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# Tributyltin: case study of a chronic contaminant in the coastal environment

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## Abstract

As early as 1975, significant and repeated disturbances were observed to occur in the *Crassostrea gigas* oyster farms of the Arcachon Bay along the French Atlantic Coastline. TBT contamination of the local breeding waters was found to be responsible for failure to reproduce and for anomalies occurring in the shell calcification of adult oysters leading to stunted growth. On 17 January 1982, the French Ministry of the Environment issued a 3 month ban on the sale of marine anti-fouling paints with an organotin compound content exceeding 3%.

The Ministerial ban was subsequently renewed and reinforced and ultimately converted into an enforcement decree transcribing an European Union directive into French law, in October 1992. The ban was the first official action in response to a growing awareness to the TBT-related pollution of some coastal areas and to its unacceptable impact on shellfish farming.

These measures were adopted as soon as the first scientific evidence of a causal relationship was established between tributyltin and oyster shell anomalies. Since then numerous research studies have been conducted on the geochemical behavior of tributyltin, its ecotoxicity and on TBT-related risks presented by antifouling paints. The knowledge gained on this topic since 1982 reveals in particular that:

- TBT is extremely toxic to aquatic organisms in general and to molluscs in particular for which the NOELs are below  $1 \text{ ng l}^{-1}$  (imposex, calcification anomalies),
- Contamination levels can reach very high values in port areas, and even exceed no effect levels beyond which mollusc reproduction and growth are affected, in estuaries or semi-enclosed areas,
- Contamination of breeding waters has a significant economic impact, jeopardizing the sustainable development of some highly exposed marine activities,
- The ban on TBT use in antifouling paints for crafts under 25 m represents an efficient way of reducing TBT inputs in coastal areas and restoring proper water quality,
- The regulations adopted by many countries to ban or restrict TBT use on ships sailing along the coastline, have prompted manufacturers to develop less toxic paints.

Fifteen years after TBT was first implicated as a major cause of coastal contamination, the issue no longer lies in finding out under which conditions TBT could still be used in antifouling paints, but rather in developing environmentally-harmless formulations. While the ban on TBT-based paints may be justified due to their harmful impact on coastal ecosystems,

substitutes based on the release of biocides (copper oxide, pesticides ... ) also give rise to major concerns. Prevention of marine biofouling is not motivated merely by esthetics: it responds to economic needs and to navigation safety requirements. Protection of the ships while preserving the coastal ecosystems remains a major challenge for future research. © 1998 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Environmental scientists and jurists began addressing the issue of tributyltin (TBT) in the early 1980s when it was shown that its presence in certain coastal areas was responsible for shell calcification anomalies in oyster farming areas [1] and for severe sexual disorders in certain gastropod species leading to sterile populations [2–3]. Since then, TBT has been regarded as a chronic contaminant of the coastal environment. Its fate and effects on marine organisms have been investigated and its use regulated in many countries.

## 2. Biogeochemistry

Several bibliographic reviews have summarized the state-of-the-art knowledge on the sources, fate and effects of TBT and organotins [4–7].

### 2.1. Sources

TBT belongs to the group of trisubstituted organotins. It is used for its biocide properties in the form of salts (chlorides, fluorides, acetate, oxide) or of copolymers (methacrylate). In 1985, the world production of triorganotins with biocide properties was in the range of 8–10 000 metric tons annually, while the production of di- and mono-substituted derivatives, non-toxic and used as PVC stabilizers or as catalysts, reached 27 000 metric tons [8]. It is estimated [6] that 70% of biocide triorganotins, essentially TBT and TPT (triphenyltin), are used as active agents in antifouling paints.

Antifouling paints are applied as a finish coat to the immersed sections of boats and floating structures to prevent the fixation of living organisms which can cause major interferences with maritime activities: loss of ship speed, excess fuel consumption, spreading of corrosion pits and increased weight of floating structures. Paint formulations are complex systems containing one or several toxicants incorporated within a matrix, along with various additives designed to provide consistency and coloration and to facilitate application (solvents) of the protective coating. The paint releases its toxic load into the water, thereby creating an adverse environment repelling the fixation of living organisms. Antifouling paints may be classified into three categories based on the release mechanism of the biologically active substances:

- conventional: the matrix is insoluble in sea water and the toxic molecules migrate to the surface via microscopic pores,

- erodable: release of the toxicants retained in the deeper layers of the coating film is facilitated by partial dissolution of the matrix,
- self-polishing: matrix and TBT are chemically bound in the form of a polymer, e.g. TBT methacrylate, which releases the TBT by reacting with sea water, thereby constantly renewing the surface coat. Such systems present several benefits: lower and time-constant leaching rate, longer protection time (5 years).

