Deciphering As and Cu cycling in sediment pore waters in a large marina (Port Camargue, southern France) using a multi-tracer (Fe, Mn, U, Mo) approach

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ABSTRACT

The sediments of the Port Camargue marina (South of France) are highly polluted by Cu and As (Briant et al., 2013). The dynamics of these pollutants in pore waters was investigated using redox tracers (sulfides, Fe, Mn, U, Mo) to better constrain the redox conditions.

In summer, pore water profiles showed a steep redox gradient in the top 24 cm with the reduction of Fe and Mn oxy-hydroxides at the sediment water interface (SWI) and of sulfate immediately below. Below a depth of 24 cm, the Fe, Mn, Mo and U profiles in pore waters reflected Fe and Mn reducing conditions and, unlike in the overlying levels, sulfidic conditions were not observed. This unusual redox zonation was attributed to the occurrence of two distinct sediment layers: an upper layer comprising muddy organic-rich sediments underlain by a layer of relatively sandy and organic-poor sediments. The sandy sediments were in place before the building of the marina, whereas the muddy layer was deposited later. In the muddy layer, large quantities of Fe and Mo were removed in summer linked to the formation of insoluble sulfide phases. Mn, which can adsorb on Fe-sulfides or precipitate with carbonates, was also removed from pore waters. Uranium was removed probably through reduction and adsorption onto particles. In winter, in the absence of detectable pore water sulfides, removal of Mo was moderate compared to summer.

Cu was released into solution at the sediment water interface but was efficiently trapped by the muddy layer, probably by precipitation with sulfides. Due to efficient trapping, today the Cu sediment profile reflects the increase in its use as a biocide in antifouling paints over the last 40 years.

In the sandy layer, Fe, Mn, Mo and As were released into solution and diffused toward the top of the profile. They precipitated at the boundary between the muddy and sandy layers. This precipitation accounts for the high (75 $\mu g\ g^{-1}$) As concentrations measured in the sediments at a depth of 24 cm.

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1. Introduction

With more than 40% of the Mediterranean coastline urbanized, coastal waters are subject to considerable human pressure (UNEP/MAP-Plan Bleu, 2009). As a consequence, recent coastal sediments in the Gulf of Lions (southern France) receive high inputs of contaminants including toxic trace elements, as demonstrated by studies of sediment records (Elbaz-Poulichet et al., 2011; Kawakami et al., 2008). These trace elements can be released from sediments during early diagenesis. This process, which is mainly driven by the mineralization of organic matter, is mediated by bacteria and follows a sequence of reactions during which the oxidants in solution and in the solid phase are used in the following order: O_2, NO_3^-, Mn(IV), Fe (III), SO_4^{2-} (Sigg et al., 1992).

Fluxes of trace elements at the sediment water interface (SWI) have already been measured in Thau lagoon using benthic chambers by Point et al. (2007). That study showed that the transfer of most elements from the sediment to the water column is enhanced by low oxygenation of the water column. Seasonal variations as well as fine 1D (or even 2D) variations in trace elements and associated diagenesis tracers in sediment pore water were the subject of several recent studies in Mediterranean lagoons

(Jézéquel et al., 2007; Metzger et al., 2007; Rigaud et al., 2013) and in the bay of Toulon (Dang et al., 2015, 2014). Altogether, these studies highlighted seasonal variations of diagenetic activity related to the effect of temperature on microbiological activity and/ or to the supply of fresh organic matter to bottom sediments. These variations affect the behavior of trace elements. The same studies also confirmed the role of Fe and Mn-oxides in the control of trace element mobility in pore water and their exchange at the SWI. Upon precipitation in oxic conditions, Fe and Mn-oxides co-precipitate and/or adsorb trace elements. Conversely, their reductive dissolution releases trace elements into the pore water. Organic matter is also important either as a carrier phase that releases trace elements upon remineralization and stabilizes them in pore water through complexation. The formation of sulfides through the reduction of sulfate is also an important process that limits the mobility of trace elements in pore water through the precipitation of insoluble metal sulfides.

Organoarsenic and Cu were used as biocides in antifouling paints up to 1960 before the use of tributyltin became widespread. From 1982 on, the use of tributyltin in paints for ships was progressively forbidden in France until its total ban in 2003, when it was replaced by Cu. In marinas and harbors along the Mediterranean coast where sedimentation rates are low, concentrations of As and Cu can be high. In the marina of Port Camargue, southern France, As and Cu concentrations of respectively 1500 and 75 $\mu g\,g^{-1}$ have been reported in sediments (Briant et al., 2013) indicating notable enrichment (up to 200 for Cu and 50 for As) compared to crustal values (Taylor and McLennan, 1985).

These polluted sediments could be a source of pollution for overlying waters. In this context, the objectives of this study were to understand the processes that control the mobility of Cu and As in heavily polluted coastal sediments.

