Sediments and Pollution in the Northern Adriatic Sea[a]

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INTRODUCTION

Most pollutants are known to have a strong tendency to interact with suspended organic and inorganic matter.[1]

Under certain conditions, the sediments may form deposits, where the substances are stored and/or mineralized and removed from the external environment. Various phenomena may, however, promote a pollutant release from the sediment towards the overlying waters. Molecular diffusion, bioturbation, resuspension of bottom sediment and pumping due to low-intensity wave motion are phenomena that cause the transport of chemical species through the water-sediment interface. The constituents that are mostly involved in these fluxes are the ones dissolved in the interstitial waters and those weakly linked to the solid.

The fine mineral or flocculated sediments, which rapidly settle in the riverine prodelta,[2–4] are the richest ones in easily exchangeable pollutants. On the other hand, the solid matter which sediments after a long transport attains a more stable equilibrium with the pollutants which are dissolved in the waters.

The study of the sedimentation and transport processes of the particulate matter and associated pollutants is of great importance to understand the evolution of the marine environmental quality.

THE ADRIATIC SEA: GENERALITIES

Problems of the open and coastal water pollution of the Adriatic Sea have been the concern of scientists and administrators for some time.

Many national research programs, both related to the whole basin or with a more local concern, were called to study the Adriatic Sea, among which the applied program called "P.F. Oceanografia e fondi marini" of the National Research Council is the most important.

Furthermore, as a result of the Italian/Jugoslavian Treaty on Cooperation, a joint multidisciplinary program investigating pollution phenomena in the Adriatic Sea, has been operating since 1978.

The Northern Adriatic Sea is a shallow semi-enclosed sea with peculiar characteristics (FIG. 1).

[a] This is contribution number 656 from the Istituto per la Geologia Marina—C. N. R., Bologna.

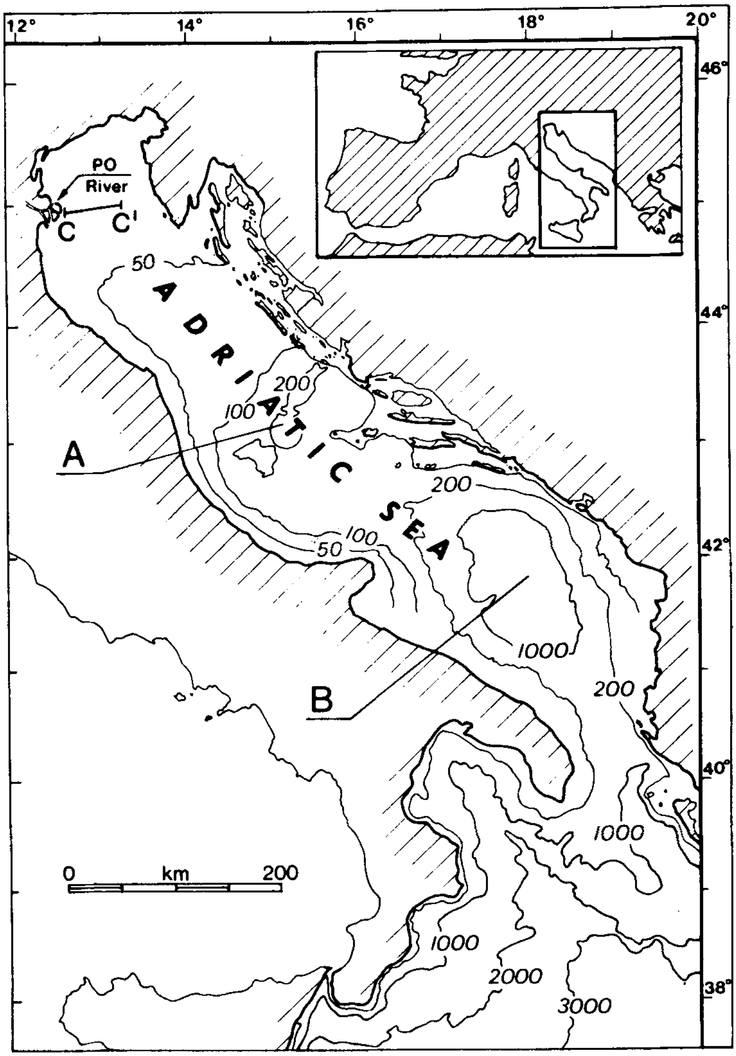

FIGURE 1. Adriatic basin showing the Po river delta: *contour lines* indicate the bathymetry in meters. **(A)** Meso-Adriatic Depression; **(B)** Sud-Adriatic Depression; C-C[1]: Location of the section of FIGURE 2.