Biofouling control thus represents a major source of TBT input into the coastal environment. It is estimated that one boat releases between 1 and 10  $\mu\text{g TBT cm}^{-2}$  of hull daily (leaching rate) to ensure antifouling protection, i.e. amounting to quantities of 0.2–2  $\text{g d}^{-1}$  for a small sailboat, and up to 50–500  $\text{g d}^{-1}$  for an average-size merchant ship.

Furthermore, Fent [9] has shown that urban effluents conveyed non-negligible quantities of TBT and of its degradation byproducts, which accumulate in the sludge from wastewater treatment plants. These urban inputs probably result from leaching of treated lumber.

## 2.2. *Physico-chemical properties*

TBT is only slightly soluble in seawater: 1–10  $\text{mg l}^{-1}$  for TBTO, and under 20  $\text{mg l}^{-1}$  for more soluble salts (halides). In natural waters, a small fraction (5%) is adsorbed onto suspended particles. The partition coefficient between particulate and aqueous phases ( $K_p = C_{\text{sed}}/C_{\text{water}}$ ) generally ranges from 1000 to 3000 ( $\text{l kg}^{-1}$ ) depending on the nature of the particles.

In aqueous solution, the  $\text{TBT}^+$  ionic form is in equilibrium with the hydro- and chloro-species. The cation predominates when the pH is lower than a  $\text{p}K_a$  of 6.51. Under normal pH and salinity conditions of the marine environment, TBT is essentially found in the TBTOH hydro-chelated form. Chemical speciation is significant in the aquatic medium since it has been shown that TBT bioavailability, i.e. its capacity to be accumulated by living organisms, increases when found in its TBTOH form ( $\text{pH} > 8$ ). Conversely, the presence of dissolved organic matter is a limiting factor.

TBT is a hydrophobic substance with an octanol/water partition coefficient ( $\log K_{ow}$ ) varying according to conditions of pH and salinity. The values published in the literature indicate that the partition coefficient ranges from 3.21 to 3.85 for TBTCI at pH values of 5.8 and 7.8, respectively [6].

## 2.3. *Persistency in the marine environment*

The tin-carbon bond represent a point of least resistance in the molecule. Alkyltins are therefore degraded by successive dealkylations caused by UV photolysis or by the action of micro-organisms.

TBT half-life in seawater is highly variable depending on the environmental conditions of pH, temperature, turbidity and light. It is generally estimated to range approximately between a few days to a few weeks [10]. Watanabe et al. [11] have shown that degradation is faster in seawaters with a high suspended matter content,

and that biodegradation by micro-organisms is the predominant mechanism. The calculated half-lives range from 5.8 days in summertime for turbid waters to 127 days in winter for non turbid ones (Table 1).

Degradation is much slower in sediments where half-lives are estimated to last several years. In the sediments of Auckland harbor (New Zealand), de Mora et al. [12] have estimated TBT half-life to be approximately 1.3–4.4 years, while Adelman et al. [13] suggested, based on mesocosm experiments, that its half-life could exceed 19 years. Moreover, the extreme stability of TBT in the sedimentary compartment has been further confirmed by the high concentrations found in the deep sediments of several harbor areas (Fig. 1).

2.4. Levels of presence in the marine environment

The data compiled since the 1980s reveal that TBT and its degradation byproducts are present in all compartments of the coastal environment: water, sediments, living organisms, including large mammals. Levels vary widely depending on the proximity of harbor-based sources and have tended to decrease in the past few years due to the regulations now applicable in several countries.

Measurements taken prior to restrictions on TBT use in antifouling paints had shown levels generally ranging between 50 and 500 ng l<sup>-1</sup> in North American

Table 1  
Tributyltin half-life in seawater measured in summer and winter in turbid (left) and non turbid (right) conditions (from [11])

	Summer	Winter
Half-life (d)	5.8–16.8	37.3–127.4
Biodegradation %	86–20	90–37
Photolysis %	14–80	9–61
Evaporation %	0.1–0.3	0.8–2.6

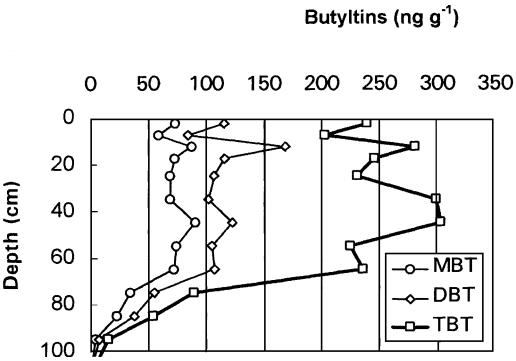


Fig. 1. TBT (ng g<sup>-1</sup> dry weight) and its degradation byproducts in La Trinité-sur-Mer (France) marina sediments (Alzieu and Michel, in press).

and European marinas, exceptionally reaching peak values in the range of  $1 \mu\text{g l}^{-1}$  in highly contaminated areas. By the late 1980s, high TBT concentrations were still recorded in European harbor waters ( $10\text{--}1500 \text{ ng l}^{-1}$ ) and coastal waters ( $< 2\text{--}50 \text{ ng l}^{-1}$ ) [5]. The highest values (above  $1 \mu\text{g l}^{-1}$ ) were found in the Mediterranean Sea (tideless sea), in major harbor areas and, on a single occasion, in the vicinity of a discharge outlet for TBT-treated cooling water.

