



## Trace elements in the sediments of a large Mediterranean marina (Port Camargue, France): Levels and contamination history

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### ABSTRACT

The study of trace elements (Cu, Zn, Pb, As, Hg) and butyltin concentrations in the sediments of Port Camargue enabled assessment of the levels and history of the contamination of the largest European marina linked with the use of antifouling paints. Surface sediments near the boat maintenance area were heavily contaminated with up to 1497  $\mu\text{g g}^{-1}$  of Cu, 475  $\mu\text{g g}^{-1}$  of Zn, 0.82  $\mu\text{g g}^{-1}$  of Hg, 94  $\mu\text{g g}^{-1}$  of Pb and over 10,000  $\text{ngSn g}^{-1}$  of tributyltin (TBT). High concentrations of Hg and TBT indicate ongoing sources of these elements despite the ban on their use as biocides in paints. Sediment cores provided records of contamination since 1969. The peak concentrations of As, Hg, Pb and TBT in the sediment profile reflect their presence on boat hulls when the marina was built at the end of the 1960s. Degradation of TBT in the sediments near the boat maintenance area is slow compared to other less contaminated area of the marina.

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### 1. Introduction

Harbour sediments generally have high concentrations of trace elements due to harbour activities. Among the many potential sources, metal based antifouling systems clearly play a major role in the contamination. Lead and copper sheets were already used in ancient times to limit biofouling of ship hulls (Yebra et al., 2004). In the 20th century, lead based paints were used to prevent corrosion and fouling. Pb was subsequently replaced by arsenic, mercury, copper and tributyltin (TBT). As and Hg based paints were banned in France in the 1960s (Miquel, 2001) and TBT was widely used from then until 2008. Copper is now the main inorganic biocide used in antifouling systems (AF). Zinc oxides and other chemical compounds are commonly added to paints as booster biocides. The widespread use of antifouling (AF) paints has resulted in high levels of contamination of the water and of the sediments (Jones and Turner, 2010).

Prejudicial effects, especially of TBT and Cu, have been observed in non-target organisms. In the 1980s, deleterious effects of TBT on oyster shell formation were reported in French oyster farms (Alzieu et al., 1986). Ecological effects on growth, reproduction, development and survival have also been reported in various marine species (Gibbs and Bryan, 1986; Maguire, 1987). In seawater,

Horiguchi et al. (1998) observed that concentrations between 1.2 and 5.6  $\mu\text{g L}^{-1}$  caused irregular swimming behaviour of gastropod larvae. At lower concentrations (0.2  $\mu\text{g L}^{-1}$ ), TBT has been reported to have an impact on the sexual organ of gastropods (Smith, 1981).

In the marine environment TBT can be successively desalkylated or dearylated from tri- to di-, monosubstituted compounds and finally inorganic tin. The persistence of TBT in the environment depends on physicochemical conditions including dissolved/suspended organic matter, pH, salinity, and temperature (Dubey and Roy, 2003) as well as on the degradation mechanism (which may be biotic or abiotic) (Maguire and Tkacz, 1985; Cooney and Wuertz, 1989). Tributyltin degradation kinetics in marine environments vary. In the water column, degradation takes days or weeks (Stewart and de Mora, 1990), whereas in the sediment, organotin compounds associate strongly with natural sorbents and are quite stable under anoxic conditions (Fent, 1996). In superficial sediment, the half-life of TBT is about two years (de Mora et al., 1989) but can be decades in deep sediments (Dowson et al., 1996; Maguire, 2000).

In the early 1980s, worrying side effects of TBT on oysters led French authorities to forbid the use of TBT on vessels less than 25 m in length (Alzieu et al., 1986). This prompted other countries to restrict its use on small vessels between 1987 and the early 1990s (Stewart, 1996). In the early 1990s, an International Maritime Organization (IMO) resolution recommended that governments ban the use of TBT on vessels less than 25 m in length;

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TBT leaching from paint should be less than  $4 \mu\text{g cm}^{-2} \text{day}^{-1}$ . Since 2008, TBT antifouling coatings have been banned by the IMO on all vessels.

Although Cu is an essential element for organisms, when its concentration exceeds nutritional requirements, it is toxic (Hall and Anderson, 1999; Rivera-Duarte et al., 2005). Most Cu contamination in estuaries and harbour sediments comes from dissolved AF paint in the seawater. However Turner et al. (2008) demonstrated that AF particles released in harbour sediments during hull clearance can contain up to 30% of Cu in a form that is bioavailable for benthic organisms and also for organisms living in the water column that ingest resuspended paint particles. A few  $\text{mg L}^{-1}$  of paint residues were shown to reduce the photosynthetic activity of the alga *Ulva Lactuca* (Turner et al., 2009a,b). Cu also inhibits diatom growth (Morel et al., 1978). Many other studies have also shown lethal and sublethal effects of Cu on marine organisms (Cid et al., 1995; Turner et al., 2009a,b; Xie et al., 2005; Karlsson et al., 2010). In sediments, infaunal diversity is reduced at concentrations of Cu above  $30 \mu\text{g g}^{-1}$  (Olgard, 1999; Piola and Johnston, 2007).

The Port Camargue marina has never been dredged and its sediments have been affected by pollution by toxic antifouling paints and other sources since it was built 40 years ago. We also expected the sediments to provide a record of the impact of environmental regulations.

The objective of this study was to assess the contamination and history of trace elements (Cu, Zn, As, Hg, Pb and TBT) used as biocides in antifouling paints in a large Mediterranean marina. To this end, concentrations of trace elements, monobutyltin (MBT), dibutyltin (DBT) and TBT were measured in the surface sediment in the marina and surrounding area. The history of trace element contamination was studied using sediment cores.