The Po River is the largest Italian river (TABLE 1), drains a very industrialized as well as an intensively cultivated area, and exerts its influence over the whole basin. The other rivers, much less important, may be meaningful on a local scale, mainly in coastal areas.

For many years, pollution phenomena have been thought likely to damage the Northern Adriatic ecosystem in a short time. In contrast, the water renewal times

TABLE 1. Average Annual Discharge of the Principal Rivers Debouching in the Northern Adriatic Sea Area

River	Discharge (m^3)	Basin Surface (km^2)
Isonzo	99	3.1
Tagliamento	37	1.2
Piave	98	3.1
Brenta	108	3.4
Adige	262	8.3
Po	1570	49.6
Reno	59	4.1
F. Uniti	21	1.2
Savio	11	0.6
Marecchia	10	0.5

are now known to be rather short (about one year),[5] and with the exception of particular local situations, serious water pollution phenomena are not yet likely to occur.

The major phenomena might occur in the zones where a continuous deposition of fine sedimentary materials of riverine origin takes place, resulting therefore in an accumulation of easily exchangeable pollutants.

WATER CIRCULATION

From the results of all the oceanographic research carried out in recent years,[6,7] the water circulation can be described as follows:

(1) The winter circulation is essentially of thermoaline origin, governed by high salinity water dilution and heat exchange processes. The heat fluxes towards

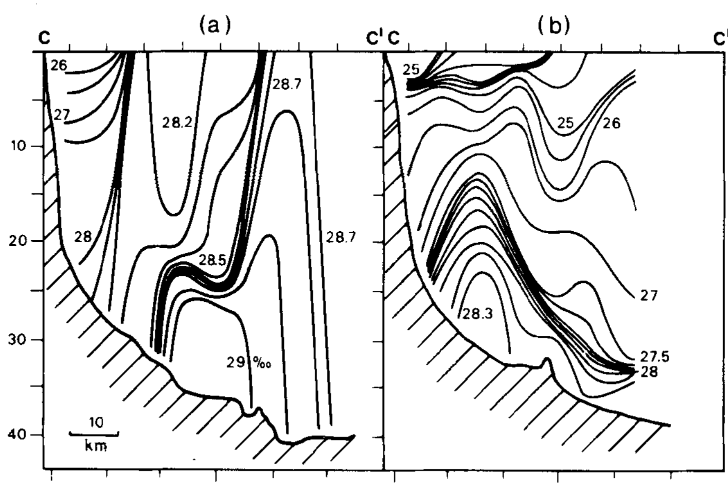

FIGURE 2. Vertical distribution of the salinity of the Adriatic waters. **(a)** winter; **(b)** summer. (Section C-C[1] from Franco.[7] Reprinted by permission.)

the atmosphere cause an instability in the water column, which is vertically homogeneous. The river's very cold waters flow southwards along the western coast, separated from the very saline water of the central part of the basin by a rapid vertical discontinuity (FIG. 2a).

In the middle of the basin the dense waters move with intermittent fluxes towards the Central Adriatic Sea, while to the east a high-salinity water flux, coming from the south, moves in the opposite direction. Therefore, the winter circulation can be described as a cyclonic system from which a secondary basin separates on the isobath of 50 m (FIG. 3). Because of the wave motion, resuspension phenomena can occur down to a depth of 30–40 m (according to Brambati *et al*[8]) or 90–100 m (according to Stefanon[9]).