Today, maximum concentrations in marina waters rarely exceed  $100 \text{ ng l}^{-1}$  along the English Channel and Atlantic coasts (average  $42$  and  $22 \text{ ng l}^{-1}$  respectively) and  $200 \text{ ng l}^{-1}$  along the Mediterranean coast (average  $42 \text{ ng l}^{-1}$ ) (Michel, unpubl.). In 1992, Law et al. [14] reported maximum concentrations of  $17 \text{ ng l}^{-1}$  in the estuaries and above  $100 \text{ ng l}^{-1}$  in the harbors and shipyards along the English and Welsh coasts. In countries where no regulations have been adopted, extremely high contaminations are recorded in harbor waters:  $14.7 \mu\text{g l}^{-1}$  in Bahrain [15],  $1 \mu\text{g l}^{-1}$  in Hong Kong [16].

Because of the great stability of the TBT adsorbed onto sediments, contamination is sometimes found to reach very high levels, reflecting the long-term storage capacity of this compartment. In harbor areas, average concentrations generally range between  $1$  and  $2 \text{ mg kg}^{-1}$  dry weight. As an example, monitoring of US coastal areas has shown that the average contamination was approximately  $54 \mu\text{g kg}^{-1}$  dry weight [17], while levels barely 10 times lower ( $5.3 \mu\text{g kg}^{-1}$ ) were recorded in top-layer sediments collected at sea  $25 \text{ km}$  from Vancouver harbor (Canada) at a depth of  $377 \text{ m}$  [18]. Additionally, concentrations exceeding  $1 \text{ mg kg}^{-1}$  dry weight were found to subsist in the sediments of the bay of Arcachon (France) 8 years after the TBT ban. Harbor sediments therefore constitute a reservoir of contamination liable to be transferred to the water column either via mechanical resuspension or by dredging operations and sludge dumping at sea.

Similarly to the data on water and sediments, most of the data on the contamination of marine organisms were acquired after 1990. In oyster samples collected along the Essex coast (UK), Waldock et al. [19] found higher contamination levels in the species *Crassostrea gigas* ( $3500\text{--}8600 \mu\text{g kg}^{-1}$  of flesh) than in the flat oyster *Ostrea edulis* ( $< 230\text{--}1990 \mu\text{g kg}^{-1}$  dry weight). Monitoring along US coasts between 1988 and 1990 [20] revealed comparable contaminations in different mussel and oyster species, with a similar order of magnitude along the West ( $10\text{--}4000 \mu\text{g kg}^{-1}$  dry weight) and East ( $10$  to  $5000 \mu\text{g kg}^{-1}$  dry weight) coasts.

TBT distribution in the organs differs according to the bivalve species. In the oyster *Saccostrea commercialis*, Batley et al. [21], found decreasing concentrations in mantle  $>$  foot  $>$  branchiae  $>$  labial palpi  $>$  viscera  $>$  adductor muscle. Extremely high levels were reported in gastropods living in British estuaries and harbor areas by Gibbs et al. [22] ( $0.3\text{--}1.6 \text{ mg kg}^{-1}$  dry weight) and by Bryan et al. [23] ( $0.9\text{--}2 \text{ mg kg}^{-1}$  dry weight).

With respect to fish, notable concentrations have been found in salmon raised in TBT-treated cages. In the herring *Clupea harengus* of the bay of Vancouver, Maguire et al. [24] recorded maximum values of  $5 \text{ mg kg}^{-1}$ .

Finally, Iwata et al. [25] have shown that the large marine mammals are equally affected by the pollution of coastal waters. These authors found maximum

concentrations of TBT and its degradation byproducts reaching up to  $770 \text{ ng g}^{-1}$  wet weight.

### 3. Biological effects

#### 3.1. Bioaccumulation

The lipophilic nature conferred to TBT by the alkyl groups tends to facilitate its bioaccumulation by living organisms. The bioconcentration factor (BCF) calculated from the octanol/water partition coefficient gives values ranging between 100 and 500 in fish, presenting major differences with experimental values. BCF values vary among groups of species (1–30 000) and within a single group. Certain results indicate that bioconcentration in the crab is higher via the food pathway, suggesting the possibility of biomagnification mechanisms along the food chain. It is well known however that crustaceans and fishes are capable of transforming enzymatically TBT into hydroxybutyldibutyltin first, then into dibutyltin and monobutyltin. Nevertheless, the possibility should not be neglected that exposure to high TBT concentrations in extremely contaminated areas may inhibit the detoxification mechanisms common to TBT and to polyaromatic contaminants. Comparatively, the absence of any cytochrome P 450-dependent system explains the capacity of molluscs to bioaccumulate TBT.

