HEAVY METAL CONTENTS (Cd, Cu, Hg, Pb and Zn) IN A SALT MARSH INFLUENCED BY PETROCHEMICAL WASTE DISCHARGE: PIALASSA BAIONA, RAVENNA (ITALY).

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This paper has not been submitted elsewhere in identical or similar form, nor will it be during the first three months after its submission to Hydrobiologia.
ABSTRACT

The salt marsh near the discharge channel from the Ravenna petrochemical plant was studied in 1982. The study was repeated in 2000/02, with the aim of detecting present-day levels of trace metals in the sediments and to evaluate if any recovery (i.e., burial) had taken place due to recent “non-contaminated” sedimentation.

Cu and Pb showed the same surface levels as in 1982, and sediment profiles measured in the core indicated an homogeneous concentrations in the top 10 cm over the last 30 years. Higher surface concentrations were measured for Zn (up to 800 mg kg\(^{-1}\) dw), peaking in the top 3-4 cm (last 10-15 years). Higher concentrations were also measured for Hg in the surface sediments of the channel, as well as in the core (20-40 mg kg\(^{-1}\) dw), although lower values were measured in recent sediments, as discharge from chloro-alkali plants ceased about 20 years ago. Those Hg values are still two orders of magnitude higher than the sediment quality guidelines of the NOAA (National Oceanic and Atmospheric Administration) and FDEP (Florida Department of Environmental Protection) (SQGs), ERM (Effect Range Median) and PEL (Probable Effect Level), respectively. Cadmium concentrations were analysed for the first time, and showed a peak in surface layers (1-2.5 mg kg\(^{-1}\) dw), with a progressive decline along the sediment column.

Through comparison with pre-industrial values detected in the deep core layers (before 1920), Hg showed the highest enrichment factor (EF) - up to 300 times. Cd and Zn occur in recent sediments at levels 2-10 times higher than background values. In terms of possible adverse effects, Hg poses the highest risk, and Cd and Zn are also, in most cases, above the recommended ERL and ERM.
INTRODUCTION

Lagoons are well-known as monitorable areas of concentration and interfaces between land and sea. This is why they are highly endangered ecosystems and protected worldwide (UNESCO, 1991). Pialassa Baiona, a coastal lagoon located 5 km north-east of Ravenna, Italy, is connected to the North Adriatic Sea through the Canale Candiano, which is the important harbour of Ravenna. Parts of this lagoon are currently used for fish and mollusc farming. Since the end of the 1950s, it has been heavily polluted by industrial discharge from an acetaldehyde plant. High levels of Cu, Pb, Zn and Hg in contaminated sediments have been reported in previous studies (Ui, 1970; Miserocchi et al., 1990; Miserocchi et al., 1993). Cu, Pb and Zn are 2-3 times the background (pre-industrial) levels, whereas mercury is up to 160 µg/g (i.e., 500 times the background). It has been estimated that 100-200 tons of mercury were discharged into the lagoon in the period 1957-1977, almost 80% of which was redistributed in the sediment of the southern ponds (Miserocchi et al., 1993). The time required to reclaim the area from Hg contamination has been estimated at 40-50 years. In addition, high concentrations of polystyrene, PAHs, PCBs and PCDD/Fs were recently found in sediment samples in the southern area (Fabbri et al., 2001a; Matteucci et al., 2001). Lastly, recent studies on mercury methylation have highlighted the fact that redistribution processes can increase the bioavailability of Hg, with some risk to human health (Fabbri et al., 2001b; Trombini et al., 2003).

The aim of the present work was to detect the present-day levels of trace metals in previously contaminated sediments, and to check if any recovery (i.e., burial) had taken place due to recent "non-contaminated" sedimentation. Core and surface sediments were collected to examine accumulations of Cd, Cu, Hg, Pb and Zn in sediments.