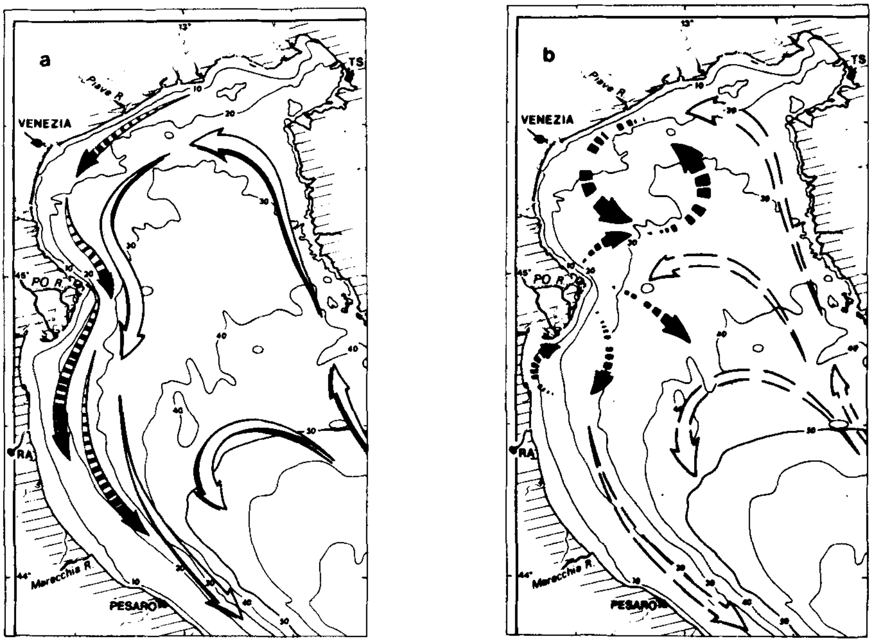

FIGURE 3. Winter (**a**) and summer (**b**) circulation of surface waters. The *dashed arrows* indicate slower circulation. (From Franco.[7] Reprinted by permission.)

(2) The summer situation is characterized by a vertical stratification of the water column due to the spring warming up of the surface layers, which become less dense (FIG. 2b).

In short, two water masses are formed in the whole Northern Adriatic, separated by an evident pycnocline. The layers may become three, owing to a particular mixing phenomena and/or a lateral injection of intermediate-density waters from the east. The deeper layer consists of low-temperature, high-salinity waters of a winter type. The thickness of this layer tends to decrease and in autumn a dome structure can be isolated north of the basin. The overall cyclonic circulation is very slow in summer (FIG. 3b).

Also, the wind effects are worth mentioning, as they may modify local circulation aspects.

The Po waters, which flow on the surface, usually show cyclonic eddies to the north and anticyclonic ones to the south.

The wave motion and the tidal currents keep the coastal zone (down to a depth of 10–12 m) free from stratifications. The waters of minor rivers (TABLE 1) often remain confined to this area. In the marine zone from Chioggia to Ancona (mainly in front of the Emilia Romagna Region) the waters have very little renewal down to a depth of 20–25 m since they are protected by the morphologic structure of the Po delta. Here, in summer, the inertial and tidal currents only cause oscillations, and an overall water stagnation may occur in late summer.[10]

PRESENT SEDIMENTATION PROCESSES

TABLE 3 shows the annual average discharge of the principal rivers debouching in the Northern Adriatic Sea area. It is evident that the prevailing sediment supply is from the Po River (approximately 70%); the smaller rivers debouching to the north and to the south contribute 20% and 10%, respectively.

The coarse materials show poor interaction with the pollutants. The recent sands settle near the riverine mouths, feeding the deltaic systems, or they distribute themselves along the coasts.

The fate of the pollutants in the marine environment is mainly associated with the transport, distribution and sedimentation phenomena of fine materials (silt and clay).

During the Würmian regression (10,000 years ago), the whole Northern Adriatic basin was emerged up to the Meso-Adriatic deep (FIG. 1). During the post-Glacial transgression the sea level underwent rise and stagnation periods. Therefore it is possible to identify traces of coastal morphologic systems[11,12] which are partly buried under more recent sediment and partly still uncovered and evident. The actual shoreline is slightly regressed in comparison with the transgression peak (nearly 2000–3000 years ago).