#### 3.2. Toxicity

At micromole concentrations, trialkyltins affect the cell metabolism by stimulating the production of adenosine triphosphate and by inhibiting its transformation into adenosine diphosphate, thereby causing malformations of the mitochondrial membranes. The sensitivity of the various zoological groups is dependent upon the nature of the alkyl radical. Thus, the methyl and ethyl derivatives are harmful to mammals and insects, while the propyl and butyl radicals confer its bactericide and fungicide properties to tin. As a general rule, alkyltin toxicity decreases along with the number of alkyl radicals:  $\text{tri-Sn} > \text{di-Sn} > \text{mono-Sn} > \text{SnO}_2$ . A notable exception to this rule was recently reported by Lascourrèges [26] who showed that, in an anoxic medium, the bacterial growth rate of the *Desulfovibrio* genus is reduced by 25% in the presence of concentrations ranging from 1.4 to  $4 \mu\text{M}$  MBTCl and from 55 to  $170 \mu\text{M}$  TBTCl.

Ecotoxicological data point to molluscs, bivalves and gastropods, as the species most sensitive to TBT exposure. The no effect levels proposed by Alzieu [5] indicate the following:

- concentrations  $< 1 \text{ ng l}^{-1}$  cause the appearance of male characters in many female gastropods, a phenomenon known as imposex. Gibbs et al. [22] described six successive stages in the dogwhelk *Nucella lapillus*, starting with the formation of a *vas deferens* and ending with blockage of the oviduct, thereby leading to sterility.

Imposex has been described in over 72 species belonging to 49 genera, and serves as a bioindicator of TBT exposure.

- concentrations exceeding  $1 \text{ ng l}^{-1}$  limit cell division in phytoplankton (diatoms) and reproduction of zooplankton (microcrustaceans, copepods).
- concentrations exceeding  $2 \text{ ng l}^{-1}$  are responsible for shell calcification anomalies in the oyster *Crassostrea gigas*, with a build-up of wafer-like chambers containing a protein gel differing from the calcification protein (conchyolin) by its high threonine content and reduced amounts of the amino-acids active in the calcium binding process, i.e. aspartic acid, glycine and serine.
- concentrations exceeding  $20 \text{ ng l}^{-1}$  cause disturbances in the reproduction of bivalve molluscs. According to the effect scale defined by His and Robert [27], the larval growth of *C. gigas* is interrupted when TBT concentration reaches  $50 \text{ ng l}^{-1}$  (total larvae mortality after 10 days).
- concentrations of  $1\text{--}10 \text{ }\mu\text{g l}^{-1}$  affects fish reproduction.
- concentrations of  $1\text{--}1000 \text{ }\mu\text{g l}^{-1}$  result in disturbed fish behavior.
- concentrations  $< 500 \text{ }\mu\text{g l}^{-1}$  result in disturbed crustacean exuviation.

#### 4. Risks to human health

Contact exposure to TBT causes irritations in the eyes and skin, potentially leading to severe dermatitis. However no case of food poisoning by direct ingestion has ever been reported. Various studies conducted on fish markets in the US and in Japan have shown that seafood consumers are exposed to TBT inputs. Nevertheless, the World Health Organization [28] considers that the safety factors calculated on the basis of various models are sufficient (10–250) to safeguard human health, even for heavy fish consumers (150 g daily).

#### 5. Case study of the Bay of Arcachon

The harmful effects of TBT on the coastal environment were first observed in the Bay of Arcachon, located along the French Atlantic coast halfway between the Gironde estuary and the Spanish border. The inland bay is triangle-shaped, stretches 20 km along each side and opens to the west into the Atlantic Ocean via a narrow sandy inlet. Shellfish farming, primarily oyster farming, and water sports tourism constitute the bulk of the area's traditional activities. Shellfish farms occupy around 1000 hectares within the bay, with an annual production of 10–15 000 tons of oysters *Crassostrea gigas*, 600 tons of mussels *Mytilus edulis*, 100 tons of carpet clams and 50 tons of cockles. The farming beds are surrounded by ten marinas, in addition to seasonal mooring berths, for a total mooring capacity of 10 000–15 000 boats in summertime.

Starting in 1975, oyster production suffered severe disturbances due to two concurrent phenomena: progressive decline of reproduction and of juvenile recruitment, along with a general outbreak of shell calcification anomalies in adult oysters. During

the reproduction process, the genital substances previously released by the oyster *C. gigas* are fertilized in the aquatic environment before giving birth to pelagic larvae which then settle onto a support to become juveniles (spat). Oysters farmers install various types of supports over which the larvae can settle at the end of their pelagic life, in order to renew their breeding stocks. The success of this operation, known as spatfall, conditions the prosperity of future oyster stocks.