To this end, sediments and pore waters were sampled in the marina of Port Camargue. Peepers were used to collect pore waters. They were embedded in the sediment at the end of summer and in winter to account for seasonal variations in diagenetic activity. Cu and As concentrations were measured in both the pore waters and the sediment solids. In order to better constrain the redox conditions in the sediments, the concentrations of redox sensitive elements (Fe, Mn, U and Mo), which have contrasted solubility depending on redox conditions (see Calvert and Pedersen, 2007 and references therein) were also systematically measured in the pore waters and in the sediment solids. The presence of pore water sulfides was also investigated. The results of this study improve our knowledge of the biogeochemical processes that control As and Cu cycling in a heavily polluted Mediterranean water body and will hopefully contribute to better management of such highly polluted environments.

2. Material and methods

2.1. Study site

Port Camargue (Fig. 1) is among the largest European marinas with a capacity of five thousand moorings. It is located in the bay of Aigues Mortes in the western part of the Rhone delta. This part of the delta receives freshwater inputs from the Vidourle River and is also under the influence of the plume of the Rhone River, which discharges 70 km east of Port Camargue. The marina was built between 1960 and 1985 and was partially dug in a sand dune formation made of Rhone river alluvium (Raynal et al., 2010).

According to bathymetric data provided by the port authorities, the sedimentation rate in the marina is heterogeneous and low (maximum 1 cm yr^{-1}). The marina has not been dredged since it was built, so its sediments have incorporated around 50 years of polluting trace elements. Briant et al. (2013) reported heavy pollution of surface (top 25 cm) sediments that were related to their past or present use in antifouling paints. Cu concentrations were particularly high, reaching 1500 $\mu g\,g^{-1}$ near the boat careening area. Arsenic concentrations reaching 75 $\mu g\,g^{-1}$ were also reported in the same study. Sediment bioturbation linked to biological activity is limited due to the absence of benthic macro-organisms, confirmed by observations of the sediment core. This is probably due to the high level of pollution, which inhibits their growth. However, sediment mixing through resuspension also probably occurs, although mostly in navigation channels. At our study site, which is located near a dock, resuspension was limited as indicated by the Cu and tributyltin sediment profiles, which reflect the history of their use in antifouling paints since the construction of the marina (Briant et al., 2013).

2.2. Sample collection and treatment

A sediment core was collected at sampling station 19 (Fig. 1) using a UWITEC® corer equipped with 40 cm long polycarbonate tubes with a diameter of 8 cm. The core was cut into 2 cm sections. Raw sediments were used for granulometry analysis. Sediments destined for trace element analysis were wet sieved with seawater using a nylon sieve, freeze dried, and ground in an agate mortar. Particulate organic carbon (POC) was determined on total sediment after freeze drying and grinding.

Pore waters were also sampled at site 19 (Fig. 1). Three sampling campaigns were carried out in September 2012 (summer 2012), February 2013 (winter) and September 2013 (summer 2013). The main physical−chemical parameters were monitored in the middle of the water column (around 1.25 m above the sediment layer) twice a month using a multi-parameter HACH HQ40d equipped with different probes for the determination of conductivity, pH, dissolved oxygen and temperature. During the winter survey, the water temperature was about 10 °C and salinity 30. In summer, the water temperature ranged from 19 °C to 21 °C, and salinity was 35. Measurements of dissolved oxygen always pointed to oxygen saturation.

Dialysis samplers or peepers were used for the collection of pore waters (Hesslin, 1976). These devices are made of a 1.8 cm thick methacrylate casing, and are 65 cm high and 18 cm wide. The device consists of two columns of 50 horizontal cells (4.6 mL) with 1 cm vertical resolution.

Prior to sampling, the peepers were acid cleaned with HCl (Suprapur® 2N, Merck Millipore), then rinsed with deionized water (Milli-Q® Millipore). The dialysis cells were filled with Milli-Q water and covered with a filtration membrane (0.22 μm, PVDF membrane, Hydrophilic, Durapore®). To prevent pollution, preparation was carried out inside a Class 100, laminar air-flow clean bench cabinet in a clean room. The peepers were stored in Milli-Q water. As the presence of oxygen in the dialysis cell when anoxic pore waters are sampled can distort the results (Bufflap and Allen, 1995), the peepers were stored in an airtight container flushed with nitrogen for two weeks before being embedded in the sediments.

Pairs of peepers were embedded in the sediments by divers and left in place over a period of four weeks, which is the time necessary for full equilibration to be reached (Stewart and Malley, 1999; Teasdale, 1995). After retrieval, the peepers were immediately placed in nitrogen filled polyethylene (PE) bags to prevent oxidation and transported to the laboratory in an airtight container flushed with nitrogen.