The fine materials which settle either in the prodelta areas in front of the mouths or further on, after having been transported in suspension by currents, are prevailingly found along the northern and western edges of the basin beyond a depth of 6–7 m (FIG. 4). The thickness of the olocenic sediment varies from 0 to 20–25 m at the points where the subsidence and/or the input (Ravenna area) is particularly high.

The remaining part of the basin is almost without deposits of recent fine materials.

We have already said that waves and streams are likely to resuspend sediment matter even at relatively great depths. The persistance of deposits in certain areas always depends on the relationship between the quantity of deposited material and resuspended matter. Many pelites are transported into the Meso-Adriatic deep trough down to a depth of 150–200 m. The Po River has a relatively high solid transport (about 14 Mt/year) in comparison with its flow, and most of the suspended matter settles down along the northwestern coast, where the fine materials coming from the northern mineralogical provinces deposit as well, owing to the particular Adriatic circulation.

The high content of dolomite in the sediments placed in a belt 20 to 25 m deep[13] in the area off the Po (FIG. 5) shows transport pathway of fine materials from Northern Italian rivers whose load is remarkably rich in dolomite.[14] The content

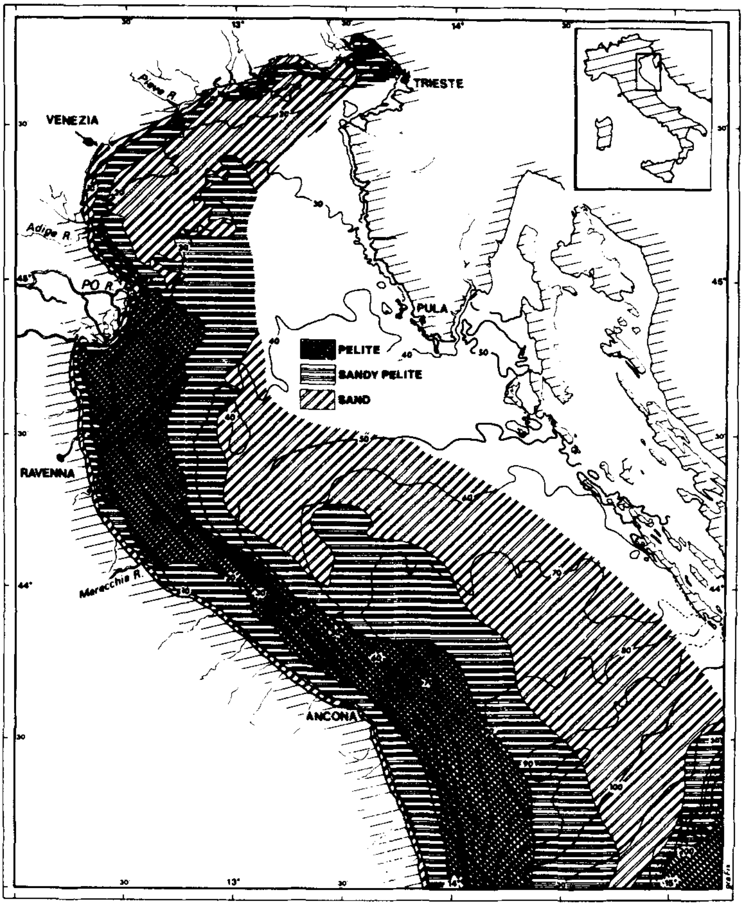

FIGURE 4. Grain-size composition of surface Adriatic sediments. (From Brambati *et al.*[73] Reprinted by permission.)

of dolomite in the zones that are directly influenced by the rivers north of the Po is much higher and is related to the coarse material content in sediments.[15] South of this area, dolomite is mostly associated with the pelitic fraction ($r = 0.50$, $p < 0.001$).