Between 1975 and 1982, spatfall in the Bay of Arcachon was very low and even non-existent in certain sectors, while it remained normal outside of the bay. Observations in the natural environment revealed that the larvae survived only for a few days, whereas larvae from the bay waters transferred to the laboratory in seawater collected outside the bay were developing normally. His and Robert [27] found that *C. gigas* larvae were highly sensitive to TBT at concentrations as low as  $20 \text{ ng l}^{-1}$ .

These authors established a toxicity scale starting at the no-effect level up to inhibition of fertilization. TBT inputs estimated at  $7.7 \text{ kg d}^{-1}$  during the oyster reproduction period, along with total tin contents measured in oyster flesh [1] both suggested that larvae mortality in the bay could be attributed to the contamination of bay waters.

Shell anomalies involving the formation of wafer-like chambers filled with an inter-lamellar gel were first observed in the Bay of Arcachon in 1974. These anomalies later spread progressively to most oyster production areas along the Atlantic coast, with various degrees of severity. The phenomenon of shell malformation occurred in three successive stages:

- hypersecretion of a gel occurring suddenly in July and simultaneously in populations of varying age,
- deposit of a thin calcium layer entirely surrounding the gel 15 days after its secretion and forming a gel-filled pocket,
- disappearance of the gel by late October and consolidation of a chamber in the shell.

This “chambering” results in an abnormally thickened shell, and in the most acute cases, in stunted lengthwise growth with a shortened palleal cavity, producing a ball-shaped oyster. The role of TBT in shell calcification malformations was identified following a combination of in situ and laboratory experiments which revealed that the phenomenon occurred simultaneously in the lab with oysters exposed to TBT-based paints and in test oysters immersed in a marina. Comparatively, control oysters raised in the laboratory and in an uncontaminated natural environment were free of any malformations. Subsequent studies confirmed these initial observations, and Chagot et al. [29] have since shown that calcification anomalies can occur at concentrations as low as  $2 \text{ ng l}^{-1}$ .

TBT contamination of the bay waters coincided with a major crisis of the oyster farming sector in the Bay of Arcachon, which prompted public authorities to question officially the chance of survival of this activity. Regulatory measures were adopted in 1982 helping to restore a normal production level as of 1984. In the meantime, production had dropped from 10 000 tons in 1979 down to 3 000 tons in 1981, with a concurrent depreciation of the merchant value of the local oysters.

Although no detailed economic study was performed at the time, it may however be estimated that losses on the sales of spat and adult oysters amounted roughly to



a total of 880 millions F. francs (1983) [30]. In addition, the need to reconquer the markets, the slowdown of the local economy and the demotivation in the oyster farming community also had an indirect but negative and durable impact impossible to evaluate.

## 6. Regulations

On 19 January 1982 following the recommendations of an ad hoc committee, the French Ministry of the Environment adopted an ordinance banning, for a renewable period of three months, the use of antifouling paints containing more than 3% organotins for boats under 25 m long. Although this ban ordinance was promulgated two months only after the ad hoc committee issued its recommendations, this “precautionary ban” reflected the uncertainties of the time:

- necessity to confirm the experimental results and to develop specific chemical analytical methods needed to evaluate the toxic levels and measure the contamination of the marine environment,
- difficulty of assessing the quantities of TBT tolerable by the environment, hence the authorization granted to the least polluting paints. Regulations have been further reinforced as greater knowledge was gained on the subject:
- enforcement decree of 14 September 1982: application to the entire French coastline, labelling providing consumer information, waiver for light-alloy hulls taking into account the unavailability of any substitute antifouling paints compatible with this material,
- enforcement decree of 2 October 1992: repeal of the waiver, ban on sales to the general public, special packaging for shipyards, ban on the use of certain active agents (Hg, organochlorinated compounds ...), in application of a European Directive.

Over the same time period, many countries adopted similar measures or regulations adapted to their respective domestic context:

- United Kingdom/1986: ban on sales and supply of paints containing more than 7.5% copolymerized organotin compounds, or more than 2.5% free organotin compounds; combined with an interim environmental threshold standard of  $20 \text{ ng l}^{-1}$  in coastal and estuarine waters – 1987: ban on sales for boats under 25 m long and for aquacultural structures, and marketing approval for all antifouling paints – 1995: ban on non-copolymerized organotin-based paints.
- United States/1987: restriction on the use of organotins (maximum leaching rate), listing of TBT-based paints as “pesticides for limited use” – 1988: Organotin Antifouling Paint Act banning the use of organotins in paints for boats under 25 m long, and prescribing a maximum leaching rate of  $4 \mu\text{g cm}^{-2} \text{ d}^{-1}$ .
- Australia/1988; Canada/1989: ban for boats under 25 m long.
- New Zealand/1993: total ban on domestic use of TBT-based marine antifouling paints.