MATERIALS AND METHODS
Study area

Being part of the Po plain, the Northern Adriatic coast is low and typically sandy, with sets of dune ridges which reveal the migrations of ancient shorelines. In the past, wetlands were widespread in the coastal area between Trieste and Ancona. During the last century, intense activity by man reclaimed lands for agriculture and, consequently, today only a small part of the original extent of wetlands survives, with considerable morphological, hydrological and chemical modifications. The Pialassa Baiona, a coastal lagoon on the Northern Adriatic, is included in the Ramsar list. It covers an area of 11 km² (Figure 1) and is formed of a number of small ponds (average water depth 60 cm) and deeper distributary channels in a herringbone arrangement (1 to 2-3 m deep). The lagoon is connected to the sea through the harbour channel of Ravenna. Thus, the salinity of the lagoon (25-30 ‰) is mainly controlled by water exchange with the Adriatic.

The hydrodynamics of the Pialassa Baiona is mainly influenced by tides, with a maximum tide level difference of 1 m. Upstream freshwater discharge occurs along various channels draining agricultural land. In the southernmost (Via Cupa) channel, industrial and municipal waste discharge also occurs.

In the ponds and distributary channels, the sediments are generally muddy in nature and black in colour, whereas dark grey sandy silt prevails in tidal inlets. This sedimentological pattern affects the redistribution of polluted sediments, mainly in the channels and southern pond (Miserocchi et al., 1993).

The study area was influenced in the past by a large chemical plant which produced acetaldehyde and vinyl chloride from acetylene. Two thermoelectric power plants, one factory producing concrete, two lampblack production plants, and several small industries are also active in the area. High contamination of sediments by trace metals has been reported in the southern area, particularly in the Canale Magni pond, near the channel most greatly influenced by direct industrial discharge.
At the moment, neither present nor past data are available to estimate the heavy metals load discharged in the lagoon from different external sources. However, the coming into force in 1976 of 319/76 environmental law has contributed to regulate the waste discharge and, as a consequence, to start the reduction of pollutants.

By making reference to the hypothesis according to which since the period included between the end of 1970s and the beginning of 1980s, waste discharge of pollutants are to be considered as negligible. In the previous detailed characterisation of all the lagoon (28 sampling stations), in 1982, the distribution of sediment surface concentrations stressed that the origin of Hg was exclusively industrial (Miserocchi et al., 1993), while the industrial source for the other elements was only partial. In particular, the atmospheric input for Pb and the agricultural one for Cu and Zn were also important (Miserocchi et al., 1990).

Sampling and analytical work

Sampling (Figure 1) focused on the most heavily contaminated part of the lagoon (southern area), in the same sites as the previous studies, together with upstream and downstream industrial and municipal waste discharge (Via Cupa Channel).

A sediment core 56 cm long and 10 cm in diameter (C00-1) was bored from the Canale Magni pond in the year 2000. Its large diameter and sharpened end minimized compaction of sediments. This core was cut into 1-cm thick slices at the top (0-16 cm) and into thicker slices at the bottom (2-5 cm), in order to reach sediment layers presumably deposited before the development of the industrial area. The sediments were dated by lead-210, as reported in Fabbri et al. (2001a) and Matteucci et al. (2001).

During 2002, superficial sediment samples (0-3 cm) were collected by a Van Veen grab in the southern part of the lagoon (BP02-3, BP02-4) and in the southernmost part of the Via Cupa channel, close to (BP02-2) and upstream (Channel) of the waste source.
All samples were digested with a strong acid mixture (HNO₃, HF and H₂O₂) in teflon bombs in a microwave oven following Guerzoni et al. (1987), modified to optimise the dissolution of organic compounds (Miserocchi et al., 2000). After digestion, Cd and Pb were determined by graphite furnace AAS, Cu and Zn by ICP-AES, and Hg by automatic mercury analyser (US-EPA, 1998).

RESULTS AND DISCUSSION

Data from 1982 showed very high concentrations of Cu, Hg, Pb and Zn, with average values of 66, 70, 47 and 148 mg kg⁻¹ respectively (Table 1). Surface data were compared with pre-industrial (background) levels found in cores from the same area, and were 2-3 times higher for Cd, Pb and Zn; Hg was 2-3 orders of magnitude higher than background values (Miserocchi et al., 1980; Miserocchi et al., 1993).

Comparisons of “old” (1980s) surface data with recent samples (2000/02) are shown in Table 1. Surface sediment concentrations of Cd, Cu, Hg, Pb and Zn and their trend concentrations versus depth are shown in Figure 2. Cu and Pb concentrations in surface sediments (2000/02) were similar to those of 1982. Instead, zinc in surface sediments showed a three-fold increase, when compared with corresponding concentrations of sediments collected in the 1980s.