Several authors have described the granulometric composition of the superficial sediments (FIG. 4). The thickness of the holocenic fine deposits allows calculation of average sedimentation rates (a few mm/year).[12] However, in order to quantify fluxes, to formulate mass balances, and to study the evolution of transport phenomena, it is necessary to know the recent sediment accumulation rate (g/cm^2 year) and its areal and annual variability. A wide research program is devoted to studying depth profiles of natural and anthropogenic radionuclides in sediments (especially Pb-210 and Cs-137) to determine sedimentation rates and mechanisms.

Useful information to ascertain the various sources of sedimentary materials has been obtained using different tracers, including clay minerals[16-19] as well as some pollutants.[20-24] If we observe the distributions of substances such as ammonia, which is subjected to rapid transformation and high riverine discharges,[22,23] we can also gather reports about the zones where the fine riverine materials settle at first. The water content is usually high in the prodeltaic deposits.

POLLUTANTS

Particularly high concentrations of pollutants have never been reported in the Adriatic Sea sediments, although the overall inputs brought by the rivers and by the atmosphere are relatively high. This may be due to the fact that the suspended solid inorganic matter transported by the Po River, which is rather elevated compared to its flow, has a dilution effect on the concentrations of the transported pollutants which are then dispersed and deposited into the sea.

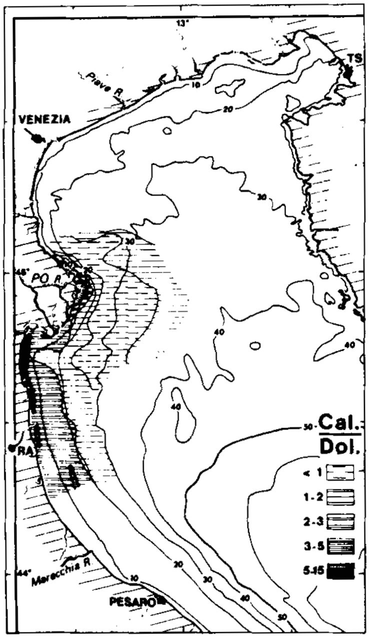

FIGURE 5. Distribution of calcite/dolomite ratio in surface sediments. (From Ravaioli.[13] Reprinted by permission.)

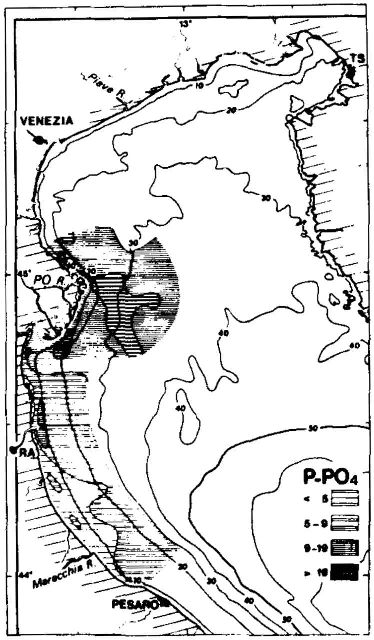

FIGURE 6. Distribution of P-PO_4 (mg/kg, dry weight) in surface sediments.

The study of pollution has given rise to a renewed interest in present and recent sedimentation phenomena.

NUTRIENTS

It is well known that nutrients promote the growth of microalgae, which constitute the first step in the food chain. If their concentration in the waters is too high (eutrophic conditions), the growth of phytoplankton turns out to be abnormal and may cause environmental decay phenomena and seabottom oxygen deficiency. This kind of situation is frequent in summer in the Northern Adriatic, along the Emilia Romagna coasts (and in the coastal lagoons).

As a rule, however, although algal blooms have been recorded even in front of the Po delta and some areas of the northern coasts,[25] the rest of the basin is in meso- or oligotrophic conditions.[7] The nutrients are brought into the North Adriatic mainly through the rivers; the waters coming from the south through the eastern ascending stream contain low levels of nutrients. In winter, the dissolved nutrients are conveyed southwards, along the western coastal zone. The fraction linked to the solid materials settles in the prodeltaic area of the rivers and, more generally, in the deposition zones of the fine materials along the northern and western coast of the basin.[22,23]

The phenomenology is more complex in summer. The minor rivers feed the coastal area, whose waters are prevailingly mixed vertically down to a depth of 10–12 m. The Po River disperses its waters in all directions (FIG. 4), feeding the superficial layer with less dense waters off shore. In the photic zone, the nutrients are utilized for the growth of phytoplankton; because of biological and physical phenomena (grazing by zooplankton and fecal pellet production, sinking of dead organisms) they quickly descend towards the bottom waters. Here the decomposition of the organic matter, with the consequent decrease of the dissolved oxygen, promotes nutrient regeneration; their reutilization is prevented, however, by the stratification of the waters.