In the laboratory, the peepers were transferred to a glove box flushed with nitrogen and the water contained in the cells was sampled through the dialysis membrane with PE syringes equipped with polypropylene pipette tips. One peeper was reserved for
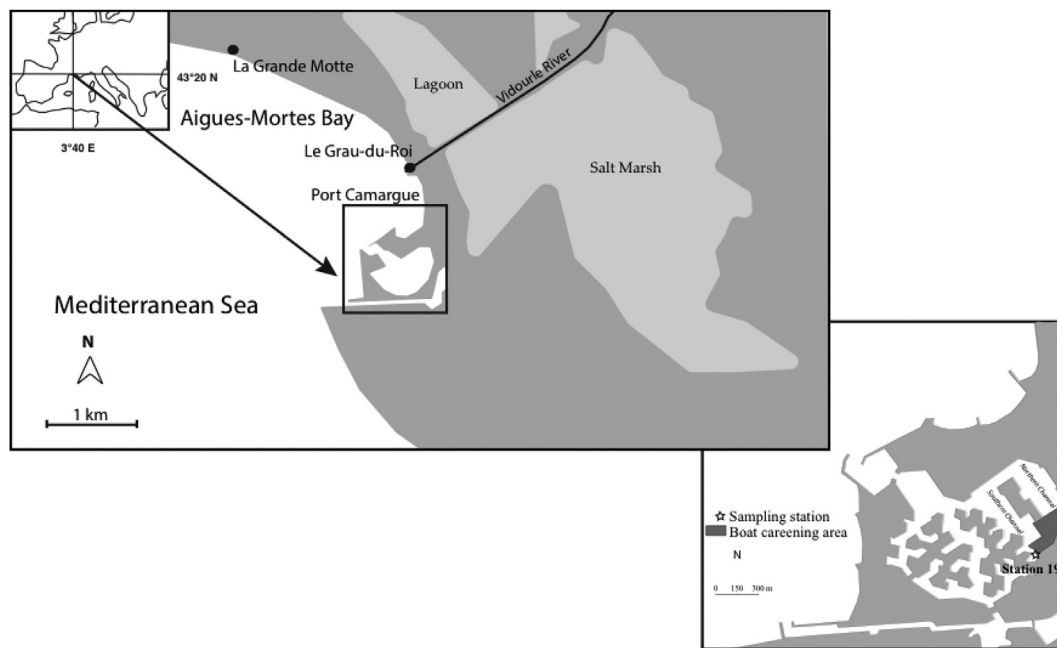
Fig. 1. Map of the study area with the location of the sampling station.

analyses of trace elements. For sulfide analysis, samples were taken from the second peeper. The position of the SWI interface in the peepers was determined visually by the change in color of the peepers. The section of the peeper above the SWI turned grey whereas the part below kept its original color. The precision of the determination of the position of the SWI was ±1 cm. Samples for trace element analysis were acidified to 1‰ with HNO_3 (Merck Suprapur) prior to analysis.

2.3. Pore water analysis

Pore water sulfides sampled during the winter and the summer 2013 surveys were analyzed using the methylene blue method (Spectroquant 114779, Merck®) at 665 nm. Detection limit was 0.70 mg L^{-1} of total sulfides ($\sum H_2S$).

Trace element (Cu, As, Mn, Fe, Mo, U) concentrations were determined using a 7700 Series ICP-MS (Agilent Technologies®) with In, Sc and Ge as internal standards. The samples collected in the 2012 survey were not diluted, whereas the samples collected in the two 2013 surveys were diluted 5 times prior to analysis. The detection limits were 0.22 µg L^{-1} for Cu, 0.05 µg L^{-1} for As, 0.06 µg L^{-1} for Mn, 1.02 µg L^{-1} for Fe, 0.29 µg L^{-1} for Mo and 0.01 µg L^{-1} for U.

The accuracy and precision of the method were tested using the CASS-5 seawater reference material certified by the Canadian National Research Council (CNRC). Measured concentrations of Cu, As, Fe, Mn, Mo and U agreed with recommended values to within ±4%.

2.4. Solid phase analysis

Sediment granulometry was determined immediately on the raw sediments using a Coulter LS 13 320 laser granulometer. The concentration of POC in the sediments was determined with a LECO analyzer at the EPOC laboratory (University of Bordeaux-CNRS) as described by Etcheber et al. (1999).

The procedure used for the analysis of trace elements (Cu, As, Mn, U, Mo) is described in detail in Briant et al. (2013). Briefly, after digestion of the sediments with HF and HNO_3 (Merck Suprapur),

evaporation to near dryness and dissolution of the residue in HNO_3 (Merck Suprapur), trace elements were determined using an ICP-MS, X Series II (Thermo Fisher Scientific), equipped with a collision cell technology (CCT) chamber. In and Bi were used as internal standards 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 ±5%.

3. Results

3.1. Physico-chemical characteristics of the sediments

3.1.1. Main physico−chemical parameters

Granulometry data (Fig. 2) showed that the fine silt and clay fraction (grain size <15 µm) was predominant in surface sediments. Below a depth of 24 cm, an increase of the fine to coarse sand fraction (grain size >125 µm) was observed.

