Reading the Chronicle of Past Industrial Pollution in the Sediments of a Coastal Lagoon

Pialassa Baiona, Ravenna

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North of Ravenna lies Pialassa Baiona, a brackish lagoon of both naturalistic (Ramsar Site) and economic value. Past industrial effluents discharge left important traces in the sediments. A map of surficial pollution by mercury is presented and preliminary results on the massive presence of polymeric materials (PVC and styrenics) and of polycyclic aromatic hydrocarbons are reported.

Approximately 10 km north of the city of Ravenna (northern Italy), lies an intertidal lagoon, named Pialassa Baiona. This 10 km^2 wide site originated as an area of marine sacs which were gradually isolated from the sea by Lamone River deposits. In the XVIII century a dendritic network of canals which separate shallow ponds (mean depth 0.6 m) were dig. Hydrodynamics are controlled by tidal flows (mean tidal range = 0.6 m, ebb tides occasionally higher than 1 m, mean water salinity 25-35‰), which cause vast expanses of muddy flats emerging. Pialassa Baiona was declared wetland of international importance under the Ramsar Convention. This Ramsar Site hosts a large number of rare fauna species which find a good habitat for feeding, nesting and breeding. The area deserves both economic and naturalistic interest. Professional eel fishing was a profitable business up to the 50s; nowadays main uses of the lagoon include recreational fishing in huts equipped with large nets, mollusc (*Tapes philippinarum*) harvesting, regulated hunting, leisure and cultural activities such as canoeing, guided tours, nature observation etc.

Historically, Pialassa Baiona has been endangered by natural phenomena (e.g. subsidence) and anthropogenic activities connected to agriculture, urbanisation and industrialisation. The basin receives freshwater from a number of drainage channels on the western border which collect the runoff of an intensely cultivated watershed (~ 340 km^2) and effluents both from a municipal sewage treatment plant and from industrial sewage treatment plants. The poor quality of the nutrient-rich freshwater causes, particularly in summer, frequent eutrophic conditions in the area. A massive industrialisation of the area started up at end of 50's in concomitance with the development of the harbour. Industrial effluents were dumped into the lagoon at its southern edge through a tributary channel (Canale Cupa) [1]. In middle 70's, when Legge Merli on the industrial effluent management was enacted, a waste water treatment plant was built and, since then, Pialassa Baiona has received better quality effluents. Nowadays, apart from an exceptional accident (18/9/2000, see local press agencies), a careful control is exerted on industrial emissions from water treatment plants, run by Ambiente Spa, to the Lagoon.

However, the signs of the past industrial activity have been preserved in the sediments of Pialassa Baiona. In particular, the Lagoon is internationally known for the heavily mercury contamination. An alerting study was carried out in 1970 by Yun Ui, Tokyo University, who underlined potential analogies between Ravenna lagoon and Minamata Bay. Mercury and methylmercury concentrations in fish (particularly eels) collected in the Ravenna area and in the hair of inhabitants [2] have been reported and, luckily, no epidemiological effects on the indigenous population have been recorded.

Ten years later, analyses performed by the Laboratorio Provinciale d'Igiene e Profilassi di Ravenna [3] testified that high amounts of mercury had been dumped in the lagoon since mid 50's and that, even though a demercuration plant, based on the reduction of water soluble mercury salts to elemental mercury, had been recently installed, a mercury leaking to the lagoon was still present through industry's rainfall and stormwater collectors. It was also noticed that muddy sediments were acting as an efficient trap for mercury and that microbiological methylation at the sediment compartment could be expected. A systematic (geochemical) study on mercury and heavy metals content on 24 samples of surficial sediments was reported by the Istituto di Geologia Marina, CNR Bologna, in 1983 [4]. Authors stressed their attention on the mercury redistribution mechanisms (tidal action and anthropogenic activities) which prevent a safe mercury burial in deep

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Presented as an invited lecture at the SCI 2000, XX Congresso Nazionale SCI, Rimini 4-9/6/2000.

