

Tributyltin levels in French Mediterranean coastal waters

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Tributyltin (TBT) and its degradation products were measured in seawater samples in 1988 and 1989 at different locations of the French Mediterranean coast, including harbours, marinas and mariculture areas. Higher levels of TBT contamination were found in harbour ($2\text{--}833\text{ ng dm}^{-3}$) and marina waters ($18\text{--}736\text{ ng dm}^{-3}$) compared with mariculture areas ($<2\text{--}111\text{ ng dm}^{-3}$). Geographical distribution of TBT degradation products showed that a TBT hot spot finally results in a diffuse contamination of dibutyltin (DBT) and monobutyltin (MBT), even far distant from input areas.

Keywords: tributyltin, seawater contamination, Mediterranean coast, France, analysis

INTRODUCTION

The high toxicity of tributyltin (TBT) for marine organisms, specially molluscs, was suspected at the beginning of the year 1980. Today, sublethal effects on bivalves and gastropods are quite well documented from field and experimental data. It has been demonstrated that shell malformation on Pacific oyster,¹ as well as irreversible damage to the reproduction of dog-whelk,² could occur when seawater TBT contamination is near 1 ng dm^{-3} . Several monitoring programmes or survey studies,^{3,4} conducted in Atlantic and North Sea areas, have shown that in most of these European coastal waters TBT levels were greater than 1 ng dm^{-3} .

The limited amount of information available for Mediterranean waters suggests that TBT contamination could be higher than in the Atlantic.⁵ In order to assess TBT levels along the French Mediterranean coast, we have analysed seawater samples from selected marinas, commercial harbours and mariculture areas.

MATERIAL AND METHODS

Sampling strategy

Seawater samples were taken at the nine zones described below, located between Toulon and Banyuls-sur-Mer (Fig. 1).

Toulon roadstead

Sampling was performed during April 1988 at 15 stations representative of inputs from several activities at this wide roadstead, viz. docks, mooring areas for big ships, marinas, aquaculture and mariculture areas. Two stations were located in inflow and outflow zones (stations 9 and 10), and another far from the coast served as a reference (station 11) (Fig. 2).

Île des Embiez marina

Four stations were sampled in September 1988 in this large marina and one as a reference point south of the island, far from inputs.

Bandol marina

In this marina near Toulon, which has a capacity for 1 350 boats, five stations were sampled in September 1988.

Marseille area

Twelve stations were sampled in April 1988 in the harbour and the adjacent marina (Fig. 3). Ten of these were located within the commercial harbour in the vicinity of mooring areas for large ships and two in the 'Vieux Port' marina, which has a capacity for 3 200 boats.

Etang de Thau

This saltwater pond 20 km long and 5 km wide, represents the largest shellfish culture area on the French Mediterranean coast ($10\,000\text{ tonne year}^{-1}$ of

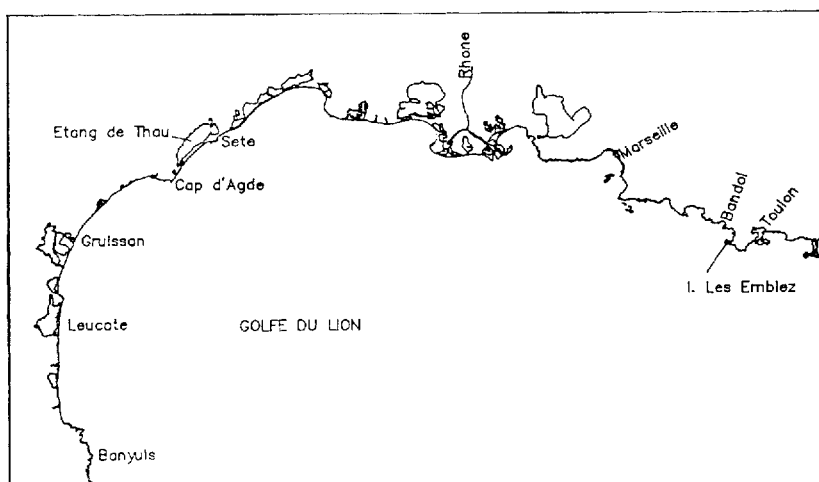


Figure 1 Selected locations for water sampling.