The highest POC values were observed in the finer particles with a maximum value of 3.45% at a depth of 19 cm (Fig. 2). Below 23 cm, the concentrations dropped dramatically, the lowest value (0.16%) being observed at a depth of 33 cm.

3.1.2. Redox tracers

Sedimentary profiles of redox tracers are shown in Fig. 3. Mn concentrations were nearly constant from the surface to a depth of 10 cm. Between 11 and 23 cm, a broad peak in concentration was observed with a maximum value of 490 µg g^{-1} at a depth of 21 cm. Below this broad peak, Mn concentrations gradually increased to the bottom of the core. The distributions of Fe, Mo and U displayed two peaks, a shallow one at a depth of 7 cm, and a deeper one at depths of 27, 29 and 30 cm. In the case of Fe, the shallow peak was weaker than the deeper one. The two Mo peaks were of the same intensity. In the case of U, the shallow peak was stronger than the deeper one.

3.1.3. Cu and As

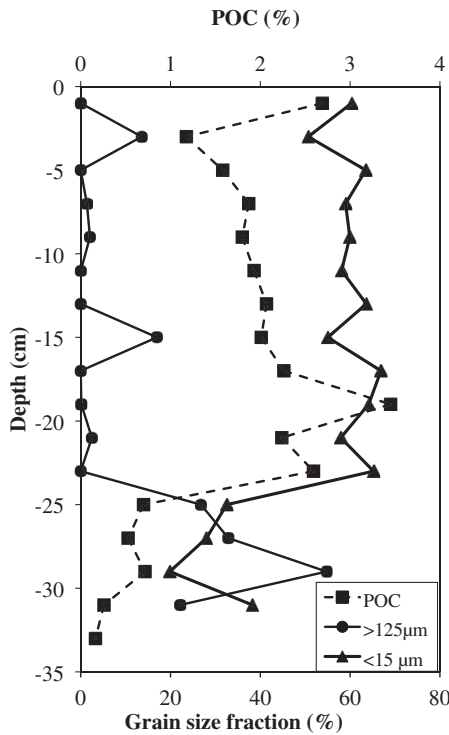As shown in Fig. 3, the concentrations of Cu increased regularly

Fig. 2. Particulate organic carbon (POC) concentrations and grain size profiles. Light/dark grey bar: sandy/muddy sediments.

from the bottom of the profile to the surface to reach a maximum value a 1973 µg g^{-1} at a depth of 7 cm, after which concentrations decreased until the surface of the profile.

Concentrations of As increased from the bottom of the profile up to a depth of 27 cm where a peak concentration of 75 µg g^{-1} was detected. Concentrations then decreased up to a depth of 7 cm where a second but very small peak was observed.

3.2. Pore water

3.2.1. Sulfides

In winter, sulfides were below the detection limit in pore waters, unlike in the summer 2013 survey when they were present at the SWI (Fig. 4). Their profile showed a broad concentration peak between 1 and 35 cm in depth, with a maximum value of 18.1 mg L^{-1} at a depth of 6 cm, after which concentrations decreased with depth. Below 35 cm, sulfides were below the detection limit.

3.2.2. Redox sensitive elements (Mn, Fe, Mo, U)

During the summer 2012 and 2013 surveys, Fe in pore waters (Fig. 4) displayed a peak concentration at the SWI with a maximum concentration of 4600 µg L^{-1}. In presence of sulfides, Fe forms highly insoluble Fe-sulfides. Because Fe and sulfides were measured in two different peepers, their simultaneous occurrence at the SWI probably reflects uncertainty in the determination of the position of the SWI, which was defined with a precision of ±1 cm for each peeper. The apparent co-occurrence could be also linked to sediment heterogeneity. Below the SWI, the concentration of Fe first decreased sharply then stabilized at 56 µg L^{-1} until a depth of 28 cm, where it started to increase and reached 1700 µg L^{-1} at the bottom of the profile.

The Mn pore water profiles were characterized by peak concentrations (55 µg L^{-1}) at the SWI. Concentrations then decreased to reach values < 11 µg L^{-1} at a depth of 14 cm. Mn concentrations increased from 14 or 24 cm in depth, respectively, in 2012 and 2013, to reach a concentration of 290 µg L^{-1} at the bottom of the profile.

Mo concentrations were 11 µg L^{-1} in the bottom water of the marina, a value typical of oxygenated seawater (Collier, 1985). The Mo pore water profiles were similar in the two surveys with concentrations decreasing from 10 µg L^{-1} at the SWI to 0.1 µg L^{-1} at a depth of 6 cm. From a depth of 24 cm, Mo concentrations increased to reach 8 µg L^{-1} at the bottom of the profile.

Concentrations of U in the bottom water of the marina (Fig. 4) ranged between 3.2 and 3.5 µg L^{-1} as expected in oxygenated seawater (Turekian, 1968). U pore water profiles were similar in the two surveys with concentrations decreasing from the SWI to a depth of 5 cm. Below this depth, concentrations ranged between 0.7 and 1.3 µg L^{-1}.

