned above, ships of >400 gross tonnage are required to undergo a preliminary check, carried out by the flag state, before entering service or before the 'International Antifouling System' (IAFS) Certificate is issued, and inspected in the case of the replacement or overhaul of the antifouling system on the ship.

The Italian administration issues antifouling system certificates for ships through a recognized organization (Registro Italiano Navale, Bureau Veritas, American Bureau of Shipping and Germanischer Lloyd), which performs inspection and control functions relating to the issuing of certificates, and actually issues the certificate on behalf of the State Administration.

Thus, all ships flying the Italian flag are certified by these bodies in accordance with Regulation (CE) no. 782/2003 [50]. In place of the certificate, vessels longer than 24 m, but with <400 gross tonnage must possess a declaration regarding the antifouling system in use (Declaration on Antifouling Systems), signed by the ship's owner or authorized agent, to which documentation describing the type of antifouling product actually used must be attached.

As far as surveillance and maritime policing are concerned, inspections are carried out by qualified coastguard personnel who, during checks effected on board, have the power to verify the existence of relevant certificates, including the IAFS Certificate [Reg. (CE) 782/2003] [50].

With regard to foreign ships, however, inspections and checks are carried out in accordance with 'Port State Control' procedures.

PSC is the power of a state, derived from international agreements, to carry out checks on foreign ships docking in their ports, with the aim of verifying compliance with international regulations relating to shipping safety, anti-pollution and onboard living conditions, for the purposes of the eventual application of relevant corrective measures.

In this context, Italy applies the Paris Memorandum of Understanding on State Port Control, which is a regional agreement between states aimed at creating a standard system of control on the part of states in whose ports ships call. This agreement aims to counter the phenomenon of substandard ships, i.e. vessels that constitute a hazard to the people on board, to the environment and to the safety of shipping. In Italy, PSC checks are carried out by qualified coastguard officials, in accordance with Ministerial Decree 305/2003, absorbing Directive 95/21/CE.

Since coming into force, the AFS Convention has become a 'relevant instrument' under the Paris MoU, allowing PSC inspectors of the state at which the ship calls to implement the provisions of the Convention in carrying out an inspection, and briefly sample products used on the ship's hull.

The PSC inspection of ships calling at national ports begins with checks on the validity of the IAFS Certificate and of the attached 'records of antifouling system'.

Because application of an antifouling system to the hull can only be effected during careening, inspection personnel also check that the dates shown on the certificate are consistent with the ship's stay in the dry dock, information which can be found in the vessel's log book and in authenticated data on the 'Safety Construction Certificate', as per Rule 10 of Chapter I of the SOLAS Convention.

For ships flying flags of countries that are not signatories to the AFS Convention 2001, declarations of compliance issued in accordance with regional agreements, such as Regulation (CE) no. 782/2003, as emended by Regulation CE 536/2008 [52], are recognized as being equivalent to the IAFS Certificate.

Where there is clear evidence of non-compliance with the provisions of the AFS Convention (lack of certification or equivalent declaration, inappropriate certification or evidence of the presence of paints other than those certified), the inspectors will subject the ship to a more thorough inspection.

In carrying out this more detailed inspection, detailed information is gathered from crew members and ship management companies to reconstruct the types and application methods of the antifouling system used.

These checks cover the date of application of the antifouling system, the name of the company commissioned, type of product used, manufacturer, commercial name and end distributor. Analogous information will be gathered in the event of a pre-existing TBT-based antifouling system having been removed or sealed over.

If considered necessary, coastguard inspectors have the power, in accordance with convention provisions, expressly referred to in EU Regulation 782/2003 [50], to take samples of the antifouling system applied, in order to verify its compliance with the provisions of the AFS 2001 Convention.

In the event of the results of the analyses carried out on the samples showing non-compliance with the antifouling products applied, the inspectors will take appropriate measures to stop the ship sailing until it has undertaken corrective measures to eliminate irregularities detected, which may include the detention of the ship in port.

If there are no dry docks suitable for performing the work of careening in the port of detention, and as long as the ship in question would not be otherwise subject to criminal sanctions as provided for by national legislation (DPR 10 September 1982, no. 904), the PSC inspectors may authorize the vessel to proceed to another dock situated in another port, in order to carry out the work necessary to bring the ship into compliance with the convention.

If the owners of the detained ship fail to show their intention to bring the ship into compliance with the convention, the inspectors of the state in whose port the ship has called may ban the ship from the port. The banning order, which is entered into the PSC inspectors' database, prevents the ship from entering all ports belonging to EU countries and signatories to the AFS Convention, thus considerably restricting its commercial operations.

With regard to control activities, taking into account the brief period of implementation of European legislation, few violations have been detected by countries of Paris MoU. In 2010, 36 violations were verified, representing 0.06% of the total violations in the maritime sector [53].

The Italian Navy has institutionally held many environmental protection duties, such as the fight against pollution, protection of biological resources and maritime policing, but the operational focus is not the only contribution made by the navy to the common cause of protecting the marine environment. Regarding the problem of the environmental hazard posed by some components of antifouling paints, in 2000, the Directorate General of Armaments of the Ministry of Defence defined the procedures for testing anti-fouling paints used by military ships, with the aim of ensuring the absence of organic or inorganic biocides based on tin, mercury or arsenic.

Approval of such procedures, even in the absence of a legal obligation, indicates a strong will on the part of the navy to minimize the environmental impact of shipping.

7. Conclusions

This article shows that the management of human activities in the context of environmental protection cannot be separated from scientific considerations. Indeed, thanks to numerous studies, we have a complete picture of the problem from various points of view: the chemical nature of compounds and their behaviour in an aquatic environment (speciation, division into environmental compartments, persistence, etc.), mechanisms of diffusion from source to target, evidence of contamination of various environmental compartments (water, sediment, biota), as well as evidence of toxic effects.

If, as stated, the various elements combine to give an overall cognitive picture which acts as a basis for legislative decisions, then it is indisputable that ecotoxicological investigations play an essential role in this process, in that they give a direct measure of the negative effects that a determined substance can have on organisms. In addition, and unlike the classic toxicological approach, which focuses on the possible negative effects on man, the ecotoxicological approach reflects a modern vision of the concept of environment, as an asset worthy of protection in its own right, and not just in relation to man.

In this context, a linearity of purpose can be seen which, starting from scientific research, proceeds through the decisions of an international legislator, and arrives at the enforcement of the law on the part of institutions. It is this aspect which involves the Maritime Administration which, via the coastguard, carries out the delicate tasks of Flag State Control and Port State Control. This is the instrument by which the international community jointly tackles issues relating to the maritime world.

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