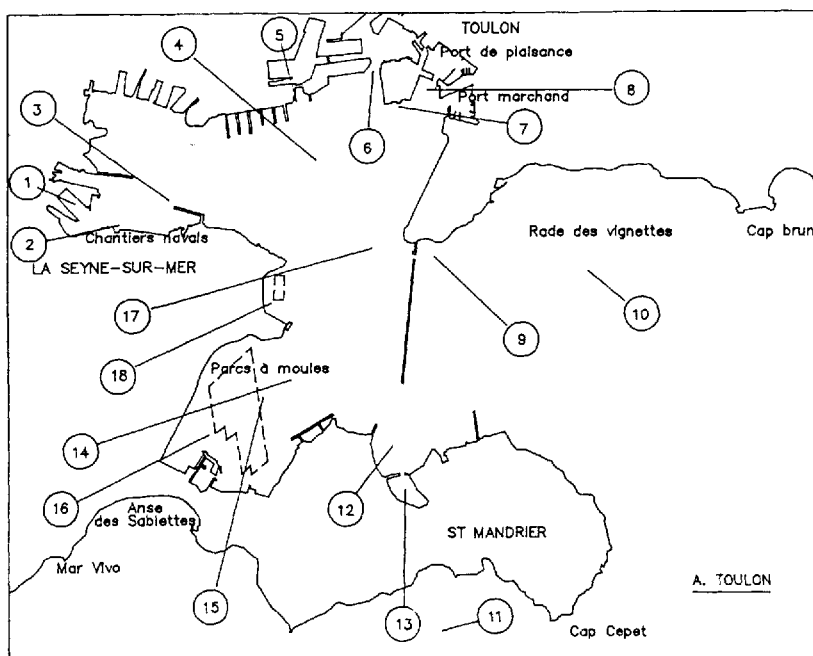


Figure 2 Sampling stations in Toulon roadstead

mussels and 5 000 tonne year⁻¹ of oysters). Ten stations were sampled in April 1988 and 1989 in marinas and shellfish areas (Fig. 4).

Cap d'Agde marina

Eight stations were sampled in April 1988 in this marina having a capacity for 1 700 boats.

Gruissan

Four stations were sampled in April and September 1988 in marina, fishing port and mariculture areas.

Leucate

This was a small saltwater pond (14 km × 6 km) having a shellfish culture area in its northern part. Five

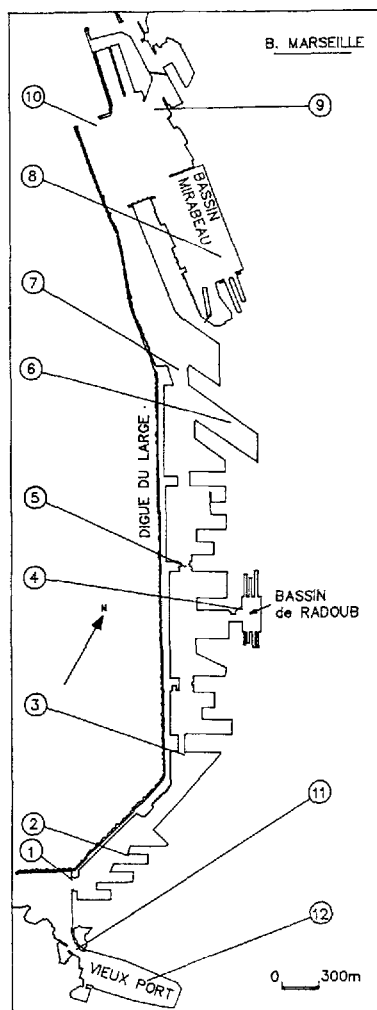


Figure 3 Sampling stations in Marseille harbour.

stations in the shellfish area and three corresponding to inputs were sampled in April 1989.

Banyuls-sur-Mer marina

Two stations were sampled in April 1989 inside the marina.

Water sampling techniques

Water samples (250 cm³) were collected, from the surface and at different depths when possible, using a Teflon sampler (Mercos). The Teflon sampling device and the glass storage bottles were acid-washed and rinsed with deionized water. All samples were

immediately acidified by 5 cm³ of 100% acetic acid, blocked by a Teflon screwcap and stored in darkness at room temperature.