In winter, the concentration and pattern of Fe differed from the patterns observed in the two summer surveys with a comparatively lower peak concentration (400 µg L^{-1}) at the SWI. The distribution of Fe was also characterized by a broad peak between the SWI and a depth of 29 cm, with a maximum concentration of 1300 µg L^{-1} at a depth of 15 cm. Fe concentrations then decreased toward the bottom of the profile, and stabilized at 760 µg L^{-1} from 30 cm downwards.

The peak concentration of Mn at the SWI was low (33 µg L^{-1}) compared to that measured in the summer surveys. A moderate increase in Mn concentrations with depth was observed from the SWI down to 22 cm. Below this depth, concentrations increased more rapidly until the bottom of the profile.

The concentration of Mo (12 µg L^{-1}) in the bottom water (Fig. 4), decreased from the SWI to reach a minimum of 1.6 µg L^{-1} at a depth of 4 cm. Concentrations then increased towards the bottom of the profile where they reached 20 µg L^{-1}.

There was a peak in the concentration of U (4.5 µg L^{-1}) at the SWI, below which concentrations in the pore water decreased
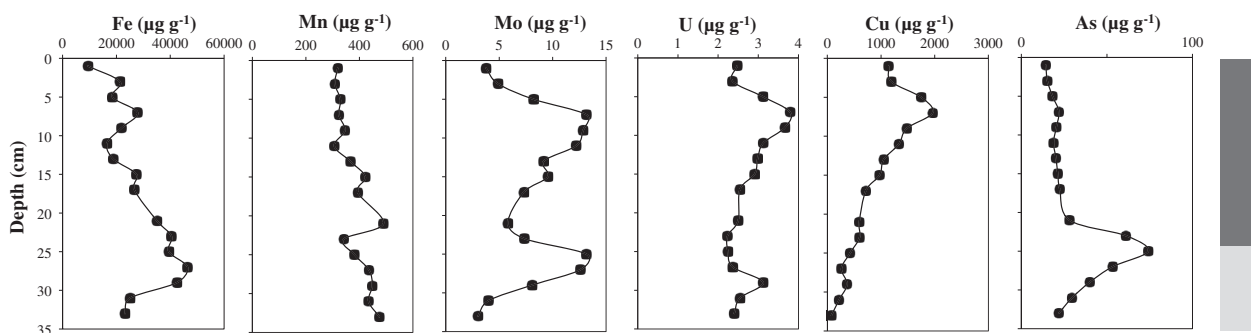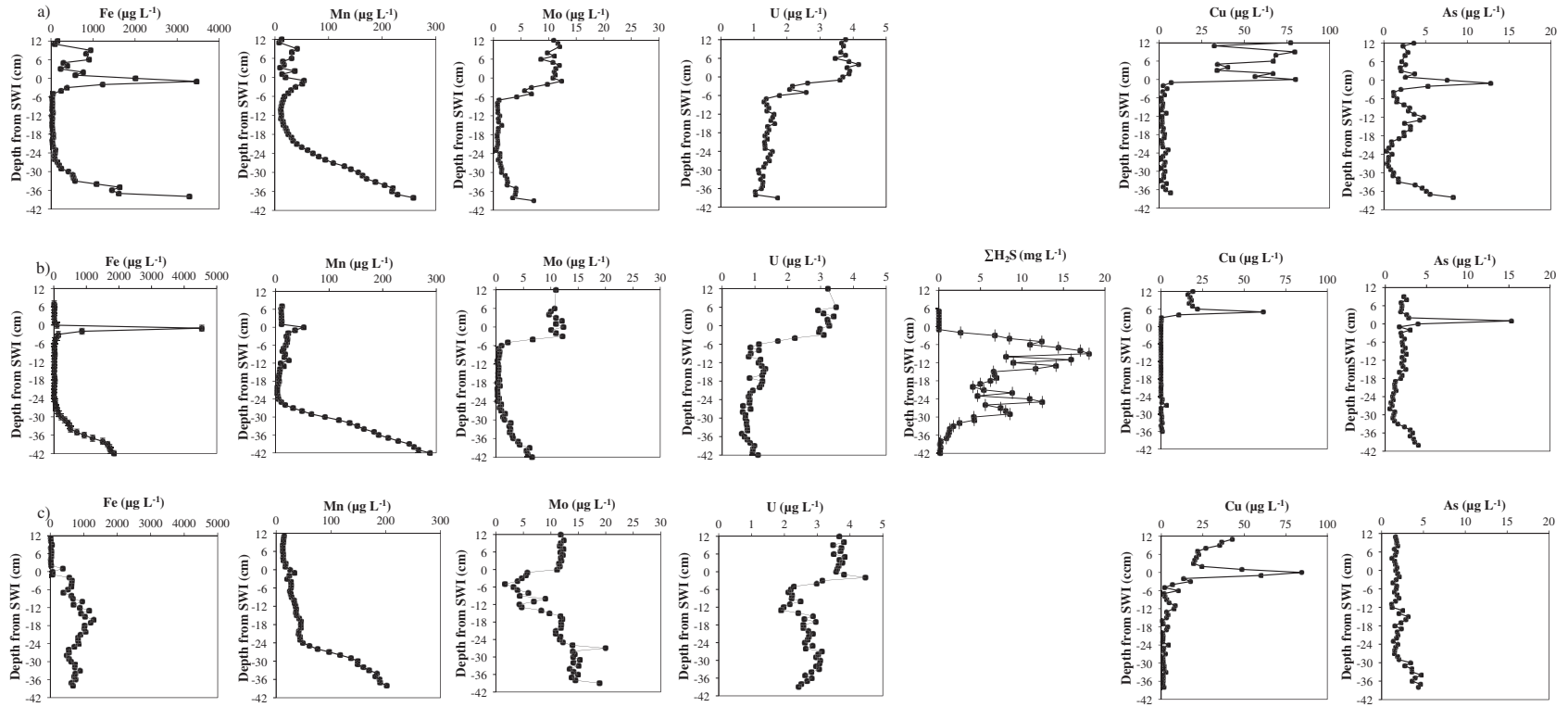