Thus the knowledge acquired over the past decade has confirmed the toxicity of organotins and of TBT in particular, and their harmful impacts on the coastal

environment. Their use in antifouling paints has been regulated by State and European authorities (EU Directive) who subsequently adopted world-scale recommendations leading to the 1990 resolution of the International Maritime Organization banning sales of TBT-based antifouling paints for boats under 25 m long and prohibiting the use of all antifouling paints with a mean leaching rate exceeding  $4 \mu\text{g cm}^{-2} \text{d}^{-1}$ .

## 7. Efficacy of regulations

Numerous surveillance programs have been set up, based on monitoring of the contamination levels and biological indicators (imposex, oyster calcification anomalies), in order to assess the efficiency of the restrictive measures adopted.

In the Bay of Arcachon, the contamination level measured in 1985 was only one-tenth of the 1982 level, as measured on total organotins in the waters and in oyster flesh [31]. TBT analyses performed between 1986 and 1992 (Table 2) have confirmed this trend: concentrations within the bay were no longer detectable as of 1992 ( $< 0.2 \text{ ng l}^{-1}$ ). The improvement of water quality was accompanied by a progressive recovery of the oyster farming activities: spatfall was back to normal in 1983 and the production of marketable oysters resumed one year later. Concurrently, the chambering phenomenon affecting oyster shells was slower to disappear, with peaks of new outbreaks in 1986 and 1990, until it finally reached a non-significant level in 1994 (Fig. 2). It should be noted however that the ban on TBT-based paints has led to increased use of copper oxide as a substitute agent, consequently increasing the levels of this trace element in water and in oyster flesh [32].

Similar observations have shown that regulations have had a beneficial effect on marine farms in different regions. In Great Britain, water quality has improved sufficiently to resume oyster culture in the Backwater River [33] and to plan oyster farms in other bays [34]. Two years after the ban in New South Wales (Australia), shell calcification anomalies in the oyster *Saccostrea commercialis* have completely disappeared, with TBT content in the tissues close to the detection threshold, contrary to copper and zinc levels which have been found to increase [21].

Table 2  
Effects of the paint regulations on TBT seawater contamination ( $\text{ng l}^{-1}$ )  
in Arcachon Bay (France).

	1986 <sup>a</sup>	1987 <sup>a</sup>	1992 <sup>b</sup>
Arcachon Marina	8–57	10–50	7
La Vigne Marina	2–89	< 2–30	3
La Hillion	< 2–51	2–5	< 0.2

<sup>a</sup>Alzieu et al. (1989).

<sup>b</sup>Michel P., unpublished.

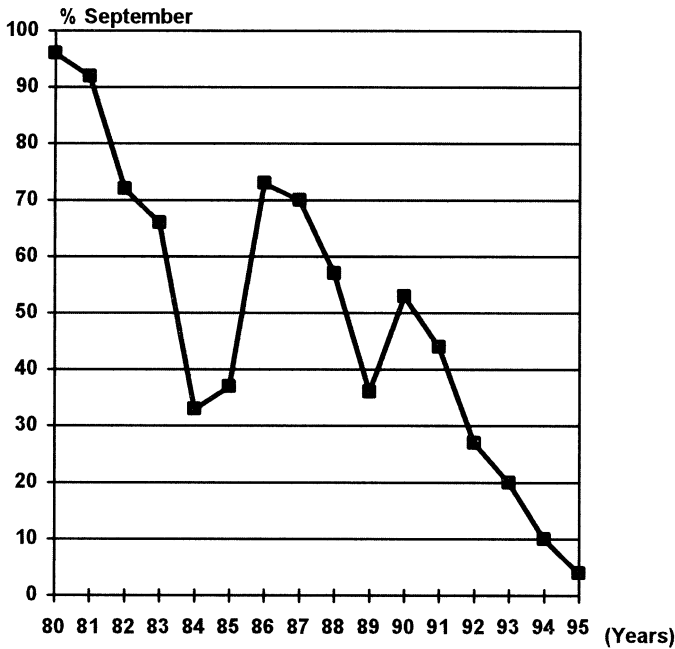


Fig. 2. Evolution of the chambering phenomenon on oysters Arcachon bay (data from IFREMER - Arcachon).

Likewise, a notable decrease of imposex matched by improved reproduction has been observed in gastropod populations in Great Britain [35] as well as in Canada [36]. Recent findings indicate that imposex should no longer be regarded as a TBT-specific effect on gastropods, since other contaminants (e.g. copper) have been shown to cause similar effects by inhibiting the transformation of testosterone into estradiol. Nevertheless, these observations do not challenge the validity of the role played by TBT in the occurrence of the phenomenon, nor by its absence in the regression of imposex. They however confirm the necessity to validate biological observations against appropriate analytical checks.