Analytical techniques

Samples from 1988 were analysed by using a purge and trap hydride generator with an atomic absorption spectrometric detector as described by Michel.⁶ This technique was used for determination of TBT, DBT and MBT levels in seawater. The concentration given for each sample is the mean value obtained from five replicates. Detection limits are around 1 ng dm⁻³ for DBT and MBT, and 2 ng dm⁻³ for TBT. For the samples taken in 1989 we used another technique based on hydride generation and simultaneous extraction by hexane of the butyltin hydrides and, finally, analyses were performed by GC/FPD for DBT and TBT hydrides. We checked that these two methodologies provide comparable values, especially for TBT levels, as validated in a European Economic Community (EEC) intercomparison exercise (EEC, 1988, not published).

RESULTS AND DISCUSSION

After regrouping the sampling zones according to their main characteristics, results are presented in Table 1 for harbours, in Table 2 for marinas, and in Table 3 for shellfish culture areas.

TBT contamination

Harbours

Table 1 shows that in surface water samples, TBT contamination is higher in Toulon than in Marseille harbour, with respective ranges of 36–833 and 2–208 ng dm⁻³. Furthermore, Toulon's wet docks appear heavily contaminated (382–833 ng dm⁻³) compared with shipyard (dry) docks in the same harbour (75–122 ng dm⁻³) and Marseille's graving dock (201 ng dm⁻³). This situation could be explained by a longer period of big ship mooring and the low exchange of water between Toulon roadstead and the open sea. As a result of these high TBT inputs a large area appears contaminated at levels near 100 ng dm⁻³. The detectable traces of TBT (8 ng dm⁻³) found at station 11 show that waters

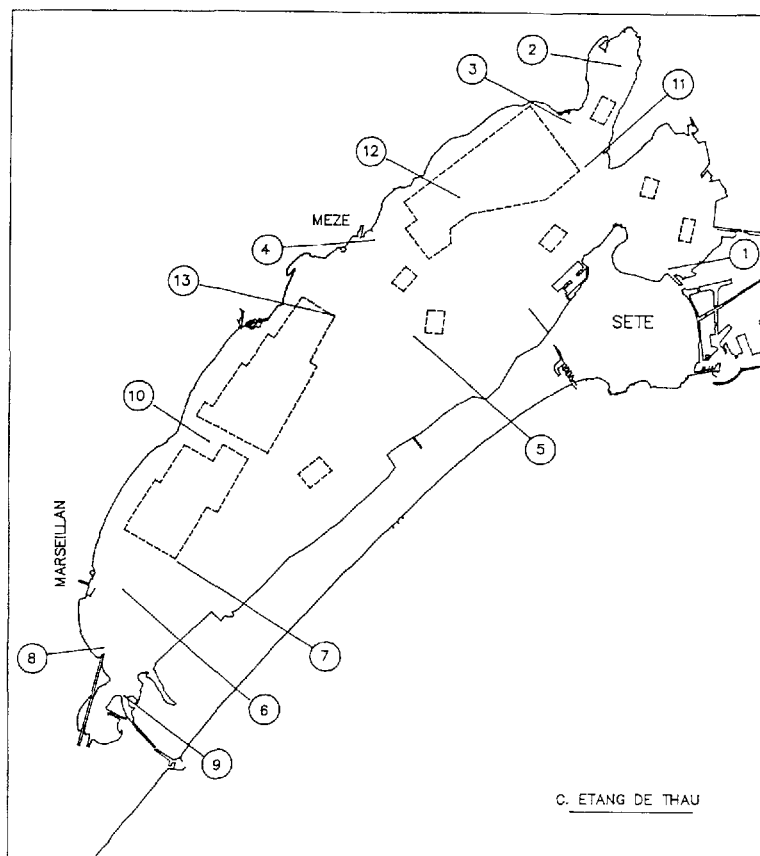


Figure 4 Sampling stations in Etang de Thau.

outside the roadstead and far from the coast are concerned. Taking into consideration results found at different depths at the central station (4) it seems that the contamination is quite homogeneous from the surface to a depth of 5 m. When sampling was made at a greater depth, levels were near 10 ng dm^{-3} (stations 4 and 10) or less (station 17).