Fig. 3. Sedimentary profiles of Mn, Fe, U, Mo, Cu and As. Light/dark grey bar: sand/muddy sediments.

Fig. 4. Pore water profiles of Mn, Fe, Mo, U and sulfides ($\sum H_2S$), Cu and As and in a) summer 2012, b) summer 2013 and c) winter 2013. In winter, sulfides (not shown) were below the detection limit (0.7 mg L^{-1}). Light/dark grey bar: sand/muddy sediments.

sharply and then stabilized at 2.2 µg L^{-1} below a depth of 4 cm and remained stable until the bottom of the profile.

3.2.3. Cu and As

Cu concentrations in the bottom waters of the marina varied considerably (from 7 to 80 µg L^{-1}) irrespective of the sampling dates (Fig. 4). These values are extremely high compared to those generally encountered in coastal waters: 1.6 µg L^{-1} in the neighboring Thau lagoon (Kawakami et al., 2008) and 0.22 µg L^{-1} in the Gulf of Lions (Morley et al., 1997), and point to significant Cu pollution of water linked to the use of antifouling paints as shown by Caro et al. (2015).

In pore water, the maximum Cu concentration (up to 85 µg L^{-1}) in winter was observed at the SWI. Below, concentrations dropped sharply to values close to the detection limit in summer and winter 2012, and below the detection limit in summer 2013.

In the bottom water of the marina, As concentrations were slightly higher in summer (3 µg L^{-1}) than in winter 2013 (2 µg L^{-1}). In pore waters, the peak in As systematically detected at the SWI in summer was absent in winter. As concentrations increased with depth from 25 cm (in winter) or 35 cm (in summer), the highest concentration was always found at the bottom of the pore water profile.

4. Discussion

4.1. Redox zonation

Early diagenetic reactions that result from the bacterial oxidation of organic matter and redox processes are inter-dependent (Van Cappellen et al., 1993). It is thus important to take redox zonation in sediments into account when investigating the reactions that control the mobility of As and Cu in pore waters.

At our study site, the POC and granulometry revealed two distinct sediment layers. The upper layer (down to a depth of 24 cm) consisted of fine mud relatively rich in organic carbon (1.18% <POC<3.45%) compared to the underlying layer, in which POC concentrations were less than 0.72% and which contained a higher proportion of sand. The coarser particles are probably "native" sediments. They originate from the dunes where Port Camargue was dug, whereas the finer surface particles were deposited after the harbor was built.

The distribution of redox sensitive elements and sulfides in the pore water also reflected the existence of the two layers of sediments and of two interfaces: the SWI, and interface between the muddy sediments and the native sediments (Fig. 4) located at a depth of 24 cm. At the SWI, reduction of Fe−Mn oxides occurred as shown by the peak concentration of Fe and Mn, evidence for the release of Fe(II) and Mn(II) into the pore waters. Below the SWI, sulfides were present in pore water in summer 2013 (Fig. 4), indicating sulfate reduction in the muddy sediments. In this zone, Fe(II) and Mn(II) concentrations were low, often near the detection limit. In the case of Fe, this is linked to the formation of highly insoluble sulfides (FeS or FeS$_2$), as widely observed in sulfidic marine sediments (Boulegue et al., 1982; Burdige, 1993; Huerta-Diaz and Morse, 1992). In anoxic conditions Mn(II) also forms solid phases. Common authigenic Mn phases in anoxic sediments are mixed Ca−Mn carbonate phases (Middelburg et al., 1987). Mn can also be incorporated in the pyrite fraction (Morse and Luther, 1999 and references therein). When sulfides in pore water exceed Fe availability, MnS can also form (Lepland and Stevens, 1998). The sharp decrease in Mo is also evidence for its removal from pore water. Removal of Mo is common in sulfidic pore water (Bertine and Turekian, 1973; Morford et al., 2009; Poulson Brucker et al., 2009; Wang et al., 2011), where Mo precipitates as sulfide, or in