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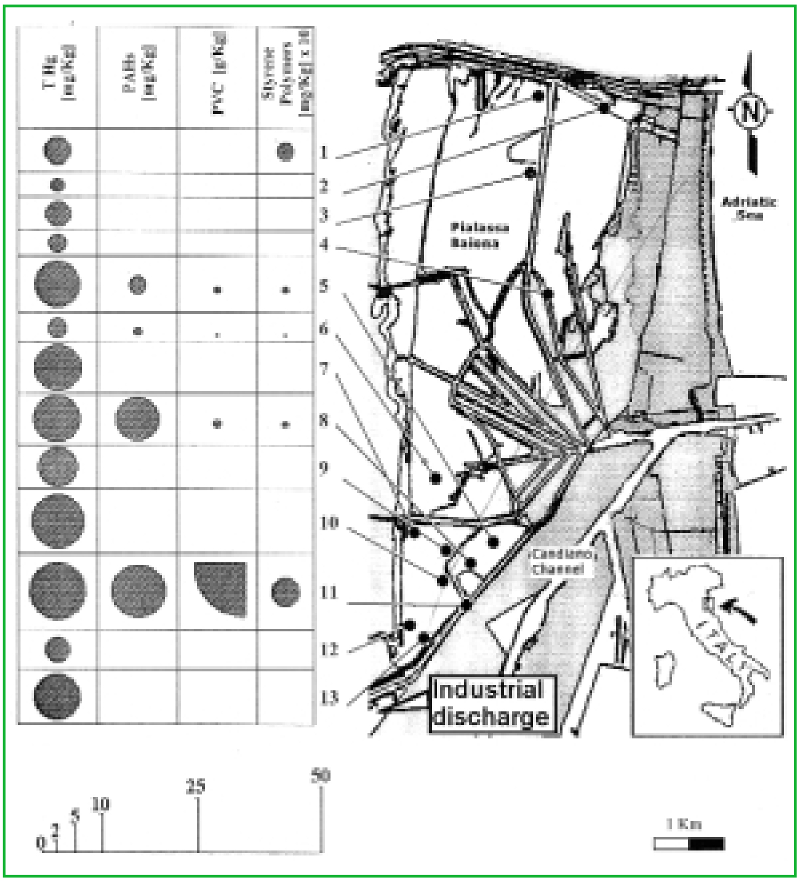

Figure 1 - Map of Pialassa Baiona and contamination load of surface sediments

sediments. Finally, an interdisciplinary analysis of the Pialassa Baiona status was published in 1994 by the Azienda U.S.L. Ravenna [4].

In the past attention was mainly devoted to mercury monitoring, but now it is necessary to understand mercury fate, speciation and bioavailabaility in order to appraise its impact on the ecosystem and its potential risk. Moreover, a possible contamination caused by organic compounds has never been considered in detail.

To fill these gaps we launched in 1994 a research program aiming at evaluating the present status of the lagoon in terms of overall pollution burden of sediments, pollutant bioavalability and analysis of contamination sources. A summary of our investigations, partly carried out in collaboration with CNR groups in Bologna (IGM) and Cesenatico and with the Strathclyde University, are presented in this report. As previously anticipated, the sedimentary compartment contains a threatening cocktail of mercury [5,6], polycyclic aromatic hydrocarbons (PAHs) [7], plastic materials and synthetic rubbers [8-10]. A collection of representative data relative to surface sediments is reported in Figure 1 in graphical form.

Sediment Characterization

Although sediment analysed in this work come from numerous locations collected in different campaigns, they share common features. They mainly consist of black mud, with high water content (50-60%) and total organic carbon (1.5 to 3.5% TOC dw), and exhibit a C/N ratio in the 10-20 range. Total sulphur lies in the range 0.4-1.1% and an important fraction is represented by acid volatile sulphides and elemental sulphur [11].

Two effects are due to the silty nature of the sediment:

- the high surface area makes it an ideal adsorbent for hydrophobic pollutants such as PAHs and vinyl polymers, as well as the high sulfur content confers it the property of an ideal Hg(II) scavenger;
- fine grains are very easily resuspended and transported by the morphodynamics of the lagoon throughout the entire basin, so representing the most efficient process of pollution redistribution.

Sediment resuspension can be brought about both by natural processes (bioturbation, erosion by wave action, high-sheer stress during flood and storm events and ebb tides action) and by anthropic activities (dredging etc).