Our data are comparable with those published⁵ for Leghorn (Livorno) Harbour in the Northern Tyrrhenian Sea: $400\text{--}810 \text{ ng dm}^{-3}$. It is noticeable that Leghorn and Toulon harbours present numerous similar characteristics e.g. high TBT input and low water turnover.

Marinas

Data reported in Table 2 show TBT contamination ranged between 18 and 736 ng dm^{-3} . Two groups of marina could be distinguished:

- (1) marinas having great capacity, high boat density and low water turnover where inner

contamination is generally greater than 100 ng dm^{-3} , e.g. Toulon, Les Embiez, Bandol, Marseille and Cap d'Agde;

- (2) small marinas located in mariculture zone and where pleasure boat activities are not well developed; contamination here is usually lower than 70 ng dm^{-3} , e.g. Etang de Thau and Leucate.

Water contamination in large marinas seems lower than that found in three marinas of the Tyrrhenian coast:⁵ $260\text{--}3\,930 \text{ ng dm}^{-3}$. Comparatively, marinas of the French Atlantic coast appear less contaminated. In a previous paper,⁴ we reported TBT values ranged between 2 and 119 ng dm^{-3} in five marinas and occasionally levels near $1\,500 \text{ ng dm}^{-3}$ in another. This difference could be explained by high tidal flush and lower boat densities in Atlantic marinas.

Mariculture areas

Results reported in Table 3 show that in sampled

Table 1 TBT and its degradation products in harbour waters of Toulon and Marseille (ng dm⁻³)

Location	Depth (m)	TBT	DBT	MBT
Toulon Harbour				
1 Ifremer Basin	0	36	36	37
2 Shipyard (wet dock)	0	122	97	90
3 Shipyard (East)	0	75	63	60
4 Roadstead (middle)	0	180	86	74
	2	168	97	74
	5	185	75	88
	10	13	29	15
5 Missiessy (wet dock)	0	833	304	48
6 New wet dock	0	382	152	24
7 New wet dock	0	537	184	21
8 Old wet dock	0	440	223	54
9 Fort Tour Royale	0	67	74	30
10 Vignettes roadstead	0	76	57	17
	15	11	13	8
11 South St Mandrier	0	8	9	8
	20	4	29	23
12 St George's Bight	0	87	55	17
17 Pointe de l'Aiguillette	0	154	98	70
	2	109	62	48
	5	56	45	17
	10	4	23	20
Marseille Harbour				
1 Joliette Port entrance	0	73	38	36
	5	12	17	42
2 Grande Joliette	0	187	46	26
	5	64	54	55
3 Arenc passage	0	92	55	62
	5	72	54	40
4 Graving dock	0	201	141	90
	5	208	132	109
5 Pont Pinède passage	0	126	75	66
6 'Commerce' basin	0	118	65	98
	5	54	22	45
7 Léon Gourret and Pdt Wilson, passage	0	57	102	46
	5	2	14	55
8 Mirabeau basin	0	147	71	71
	5	69	57	72
9 Tugboat port	0	47	62	47
	5	35	80	35
10 North entrance	0	45	47	20
	5	2	21	58

mariculture areas TBT contamination ranges between <2 and 111 ng dm⁻³. The mussel culture area of Baie du Lazaret (Toulon), which produces annually 250–300 tonnes, appears the most polluted with a median level equal to 100 ng dm⁻³. This situation is the consequence of the high contamination of Toulon roadstead as explained above. As a biological

consequence, these concentrations will have an undoubted adverse effect on reproduction as well as an impairment of the growth of juvenile mussels.

The contamination is much lower in the other areas and seems comparable in Etang de Thau and Leucate where mussels (*Mytilus galloprovincialis*) and Pacific oysters (*Crassostrea gigas*) are grown. No significant difference has been found between 1988 and 1989 sampling in Etang de Thau. In these two areas TBT concentrations occasionally exceed the level of no effect on oyster reproduction,⁷ fixed at 20 ng dm⁻³. However, contamination levels are sufficiently high to produce anomalies of calcification observed in adult oyster.⁸ Furthermore, it is noticeable that the fleets cruising in Etang de Thau and Leucate are formed by small boats, with a majority used by shellfish farmers. So, according to the ban on the use of TBT antifouling paints for boats less than 25 m long, the contamination should be lower than measured here.