association with Fe-sulfides (Helz et al., 2011, 1996; Zheng et al., 2000). The marked decrease in U concentrations at the SWI probably reflects its reduction, which generally occurs at the Fe(III)/Fe(II) transition zone (Klinkhammer and Palmer, 1991; Calvert and Pedersen, 1993; Cochran et al., 1986) and produces U(IV) or U(V) species, which are less soluble than U(VI) as they adsorb strongly onto particles, or form UO$_2$(s) (Anderson, 1982; Anderson et al., 1989; Barnes and Cochran, 1993, 1990; Chaillou et al., 2002; Sundby et al., 2004).

Below 24 cm, in the native sediments, sulfide concentrations decreased markedly with depth and finally disappeared at a depth of 35 cm in summer 2013. During the two summer surveys, Fe, Mn, and Mo concentrations increased with depth. This pattern suggests the native sediments are a source of pore water Fe, Mn and Mo.

In contrast to the summer 2013 survey, sulfides were below detection limit in pore waters in winter. Seasonal variations in sulfide production have been observed elsewhere and found to depend on the input of organic matter and temperature (Dang et al., 2014; Lourino-Cabana et al., 2014; Thamdrup et al., 1994). In winter, low temperatures inhibit the activity of sulfate reducing bacteria. In addition, there are fewer inputs of organic matter to the sediment than in summer due to low primary production, and less oxidant is consumed. Disturbance of sediments during winter storms can favor oxygen penetration into the sediment but in a sheltered enclosed system like Port Camargue especially at station 19, this is unlikely to play an important role. Here, sediment resuspension is mainly due to the passage of boats, which, on the contrary, increases in summer.

Less pore water Fe was found at the SWI compared to summer, but Fe was mobilized from muddy sediments and a maximum concentration of 1292 µg L^{-1} was detected at a depth of 16 cm. This is probably due to oxidation of the Fe-sulfides that were formed during summer. Oxidation has been shown to occur in absence of oxygen. FeS oxidation, coupled with abiotic Fe oxide reduction, has also been demonstrated experimentally (Mortimer et al., 2011). In the Great Marsh (Delaware, USA), Luther III et al. (1992) proposed a mechanism to explain Fe cycling in pore waters involving the oxidation of soluble and solid sulfides by Fe(III) complexed by organic ligands in anoxic conditions. In winter, native sediment releases also Fe into pore waters.

A small release of Mn into solution was detected at the SWI. Mn concentrations between the SWI and a depth of 24 cm were higher than in summer. Like in summer, the distribution of Mn points to the existence of a pore water Mn source in native (>24 cm) sediment.

The solubility of Mo in muddy sediment pore waters increased dramatically in comparison with measurements made during the summer surveys, but a minimum Mo concentration was still detected between the SWI and a depth of around 15 cm. Although pore water sulfides were below detection limit, this nevertheless suggests that their concentration is sufficient for the precipitation of authigenic Mo sulfides. Below a depth of 15 cm, the concentration of Mo increased markedly with depth. Like in summer, this distribution indicates the existence of a Mo source in native sediment and the diffusion of Mo towards the SWI.

The concentrations of U were generally higher along the profile than in summer, but U concentrations also evidenced removal immediately below the SWI. As in summer this removal of U is probably due to biotic/abiotic reduction or adsorption/(co)precipitation with the secondary mineral (Chaillou et al., 2002).

In winter, the solubility of Mn, Fe and Mo in the muddy sediment increased compared to summer, as would be expected owing to the less reducing conditions and the absence of sulfides. The redox sensitive elements and sulfide profiles also revealed the occurrence of ferrous and manganous conditions in the native

sediments below the sulfidic zone. This probably reflects diagenesis in the native sediments. When recovered by organic-rich mud, the native sandy sediment acted as a source of pore water Fe(II), Mn(II). This process was described by Mucci and Edenborn (1992) and Mucci et al. (2003) in the Saguenay Fjord, where an organic-poor layer of flood material was progressively recovered by organic-rich mud. In that study, the process involved reduction of the Fe—Mn oxy-hydroxides in the organic-poor layer, especially at the original SWI, and migration toward the overlying sulfate reducing organic mud.

In our study, the sedimentary record of redox sensitive is generally in agreement with the processes observed in the pore water. Fe displayed two concentration peaks, one reflecting Fe-sulfide precipitation in the muddy sediments under the SWI, and the other at the boundary between the muddy and native sediments. The upper peak was less intense than the deeper one because of partial Fe mobilization during winter. The distribution of Mn is consistent with a diffusive flux from the native sediment to the overlying layer and with Mn adsorption or precipitation in the sulfidic zone.