These substances are conveyed southwards when the autumn/winter circulation starts. For this reason, owing to the particular hydrodynamics of the basin, the eutrophication phenomena take place largely in summer, especially in those zones where particular conditions exist, connected to the riverine inputs and to the presence of a decreased rechange of the coastal waters. One of these areas, where the decrease of water circulation ends in late summer and stagnation phenomena occur, is the one in front of the coast between Cervia and the Po delta. Therefore the low oxygenation of the bottom might also cause orthophosphate-releasing phenomena from the sediments previously deposited. Recent data[26] tend to emphasize the importance of the sediment in the regeneration and remobilization of ammonia.

Even though the role of the sediments in the development of the algal blooms in this area has not yet been cleared up, we know the accumulation zones and we suppose that sediment fluxes may significantly contribute to the balance of the nutrients in the water mass.

Diffusion can be the most probable and constant release mechanism of nutrient from the sediments in bottom anoxic conditions. Resuspension can episodically mobilize large amounts of nutrients from the superficial sediments, which is especially important if the concentration in the water is low.

The sediments coming from the Po River are primarily rich in phosphorus compounds (FIGURE 6 reports exchangeable P-PO_4 of bottom sediments in September 1977) as well as in reactive silica. Nitrogen compounds, mainly ammonia, accumulate in the shallow sediments between Cervia and the Po delta.

Hammond *et al.*[25] and Frignani *et al.*[27] presented data of benthic fluxes of nutrients (phosphate, ammonia, nitrite and silica) from *in situ* and laboratory experiments carried out from 1979 to 1982. Fluxes measured in the laboratory systems are mostly in the sediment-water direction. The diffusive fluxes, as well, show that the sediment can act both as a source and a sink for all the nutrients: this is particularly true for phosphate, since the other species are more often released from sediments to the overlying waters.

ORGANIC CHEMICALS

Among all the organic chemicals that can be considered to be environmental pollutants, PCBs and chlorinated pesticides (mainly DDT and its analogues) have received the most attention.

Exposure to PCBs has been linked to chloracne, nervous disorders, and hyperpigmentation of the skin in humans, and to reproductive failure and liver abnormalities in birds, rats and dogs.[28] However, the problem of toxicity is not simply one of acute effects: it is more often a matter of chronic, long-range effects.[29]

Pesticides dissolved in waters may have a number of fates. They may be sorbed by suspended matter and sediments, degraded by microorganisms, taken up by organisms, or diluted off shore. Uptake and concentration by organisms, while important for ecologic and public health aspects, are very small compared to the total amount of pesticides (and PCBs) in the environment.[30] The most important factor governing the distribution of chlorinated hydrocarbons in the aquatic environment is the interaction with suspended matter and sediment: in natural water systems the nonpolar molecules have a strong affinity for solid particles. A distribution coefficient of 2×10^5 has been reported by Harvey and Steinhauer[31] for Aroclor 1254 between suspended matter and seawater.

The suspended matter concentration is undubitably the factor that determines the major transport mechanism of these chemicals. It is likely that a big load of suspended solids in a water body will scavenge nearly all the chlorinated hydrocarbons from the water. On the contrary, in an ocean sample with a suspended matter concentration of 0.1 mg/L, less of 1% of the mass of a compound with a distribution coefficient of 10^5 will be associated with the suspended material.[32] In a coastal area, where the particulate concentration is relatively high, a substantial part of the input of these chemicals will settle on the bottom and the other part will leave the system towards the open sea.