DBT and MBT contamination

Dibutyltins (DBTs) and monobutyltins (MBTs) are the intermediate products of TBT degradation to mineral tin. So, we can observe especially in the highly contaminated harbours (Toulon and Marseille) that the geographical distribution for DBT and MBT is less close to the main sources. At Toulon, the average and relative standard deviation (RSD, %) are respectively 161 ng dm⁻³, ±130% for TBT, 86 ng dm⁻³ ±86% for DBT and 40 ng dm⁻³, ±67% for MBT. At Marseille values are respectively 88 ng dm⁻³, ±72% for TBT, 59 ng dm⁻³ ±59% for DBT and 57 ng dm⁻³, ±40% for MBT. In these two locations, lower RSD values for DBT and MBT in comparison with TBT demonstrate that local hotspots of TBT finally result in a diffuse contamination by DBT and MBT even in reference stations, far from TBT inputs.

These observations on the relative geographical distribution of TBT, DBT and MBT are reinforced when we compare vertical distribution for the same products. For example, at Pointe de l'Aiguillette (Toulon Harbour), percentages of MBT in relation to total organotin are 22, 22, 27 and 43% respectively for samples taken at 0, 2, 5 and 10 m depths. The reason is that vertical transfer of the organotin pollutant requires enough time for partial TBT degradation to DBT and MBT.

CONCLUSION

Our survey conducted at different locations of the French Mediterranean coast shows that high levels of contamination could be observed in harbours and marinas where high TBT inputs from big ships or a

great density of pleasure craft and low water turnover exist simultaneously. Levels found in any mariculture area appear sufficiently high to produce sublethal effects or reproductive failure on cultivated mollusc populations; exceptionally (Baie du Lazaret) they reached values that would have adverse effects on juvenile growth.

Table 2 Range of butyltins in seawater marinas (ng dm^{-3})

Location	Depth (m)	Date	TBT	DBT	MBT
Toulon/St Georges	0		408	107	72
Les Embiez					
Pte Gabrielle (reference)	0		2	< 1	< 1
Inner marina (4 stations)	0		98–480	94–185	40–50
Bandol					
Reference station	0		10	< 1	< 1
Inner marina (five stations)	0		175–390	106–147	56–83
Marseille 'Vieux Port'					
Entrance	0		736	190	78
Inner	0		410	119	98
Etang de Thau					
Mèze marina (station 4)	0	April 1988	59	25	38
		April 1989	58	—	—
Marseillan marina (station 6)	0	April 1988	54	23	8
		April 1989	79	—	—
Cap d'Agde					
Entrance (reference)	0		34	36	19
Inner marina (seven stations)	0		147–536	65–163	16–56
Gruissan					
Fishing boat port	0		16	17	4
Marina	0		102	26	9
Leucate (three stations)	0		18–70	—	—
Banyuls-sur-mer (two stations)	0		129–161	41–44	—

Table 3 Range of butyltins in seawater samples of mariculture areas (ng dm^{-3})

Location	Depth (m)	Date	TBT	DBT	MBT
Toulon					
Baie du Lazaret (shellfish; three stations)	0		98–111	41–103	38–59
Baie de Balaguier (fish-farm; one station)	0		58	63	46
Etang de Thau					
Stations 1, 2, 3, 5, 7, 8, 9, 10	0	April 1988	<2–16	<1–8	<1–27
	2		<2–16	<1–38	1–26
	0	April 1989	5–23		
Stations 11, 12, 13	0	April 1989	6–10	—	—
Gruissan (shellfish storage zone; two stations)	0	April 1988	13/17	16	10
	0	Sept. 1988	<2/20	<2/30	<2/2
Leucate (shellfish culture area; six stations)	0	April 1989	<2–27	—	—

Harbour pollution could be easily linked with big ships allowed to use organotin paints, but on the other hand marinas and mariculture areas have contamination that could not be explained only by legal inputs from pleasure boats greater than 25 m long. In comparison, in all locations sampled in the Mediterranean, TBT contamination could be considered higher than that found in similar zones of the Atlantic coast.

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