The Mo sedimentary profile was characterized by two peaks, the first under the SWI, and the second at the boundary between the muddy and native sediments, perfectly mirroring the pore water profile. The precipitation of Mo, and the probable formation of authigenic Mo—Fe-sulfide phases were clearly reflected by the peaks of Mo at the boundaries of the sulfate reduction zone. A major peak in U in the sedimentary profile was observed below the SWI, in agreement with pore water distribution, which showed U removal. The very small peak in U concentration at the boundary between the muddy and native and sediments despite the absence of U removal in pore waters during our surveys suggests that U was only removed occasionally or that U enrichment in native sediments occurred independently of early diagenesis.

4.2. Cu and As cycling

The Cu pore water profile is consistent with the sedimentation of particles heavily polluted with Cu linked to the use of Cu as a biocide in antifouling paints. A fraction of Cu was released into pore water when the main carrier phases (Fe—Mn oxy-hydroxides and organic matter) were solubilized, as widely observed elsewhere (François, 1988; Gaillard et al., 1986; Klinkhammer, 1980; Lapp and Balzer, 1993; Millward et al., 1998; Rigaud et al., 2013; Tankere-Muller et al., 2007; Teasdale et al., 2003). Cu can then diffuse upward to the water column and downward to the sulfidic zone where it is removed by incorporation into pyrite, as shown by Boulegue et al. (1982), Huerta-Diaz and Morse (1992) and Sullivan and Aller (1996). Although pore water sulfides were below detection limit in winter, this suggests that sulfide concentration was sufficient to promote Cu precipitation with sulfides. Nevertheless the higher Cu concentrations in pore water compared to summer, indicates less efficient removal.

The Cu sedimentary profile confirms the role of the muddy sediments as a sink for Cu, and the Cu distribution in the sediment can be considered as reflecting the history of the use of Cu in antifouling paints since the building of the harbor, in agreement with the findings of Briant et al. (2013).

Arsenic is released into solution at the SWI in summer but not in winter, suggesting that surface sediments do not contain diagenetically mobile As in winter. In the pore waters of native sediments (below a depth of 24 cm), As increased with depth. This distribution can be accounted for by release of As into solution during the reductive dissolution of Fe-oxides in the native sediments. Arsenic was released into solution in the form of As(V) and/or As(III), which diffused toward the organic-rich muddy sediments where they adsorbed on Fe-sulfides according to the mechanism modeled by Dang et al. (2014). This led to the accumulation of As in the solid phase at the boundary between the muddy and the native sediments (Fig. 3). Thus the high concentrations of As (75 µg g^{-1}) measured at this boundary appear to be due to a natural process linked to diagenesis rather than to the use of organoarsenic as a biocide in antifouling paints, suggested by Briant et al. (2013).

5. Conclusion

The sediments in the Port Camargue marina are heavily polluted with Cu and As the careening zone. The processes that control the mobility of these trace elements in pore waters were investigated using redox sensitive elements (Fe, Mn, Mo and U) and sulfides to better constrain redox conditions in the sediments. Our results show that the redox zonation in the sediment depends on sedimentation. Two sediment layers can be distinguished. The deeper layer (>24 cm depth) is mainly composed of sand and is impoverished in organic matter compared to the shallower layer, which consists in fine organic rich particles. The deeper layer was identified as native sediments and predates the building of the marina, whereas the upper layer was deposited later. In the upper layer, sulfidic conditions developed in summer. In the deeper layer conditions were Fe and Mn reducing and no sulfide was detected in pore waters during our surveys.

At the SWI, Fe—Mn oxyhydroxides underwent reductive dissolution linked to the mineralization and release of As and Cu associated with organic matter. Under the SWI, sulfate reducing conditions occurred during summer in the muddy sediment layer, leading to the precipitation of Fe-sulfides, the (co)precipitation of Mo and Mn, the immobilization of U. Cu was also immobilized in this zone thereby acting as an efficient trap for Cu. Reductive dissolution of Fe—Mn oxy-hydroxides occurred in the sandy layer. Fe, Mn and Mo diffused toward the top of the profile and precipitated at the boundary between the muddy and the sandy layer. Arsenic, whose cycle is tightly linked to that of Fe, was also released into solution, diffused toward the interface between the muddy and the sandy layer where it precipitated, probably with Fe oxy-hydroxides.

In winter, the muddy layer continued to act as a trap for Cu. Finally, due to strong immobilization of Cu in the muddy sulfidic sediments, the Cu sediment profile likely reflects the increasing use of Cu as biocide in antifouling paints since the building of the marina. Conversely, the high concentration of As observed at a depth of 25 cm is the result of diagenetic processes and not of the former use of organoarsenic in antifouling paints.

Acknowledgments

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