Total Mercury (THg) distribution

Mercury is widely distributed across Pialassa Baiona. Even though THg distribution locally presents dispersed concentration values (in the south sub-basin ranges in the 10.7-38.5 μg/g interval) due to variable water dynamic conditions associated to the high bottom roughness, analysis of surface sediments (0-5 cm) reveals the presence of a south-north pollution gradient depending on the distance from the hot discharge point (Figure 1).

A subsurface concentration maximum is generally located at 10-20 cm in sediment cores both in the north and south sub-basin, as shown in Figures 2 and 3. These data are in agreement with a significant northward transport of pollutants, as shown by the 4.7-4.8 μg/g values in northern stations and reflect a persistent mixing of surface sediment which prevents a “safe burial” of mercury in the deeper strata.

A further redistribution mechanisms was identified in floating agglomerates of dead algal biomasses. Owing to the high degree of eutrophication of the lagoon, *Ulva rigida* blooms generally occur in summer time; in late summer the *Ulva* biomass collapses, part of it starts floating across the lagoon under the action of tidal currents, thus contributing to the mercury redistribution, and part of it sinks on the sediment where decomposition starts, thus acting as new mercury input to the surface sediment. Samples of *Ulva* collected in spring 1998 across the lagoon revealed values of THg ranging from 100 to 2,260 ng/g (dw) depending on the distance from the discharge point.

In order to better evaluate the tendency of mercury to be accumulated by organisms living in the lagoon, an active biomonitoring experiment was carried out in 1997. Mussels (*Mytilus galloprovincialis*) were transplanted in three stations selected along the south north axis [12]. Following a 52 days field exposure, mercury concentrations in soft tissues of organisms located at the most polluted south basin, were found to be 4.4 times the initial background level and organisms were still accumulating mercury. Mussels located in the more distant stations reached a steady state concentration of 323 and 412 ng/g.

All these data relative to biota, unambiguously confirm that part of mercury is able to enter the food web.

Aromatic Polycyclic Hydrocarbons (PAHs)

PAHs were observed in all the cores investigated and this finding could be not surprising. In fact, PAHs are ubiquitous environmental contaminants released into water bodies by different sources both natural and anthropogenic, pyrogenic (e.g. combustion) and petrogenic (e.g. oil spills). Most striking is the high level of contamination (in some samples well above the ppm range) and the unusual abundance of PAHs with five carbon rings, dominated by cyclopenta[cd]pyrene, which is generally a minor PAH in sediments. The distribution of the single PAHs pointed toward a high temperature process as the responsible for PAHs emission [13]. The pattern of the PAH concentrations in sediments, characterised by a south-north gradient and a strong correlation with mercury and plastics, indicated that the process was associated to the past industrial activity. A decisive hint on the origin of PAHs came from the $^{13}C/^{12}C$ relative abundance of each single PAH, usually indicated as $\delta^{13}C$ (the higher is the ^{12}C content relative to ^{13}C, the more negative is the $\delta^{13}C$ value). In fact, the $\delta^{13}C$ value of a PAH reflects the source it is derived from. PAHs found in the environment typically exhibit $\delta^{13}C$ values in the -15 to -34‰ range, as they are generally derived from the combustion of biomass and fossil fuels [14]. Surprisingly, PAHs extracted from the sediments of Pialassa Baiona are exceedingly isotopically light, their $\delta^{13}C$ values being well below -31‰ (down to -62‰) [7]. This finding strongly supports the starting material producing PAHs found into the Lagoon sediments was biogenic methane (*vide infra*).