A pesticide, once in the sediment, may be released into the overlying water, taken up by organisms, altered or degraded by microorganisms, or simply buried. Therefore the accumulation of compounds such as DDT into sediments is desirable because it places them in an environment that promotes their immobilization and degradation.[29] This should be valid also for PCBs, although these chemicals are even more resistant to degradation and remain unaltered for a long time.

It is known that the major way for the ubiquitous distribution of most of chlorinated compounds is the atmosphere. In a coastal area, however, the presence of these chemicals is mainly influenced by local sources, especially by river outflows.

We report here together the results of two studies carried out on sediment samples of the northwestern Adriatic coastal area.[33,34] FIGURES 7 and 8 summarize the areal distributions of PCBs and total DDT (pp′ DDT and its analogues) concentrations, respectively. Using nearly the same methodology, the authors studied two important areas: the one in front of the Po delta and that from Po di Levante to the Sile River.

The area of the Gulf of Venice is mainly influenced by canals and rivers and by the lagoon sediment. In the very northern zone, where sediments are mainly from Piave and Sile rivers, a relatively high ratio (3.3) between total DDT and PCB concentrations points to a major agricultural contamination.[34] In the southern part of this area the industrial pollution prevails (PCBs/total DDT = 3–2.4). Furthermore in the coastal area adjacent to the lagoon, some evidence exists that pollution should be related to direct dumping of industrial tailing and/or dredged material from the lagoon canals.[34]

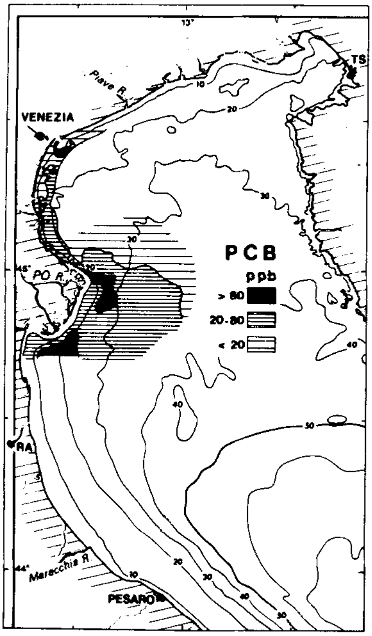

FIGURE 7. Distribution of PCBs in surface sediments.

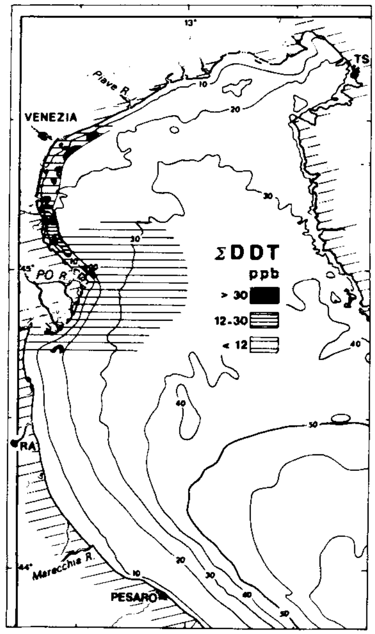

FIGURE 8. Distribution of Σ-DDT in surface sediments.

The area influenced by the Po River distributaries is low in total DDT concentrations. It can be divided into a northern and a southern zone (FIG. 8). The first is characterized by sandy sediments and little or no sedimentation: in this case the lowest levels of contaminants are found. The second one shows two zones with accumulation of PCBs and total DDT, clearly related to the principal outflows of the river, and a large zone where the concentrations are below certain limits, mainly because of the strong dilution due to the relatively large transport of suspended matter characterizing the Po River. It is noteworthy that the industrial pollution here strongly overcomes the one due to the pesticide use.