The fate of dredged sediments is strictly regulated by both national regulations and international conventions (London, Paris, Barcelona). In some cases, dumping dredged sediments at sea is forbidden, instead they must be discharged on shore in sites dedicated to toxic chemical wastes. Another objective of this study was to undertake fine characterization of the sediments in the Port Camargue marina to plan their management after dredging.

## 2. Materials and methods

### 2.1. Site description

The construction of Port Camargue marina (Fig. 1) began in 1960. The southern channel was finished in 1969 and the northern channel in 1979. In 1989, Port Camargue became the largest European marina with a 60 ha basin and more than 5000 moorings. The boat maintenance area covers an area of 4.5 ha and groups 20 companies specialized in the maintenance of leisure vessels. About 2000 hull cleaning operations are carried out each year. The regulation that is applied is the European Commission's Integrated Pollution Prevention and Control Directive (IPPC; EC/61/96) and its transcription in French Right: the Water Law (No. 92-3, January 1992). In this context, sedimentation tanks were installed in 2004 in this area for hull cleaning water wash down and other wastewater. Tanks are cleaned twice a year and the sludge is disposed in discharges dedicated to toxic chemical wastes. However, the wastewater is not treated before disposal.

Port Camargue also receives inputs from runoff from a very small (200 ha), densely urbanized drainage basin and from the sea.

The sedimentation rate in the marina is heterogeneous and low (around  $1 \text{ cm yr}^{-1}$ ) according to bathymetric data provided by the port authorities. This explains why the marina has never been dredged since it was built.

### 2.2. Sampling and sample preparation

Two sampling campaigns were carried out. In February 2009, surface sediments were collected using a Shipeck® sampler at 25 sites inside the marina (PC2 to PC25), in Aigues Mortes Bay (PC26) and at one site in the Vidourle river (PC1) at the entry of the Grau du Roi fishing harbour (Fig. 1). Sediments samples collected in the 2009 campaign were not sieved.

In September 2011, a second sampling campaign was conducted to assess the vertical distribution of trace elements and butyltin compounds in the sediments. Sediment cores were removed at 10 sites (Fig. 1) using an UWITEC® corer equipped with 40 cm long polycarbonate tubes with a diameter of 8 cm. All the cores were stored at  $4^\circ\text{C}$  until analysis. Two-centimetre sections of sediment were removed and each aliquot was wet sieved with seawater. The  $<63 \mu\text{m}$  fraction was recovered using a nylon sieve.

Samples from both campaigns were freeze dried. Shell debris visible to the naked eye in unsieved samples were discarded. Macroscopic or microscopic observations using scanning and transmission electron microscopy did not detect paint chips in either the sieved or unsieved samples. The sediments were then ground in an agate mortar and stored in the dark at  $-20^\circ\text{C}$  until analysis.

### 2.3. Sediment analysis

In preparation for analysis of the concentrations of inorganic metals, 100 mg aliquots of sediments were digested using a mixture of 2 mL HF (Suprapur 40%, Merck Millipore®) and 4 mL  $\text{HNO}_3$  (Suprapur 65%, Merck Millipore®). Digestion was carried out in a microwave oven (Discover SP-D Plus, CEM®) using the U.S. EPA method SW 846-3052. To prevent contamination, samples were prepared in a clean room inside a Class 100, laminar air-flow clean bench cabinet. Contamination of samples during digestion (vials, acids) was negligible ( $<0.01\%$ ) compared to the concentrations measured.

Trace elements (Cu, Zn, As, Pb) and Al were then determined using an ICP-MS, X Series II (Thermo Fisher Scientific®), equipped with a collision cell technology (CCT) chamber. A solution containing  $30 \mu\text{g L}^{-1}$  of In and Bi was added on-line to the sample and used to correct signal drift. Certified reference marine sediment from the Canadian National Research Council, MESS-3, was used to check analytical precision and accuracy. Measured concentrations agreed with recommended values to within  $\pm 5\%$  for Al, Cu, Zn and As and  $2\%$  for Pb. Internal precision was better than  $\pm 4\%$ . The detection limits in the sediment were  $0.06 \mu\text{g g}^{-1}$  for Cu,  $0.045 \mu\text{g g}^{-1}$  for Zn,  $0.015 \mu\text{g g}^{-1}$  for As and  $0.06 \mu\text{g g}^{-1}$  for Pb.

For analysis of butyltin compounds, sediments were extracted gently to prevent any modification of Sn speciation (Bancon-Montigny et al., 2001) using glacial acetic acid under agitation for one night. Derivatization of organotin compounds on acidic extracts was then performed as described by Carlier-Pinasseau et al. (1996). The organo species monobutyl (MBT), dibutyl (DBT) and tributyl-tin (TBT) were determined using a gas chromatograph (Focus GC – Thermo Fisher Scientific®) coupled with an inductively coupled plasma mass spectrometer (ICP-MS X Series II-Thermo Fisher Scientific®). The mass spectrometer was used for time-resolved analysis of  $^{120}\text{Sn}$ ,  $^{118}\text{Sn}$  and  $^{117}\text{Sn}$ .

The sediment certified reference material PACS-2, certified for MBT, DBT and TBT ( $700 \text{ ngSn g}^{-1}$ ,  $1100 \pm 135 \text{ ngSn g}^{-1}$  and  $832 \pm 95 \text{ ngSn g}^{-1}$ , respectively) was obtained from the National Research Council, Canada (NRC, Ottawa, Canada). The recovery of TBT, DBT and MBT were within the 95% confidence interval of the certified value.

The 7473 EPA standard method was used for the determination of total Hg concentrations in the sediments. A detailed description of the technique is given in Cossa et al. (2002). It involves a pyro-

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