Synthetic polymers

Synthetic polymers probably represent the largest class of pollutants of the Lagoon. They have been analysed in sediments by developing an isolation procedure valid for synthetic resins or by applying pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) directly to the sediment [8-10]. Py-GC/MS of isolated plastics and polluted sediment samples produced elevated levels of styrene and benzene along with a typical product distribution pattern indicative for the presence of polyvinyl chloride (PVC), polyvinyl acetate (PVA) and styrene polymers (*e.g.* acrylonitrile-styrene copolymers and styrene-butadiene rubbers). In particular, PVC and PVA were marked by the presence of benzene, indenes and naphthalenes (chlorobenzene and acetic acid were indicative for PVC and PVA, respectively); α-methylstyrene, vinylcyclohexene (Diels-Alder dimer of 1,3-butadiene), 4-phenylcyclohexene (Diels-Alder adduct of 1,3-butadiene and styrene) were typical of thermal fragmentation of styrene-butadiene rubbers; phenylbutanenitrile was identified as a marker of acrylonitrile-styrene copolymers. Using styrene as marker for quantitative purposes, it was possible to determine the profiles of styrene polymers in sediment cores, expressing the concentrations in terms of polystyrene equivalents. In the most polluted area, the total concentration of extractable synthetic polymers could be established simply by weighing the polymers isolated from a given amount of sediment sample [10]. Polymer concentrations showed a strong correlation with THg in sediment cores (Figures 2, 3) and, in turn, with PAHs. Analogous excellent correlation between styrene polymers and THg ($R^2 = 0.93$) was found in suspended matter of nepheloid layers sampled in five sites at the Chiaro del Pontazzo (southern sub-basin) [9]. Since polystyrene-based polymers display a much lower density (d~1.05) than PVC (d~1.40), they are expected to be found in major amount in suspended particulate matter.

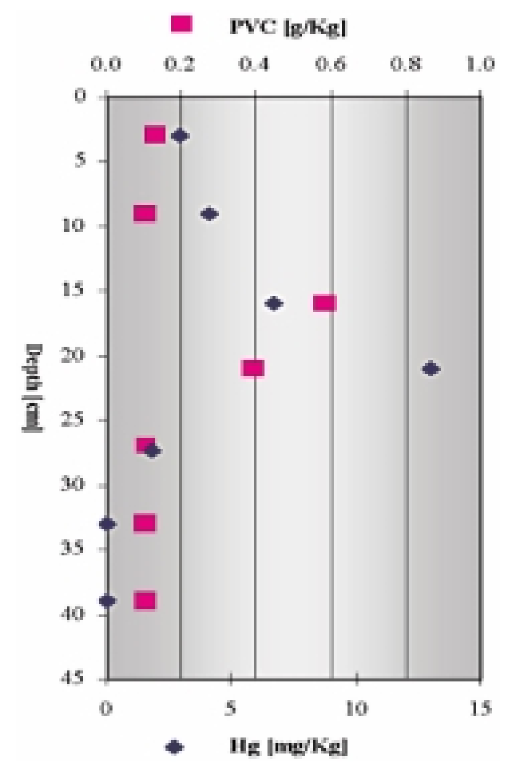

Figure 2 - THg vs PVC vertical profiles in site 6

Chemical pollution: historical background and source analysis

Total mercury, PAHs and polymers are similarly distributed into the Lagoon, they display peak maxima almost at the same depth in sediment cores and their concentrations steeply increase approaching to the industrial discharge point. As far as PAHs are concerned, their product distribution and isotopic signature indicated that a high temperature process using biogenic methane is at the of their origin. Actually, after the II World War significant natural gasfields containing practically pure methane and no sulfur were discovered in the Po Valley, including the Adriatic Sea, offshore Ravenna. Po Basin has been filled since Miocene time of clastic sediments that are gas producing in some parts and their bacterial origin was testified by a number of $\delta^{13}C$ measurements, values ranging between -43 and -76‰ [15]. It was on this easily available and plentiful raw material that Italy began developing a petrochemical industry in early 50s. In 1955 ENI (Ente Nazionale Idrocarburi) subsidiary ANIC started the construction of the first petrochemical district in Ravenna which was active in 1958 [16]. Thermal cracking of methane was adopted in Ravenna to produce acetylene; it is a two-stage process where partial combustion first imparts the necessary energy to the feedstock (T~1600 K) which, then, is passed through a refractory brick reactor at T<700 K [17]. Acetylene is thermodynamically more stable than any other hydrocarbon at T≥1600 K but less stable than its component elements (carbon and hydrogen). Acetylene yield (generally it ranges from 5 to 15%) depends on contact time, which must be as short as possible and on burner design. The cracked gas contains predominantly a mixture of hydrogen (used in Ravenna for ammonia synthesis), carbon monoxide, higher homologues of acetylene, PAHs, accompa-