Analytical monitoring studies generally reveal a rapid decline of TBT concentration in waters along with a certain stability of the levels recorded in surface sediments. In large bays harboring both regulated pleasure boats and merchant ships, water contamination, although relatively low, has been found to exceed allowable thresholds [37].

## 8. Conclusion and prospects

For the past 15 years, tributyltin has been regarded as a contaminant of coastal waters, and it has been studied and regulated as such. TBT contamination presents

the following three major characteristics:

- ecotoxicological data show that TBT degrades slowly in the water column (half-life ranging from a few days to a few months), that it is stable in the surface and deep sedimentary compartment, and that no effect levels for mollusc growth (most sensitive species) are very low and likely to be under one  $\text{ng l}^{-1}$ . Because of these properties, it is difficult to guarantee that the use of TBT as a biocide could be compatible with certain marine activities (e.g. oyster farming);
- the regulatory measures adopted by many countries, all of which involve a ban on the use of TBT-based antifouling paints for boats under 25 m-long, have resulted in a significant decrease in contamination, accompanied in certain areas by a recovery of shellfish culture and restoration of normal gastropod fertility. Special attention should however be directed to two specific problems: the potential environmental hazard presented by harbors sediments during dredging operations or dumping at sea of dredge spoils, as well as the contamination of coastal areas subjected to heavy maritime traffic;
- because of their high efficiency, TBT-based antifouling paints were largely used prior to the regulatory restrictions. Although substitute paints are based on less toxic agents, most of them still work according to the same principle, i.e. release of a toxic substance, which ultimately could lead to unacceptable inputs into the marine environment. The development of environmentally non-dangerous antifouling paints has therefore become a priority. Research in toxicant-free techniques should accordingly be encouraged and supported.

## References

- [1] Alzieu Cl, Héral M, Thibaud Y, Dardignac MJ, Feuillet M. Influence des peintures antisalissures à base d'organostanniques sur la calcification de la coquille de l'huître *Crassostrea gigas*. Revue des Travaux de l' Institut des peches Maritimes, (1981–1982);45(2):101–16.
- [2] Smith BS. Tributyltin compounds induced male characteristics on female mud snails *Nassarius obsoletus* = *Tlyanassa obsoleta*. Journal Applied Toxicology, 1981;1(3):141–44.
- [3] Féral C, Legall S. Induction expérimentale par un polluant marin, le tributylétain, de l'activité neuro endocrine contrôlant la morphogénèse du pénis chez les femelles d'*Ocenebra erinacea*, Mollusque, Prosobranchie gonochorique. Comptes Rendus des Searces de l' Academic des Sciences Paris 1982;295, III:627–30.
- [4] Maguire RJ. Environmental aspects of tributyltin. Applied Organometallic Chemistry; 1987; 1:475–98.
- [5] Alzieu Cl. L'étain et les organoétains en milieu marin: Biogéochimie et Ecotoxicologie. Rapports scient. et tech. de l'IFREMER, 1989;17:1–93.
- [6] Fent K. Ecotoxicology of organotin compounds. Critical Reviews in Toxicology, 1996;26(1):1–117.
- [7] de Mora SJ. Tributyltin: case study of an environmental contaminant. Cambridge Environmental Chemistry Series, 1996;8:311.
- [8] Blunden SJ, Chapman AH. Organotin compounds in the environment. In: Craig PJ, editor. Organometallic compounds in the environment, New York: Longman, 1986.
- [9] Fent K. Organotin speciation in municipal wastewater and sewage sludge: ecotoxicological consequences. Marine Environmental Research, 1989;28:477.
- [10] Stewart C, de Mora SJ. A review of the degradation of tri(n butyl)tin in marine environment. Environmental Technology, 1990;11:565–70.