Recent Hg concentrations in surface sediments were three times lower than in the same sites in 1982 (24 mg kg⁻¹ dw vs. 70 mg kg⁻¹ dw). The contamination level only decreased upstream from the industrial and municipal waste discharge (Via Cupa channel) for Cd, Zn and Hg.

Lead and copper concentrations showed homogeneous values or a slight decline with depth for the top 8-10 cm, covering the last 30 years (calculated with an estimated sedimentation rate of 0.36±0.04 cm yr⁻¹ and an accumulation rate of 0.24±0.02 g m⁻² yr⁻¹; Matteucci et al., 2001). Below this layer, concentrations decreased to close to background values (15 mg kg⁻¹ dw) at a depth of 20
Cadmium was analysed for the first time, and showed a peak in surface samples (1-2.5 mg kg\(^{-1}\) dw) with a continuous decrease to a background value of 0.2 mg kg\(^{-1}\) dw, down to 20 cm (Figure 2). Zinc showed an increasing trend from the 10-cm layer towards higher values on the surface, up to 800 mg kg\(^{-1}\) dw, with a peak in the top 3-4 cm (last 10-15 years). Mercury showed very high values in surface sediments in all sites of the southern lagoon (24.3±12.7 mg kg\(^{-1}\) dw), but there were some signs of reduction in recent sediments, as indicated in the concentration profile along the sediment column - as expected, since discharge of mercury from chloro-alkali plants ceased some 20 years ago. Peak Hg concentrations were found in the 3–7-cm layer (last 15-20 years) with values of 30-40 mg kg\(^{-1}\) dw.

In order to evaluate the ecotoxicological significance of heavy metal concentrations, 1982 and 2000/02 sediment data from the Pialassa Baiona were evaluated according to the sediment quality guidelines of the National Oceanic and Atmospheric Administration (NOAA; Long et al., 1995) and Florida Department of Environmental Protection (FDEP; MacDonald, 1994) (Table 2). The concentration levels of Pb and Cu for 1982 and 2000/02 are similar. The average contents of Cu were above the TEL (Threshold Effect Level) and ERL; Pb was close to the ERL but higher than the TEL in both years. The average Zn concentration has increased over the last 20 years from 148 to 501 mg kg\(^{-1}\) dw, and exceeded the higher thresholds of PEL (271 mg kg\(^{-1}\) dw) and ERM (410 mg kg\(^{-1}\) dw).

Mean Hg content (70 mg kg\(^{-1}\) dw) was two orders of magnitude higher than ERM and PEL. However, its contamination level decreased in recent surface sediments from 70 to 24 mg kg\(^{-1}\) dw, although it was still two orders of magnitude above the sediment quality recommendations. The reduction in Hg contamination is probably the result of two main processes: burial of old contaminated sediments (as shown by the core profile) and sediment redistribution on the surface of the lagoon (Miserocchi et al., 1993). Nevertheless, studies on mercury methylation have emphasized how redistribution processes seem capable of increasing the bioavailability of Hg.
Cattani et al. (1999) focused their attention on biota: total Hg (THg) was found to range from 0.1 and 2.2 mg g\(^{-1}\) d.w. in samples of the green seaweed *Ulva rigida* collected across the lagoon, while in an active biomonitoring experiment carried out with transplanted mussels (*Mytilus galloprovincialis*), THg in soft tissues was found to be 4.4 times the initial background level after a 52-day exposure in the southernmost contaminated sub-basin (Fabbri et al., 2001b). During a campaign in 1997–1998, Trombini et al. (2003) showed that the southern sub-basin still had values of total Hg and methyl Hg which pose an ecotoxicological risk.

Cadmium, copper, mercury and zinc values in the southern area of the lagoon were higher than those determined upstream in the input (Via Cupa) channel. Concentrations in surface sediments and the upstream channel ratios ranged between 2 for copper to 27 for mercury, and were 4-5 for cadmium and zinc (Table 1). Instead, lead contents were homogeneous in the channel and lagoon sediments (42 vs 43 mg kg\(^{-1}\) dw).