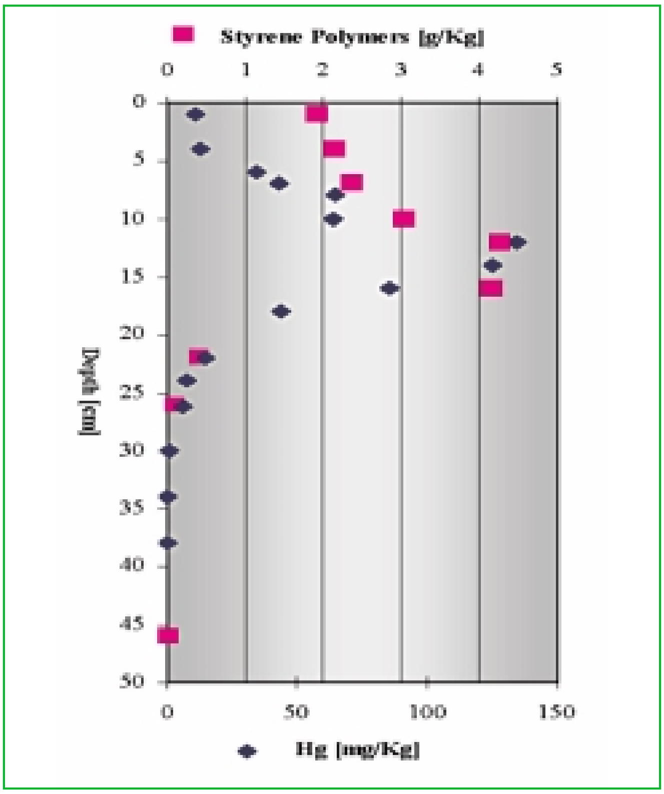

Figure 3 - THg vs styrenycs profiles in site 5

nied by the formation considerable amount of tars and carbon-black, a colloidal-size aggregate of highly aromatic structures described best as amorphous graphite or soot. PAHs are intermediates in the formation of tar and soot.

Acetylene was used as starting material to produce vinyl chloride and acetaldehyde and both processes made use of mercury catalysts. Thus, mercury, the most risky contaminant in the lagoon, is without any doubt, related to the classical acetylene chemistry, based on mercury-catalysed electrophilic additions to the triple bond. In turn, vinyl chloride and acetaldehyde were used to manufacture PVC and PVA, respectively, which are the ultimate products of acetylene chemistry. PVC and PVA, which are present in large amount in sediments of the lagoon, should preserve in their structure the isotopic ‘imprint’ of the methane they are derived from. To this regard, it is worth mentioning that the $^{13}C/^{12}C$ isotopic ratio of polymers extracted from sediments was found to be relatively low ($\delta^{13}C$=-44) [7].

Concluding remarks

Data presented here unambiguously support the following conclusions:

- the total contaminant load is not undergoing an efficient burial, mainly because of the geomorphology of the sediment which favours sediment mixing and transport and hence redistribution of sediment contamination,
- a northward horizontal redistribution of pollutants is in action,
- the good correlation generally found between PAHs, THg and polymers indicates not only a common discharge period, but also a common transport mechanism through the lagoon which is represented by the muddy sediment very easily resuspended and remobilised.

Among physical processes, tide-induced currents represent the major hydrodynamic forcing mechanism for suspended sediment convective and dispersive transport. Moreover, circulation of suspended sediment in the lagoon is also promoted by annual dredging and embankments maintenance activities regularly authorised by public environmental managers in the area. In fact, the silty nature of sediment produces plumes of fine suspended matter rich of contaminants, which may settle at long distance depending on the current rate, both during grab dredging, sediment transport and final disposal [18]. One of the most recent works was performed in 1997-8 when the highly contaminated south-western sub-basin (Pontazzo) was isolated from the lagoon with new embankments for freshwater phyto-depuration and to prevent the saline wedge from entering the San Vitale Pinewood aquifer due to subsidence.

In our opinion, a complete quali- and quantitative “radiography” of the Lagoon contamination load is necessary (horizontal and vertical distribution of pollution load, sediment elutriate tests etc), in order to start a suitable remedial investigation and to recover clean-up costs from responsible parties.

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