- [11] Watanabe N, Sakai S, Takatsuki H. Examination for degradation paths of butyltin compounds in natural waters. *Water Science Technology*, 1992;25(11):117–124.
- [12] de Mora SJ, Stewart C, Philips D. Sources and rate of degradation of tri(butyl)tin in marine sediments near Auckland, New Zealand. *Marine Pollution Bulletin*, 1995;30(1):50–57.
- [13] Adelman D, Hinga KR, Pilson MEQ. Biogeochemistry of butyltins in an enclosed marine ecosystem. *Environmental Science–Technology*, 1990;24:1027–32.
- [14] Law RJ, Waldock MJ, Allchin CR, Laslett RE, Bailey KJ. Contaminants in sea water around England and Wales: results from monitoring surveys, 1990–1992. *Marine Pollution Bulletin*, 1994;28:668.
- [15] Hassan MA, Juma HA. Assessment of tributyltin in the marine environment of bahrain. *Marine Pollution Bulletin* 1992;24:408.
- [16] May-ming Lau M. Tributyltin antifoulings: a threat to the Hong Kong marine environment. *Archives in Environmental Contamination and Toxicology* 1991;20:229.
- [17] Wade TL, Garcia-Romero B, Brooks JM. Butyltins in sediments and bivalves from US coastal areas. *Chemosphere*, 1990;20:647.
- [18] Stewart C, Thompson JAJ. Extensive butyltin contamination in southwestern coastal British Columbia, Canada. *Marine Pollution Bulletin* 1994;28:601.
- [19] Waldock MJ, Thain JE, Miller D. The accumulation and depuration of bis, tributyltin oxyde in oysters: a comparison between the Pacific oyster, *Crassostrea gigas* and the flat European oyster, *Ostrea edulis*. ICES, C.M. 1983/E: 59.
- [20] Uhler AD, Durell GS, Steinhauer WG, Spellacy AM. Tributyltin levels in bivalve mollusks from the east and west coast of the United States: results from the 1988–1990 national status and trends mussel watch project. *Environmental Technology and Chemistry*, 1993;12:139–53.
- [21] Batley GE, Scammell MS, Brockbank, CI. The impact of the banning of tributyltin-based antifouling paints in the sydney rock oyster, *Saccostrea ccommercialis*. *The Science of the Total Environment*, 1992;122:301–14.
- [22] Gibbs PE, Bryan GW, Pascoe PL, Burt GR. The use of the dogwhelk (*Nucella lapillus*) as an indicator of TBT contamination. *Journal of the Marine Biological Association of the United Kingdom*, 1987;67:507–24.
- [23] Bryan GW, Gibbs PE, Burt GR, Hummerstone LG. The effects of tributyltin TBT accumulation on adult dog-welks, *Nucella lapillus*: long term field laboratory experiments. *Journal of the Marine Biological Association of the United Kingdom*, 1987;67:525–44.
- [24] Maguire RJ, Tkacz RJ, Chau YK, Bengert GA, Wong PTS. Occurrence of organotin compounds in water and sediment in Canada. *Chemosphere*, 1986;15:523–74.
- [25] Iwata H, Tanabe S, Miyazaki N, Tatsukawa R. Detection of butyltin compound residues in the blubber of marine mammals. *Marine Pollution Bulletin*, 1994;28:607.
- [26] Lascourrèges-Berdeu JF. Rôle des sulfatobactéries dans la remobilisation et la transformation des métaux et des composés organostanniques (butylétain et phénylétains) stockés dans les sédiments lagunaires. Thèse – Université de Bordeaux I (France) (1996) no 1530, 232 pp.
- [27] His E, Robert R. Développement des véligrès de *Crassostrea gigas* dans le bassin d’Arcachon. Etudes sur les mortalités larvaires. *Revue des Travaux del ’Institut des Peches Maritimes* 1983–1985;47:1–2, 63–88.
- [28] IPCS, Environmental Health Criteria 116 – Tributyltin compounds. WHO, Geneva, 1990;273 pp.
- [29] Chagot D, Alzieu CI, Sanjuan J, Grizel H. Sublethal and histopathological effects of trace levels of tributyltin fluoride on adult oysters *Crassostrea gigas*. *Aquatic Living Resources*, 1990;3:121–30.
- [30] Alzieu CI. Environmental problems caused by TBT in France: Assessment, regulations, prospects. *Marine Environmental Research*, 1991;32:7–17.
- [31] Alzieu CI, Sanjuan J, Deltreil JP, Borel M. Tin contamination in Arcachon bay: Effects on oyster shell anomalies. *Marine Pollution Bulletin*, 1986;17(11):494–98.
- [32] Claisse D, Alzieu CI. Copper contamination as a result of antifouling paint regulations? *Marine Pollution Bulletin*, 1993;26(7):395–97.
- [33] Waite ME, Waldock MJ, Thain JE, Smith DJ, Milton SM. Reductions in TBT concentrations in UK estuaries following legislation in 1986–1987. *Marine Environmental Research*, 1991;32:89–111.

- [34] Dyrnya EA. Incidence of abnormal shell thickening in the Pacific oyster *Crassostrea gigas* in Poole Harbour (UK), subsequent to the 1987 TBT restrictions. *Marine Pollution Bulletin*, 1992;24:156–63.
- [35] Evans SM, Leksono T, McKinnel PD. Tributyltin pollution: a diminishing problem following legislation limiting the use of TBT-based anti-fouling paints. *Marine Pollution Bulletin*, 1995;30(1):14–21.
- [36] Tester M, Ellis D. TBT controls and the recovery of welks from imposex. *Marine Pollution Bulletin*, 1995;30(1):90–91.
- [37] Huggett RJ, Unger MA, Seligman PF. The marine biocide tributyltin: assessing and managing the environmental risks. *Environmental Science Technology*, 1992;26(2):232–37