Comparisons with pre-industrial values detected in deep layers of the core (before 1920) and in previous studies (Miserocchi et al., 1990; Miserocchi et al., 1993), showed that Hg had the highest enrichment factor (EF) - up to 300. Cd and Zn contents in recent sediments were from 5-6 to 10-12 times higher than background levels (Figures 3, 4). It therefore seems that Cu and Pb contamination is the same as it was 10 years ago, Hg is undergoing redistribution; and Cd and Zn have increased in the past 10 years. In terms of possible adverse effects, Hg poses the highest risk, and in most cases Cd and Zn are also above the ERL and ERM.

**CONCLUSIONS**

Cu and Pb concentrations in surface sediments (2000/02) were similar to those of 1982, as also shown in the core. The concentrations of these two trace metals were constant from -8 cm (ca.
1980) to the surface, showing that contamination, which started 50-60 years ago (ca.-20 cm in the core) is at the same level as it was 20 years ago.

Instead, zinc in surface sediments showed a three-fold increase when compared with concentrations of corresponding sediments collected in the 1980s. This enrichment was also continuously observed in depth, the highest values being found in surface sediments (0-3 cm). The first data published on cadmium showed the same zinc concentration trend, highlighting permanent pollution which still affects sediments in the lagoon.

Recent Hg concentrations in surface sediments are three times lower than in samples collected in the same sites in 1982 (24 mg kg⁻¹ dw vs. 70 mg kg⁻¹ dw). After reduction of Hg loads from industrial waste to the lagoon, restoration of Hg in surface sediment is the result of two main sedimentation processes: (i) burial of the contamination (evident at the 3-7 cm level, as shown by the core profile); (ii) redistribution of sediments on the surface of the lagoon.

Contamination levels of Cd, Zn and Hg only decrease upstream from the industrial and municipal waste discharge point (Via Cupa channel). Although it is evident that Cd and Zn are currently discharged through industrial and/or municipal waste, Hg is not, or in any case there is no evidence that it is.

Instead, comparisons of surface sediment concentrations with international SQGs reveal that, in terms of possible adverse effects, Hg together with zinc, values of which are always above the ERM, pose the highest risk. This theoretical risk is partially confirmed by recent biomonitoring studies (Cattani et al., 1999; Trombini et al., 2003). Hg concentrations above the ERM persist also upstream in the channel, probably as the result of sediment redistribution due to tidal dynamics.

In conclusion, 20 years after the first studies, the processes of sedimentation and consequential burial of mercury have led to partial decontamination of the Pialassa Baiona. However, the high concentrations still found in surface sediments, and the trend toward increased concentrations of cadmium and zinc constitute a risk, associated mainly with how sediments are distributed inside the lagoon, and to biota-sediment interactions. To pave the way for appropriate intervention, further
studies are needed into the main processes of distribution and introduction of contaminants to the lagoon.

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REFERENCES


FIGURE CAPTIONS

Figure 1. Map of Pialassa Baiona lagoon and location of sampling stations in 2000/02.

Figure 2. Vertical profiles and surface sediments of cadmium, copper, lead, zinc and mercury concentrations, in mg kg$^{-1}$ of dry weight.

Figure 3. Enrichment factor in surface sediments calculated by actual surface sediment concentrations (0-3 cm) and pre-industrial concentration detected in deep layers of core and from regional background value ratios. (a) Cadmium, copper, lead and zinc; (b) mercury for 1982 and 2000/02 samples.

Figure 4. Vertical profiles of enrichment factor of cadmium, copper, lead and zinc (a) and mercury (b). For mercury, background value was considered to be 0.13 mg kg$^{-1}$ dw, regional background value considered in Miserocchi et al. (1993).
Fig. 1
Fig. 2

Superficial sediments (0-3 cm)

- Cd (mg/kg dw)
- Cu (mg/kg dw)
- Pb (mg/kg dw)
- Zn (mg/kg dw)
- Hg (mg/kg dw)

Fig. 3
Table 1: Heavy metal concentrations (mg kg\(^{-1}\) dw) in surface sediments (0-3 cm) and channel (sampled upstream from the water discharge). (*) Miserocchi et al., 1990