Frignani and Ravaioli[33] found that the fine-silt fraction has the higher correla-

TABLE 2. Comparison of Concentrations of PCBs in Sediments of Different Areas

Areas	Reference	Range (ng/g)
Tyrrhenian Sea (near Tiber River)	Frignani *et al.*,[67] 1984	8.7–70
Northern Adriatic Sea	Frignani and Ravaioli,[33] 1982	6.7–149.1
Hudson River	Bopp *et al.*,[32] 1981	700–140,000
Coast of Turkey	Basturk *et al.*,[69] 1980	<4
Clyde sediments	Halcrow *et al.*,[70] 1974	10–2,890
Brisbane River estuary	Shaw and Connel,[71] 1980	25–58
Gulf of Lion	Aloisi *et al.*,[2] 1975	50–700
Gulf of Venice	Donazzolo *et al.*,[34] 1983	1–185

tion with the chlorinated hydrocarbon concentrations in front of the Po delta. No correlation was evidenced with the organic carbon: perhaps these data cannot represent the variety and different roles of the organic matter in the sediments.

Fossato and Frignani[35] calculated a mass balance for PCBs in the area (33 × 33 km × 25 m average depth) in front of the Po delta: because of the lack of data on PCB concentrations in core sediments and some wrong ideas (still accepted at that time) about the rates of modern sediment accumulation, the amount of PCB in sediments was underestimated. Nevertheless, those results show that PCB sediment content was more than 94% of the total amount in the area. In the period of time considered (17 days in June 1978) the suspended matter, waters and biota were carrying PCBs with a ratio of 3.2 : 1.9 : 1, respectively.

TABLE 2 summarizes some PCB data from a number of different sources for comparison with the Adriatic sediment pollution. In Italy DDT use has been greatly limited and then definitively prohibited since 1970 and 1978, respectively. Therefore, a decrease in environmental levels of chlorinated pesticides is to be expected for the future. The use of PCBs has been regulated by a directive of the Council of the European Economic Community, but it is still produced and used,[34] so pollution phenomena are still probable, at least on local scale.

RADIONUCLIDES

In describing the natural background radiation in the marine environment emphasis has been given to contributions from K-40 and cosmic rays; much less has been said about the alpha-emitters[36] or other radionuclides. This is valid also for the Adriatic Sea: only in very recent times have systematic samplings been carried out to study present levels of natural and artificial radionuclides so that further changes can be assessed in concentration due to the activity of present or future nuclear power plants.

Most of the analyses of sediment samples from the Northern Adriatic Sea have been carried out especially using radionuclides (mainly Cs-137) as tracers of sedimentation phenomena.[21] Many radionuclides, in fact, have a sufficient affinity for fine particles to be a useful instrument to trace their transport and distribution.[21] Furthermore, radionuclides are natural clocks for the environment and can be used to associate a proper temporal scale with events of both physical and geochemical nature.

Since the early 1960s some laboratories (CISE, Milan; Institute of Zoology, Parma University) have made radioactivity measurements on natural samples.[37] Mezzadri and Triulzi[38] evaluated the contribution of Sr-90 carried by Italian rivers (mainly the Po River) into the Adriatic, compared with the radioactivity directly delivered from local fallout on the marine surface. These authors calculated a contribution of the river waters with respect to the local fallout of the order of 7.6%. It seems likely also that Cs-137 had the same behavior even if it has a stronger tendency to interact with particles than does Sr-90.[39] Although the greatest part of these radionuclides came into the Adriatic from atmospheric fallout, the coastal areas show clear influences from river inputs.

Radionuclides sorbed on suspended matter follow its fate: transport and sedimentation. Sometimes marine sediments demonstrate a lack of correlation between radionuclide sorption and grain size, and selective sorption of fine particles is not always directly proportional to the specific surface area.[21] It depends on the specific minerals and radionuclide involved.[39] Albertazzi *et al.*[21] found a clear correlation between Cs-137 activities, fine silt, and clay fraction above 7 and 11 phi. The radionuclides are somewhat more strongly sorbed in sediments with a large cation exchange capacity. The carbonate content is inversely correlated with the radionuclide uptake and this can be explained as resulting from lower cation exchange capacity of carbonate minerals.[39]

In 1970 Cerrai *et al.*[37] reported Sr-90, Ra-226, Cs-137, Ce-144, Pm-147, Eu-155, Co-60 and Sb-125 concentrations in superficial sediments collected in the Northern Adriatic Sea. The aim was to compare radionuclide contents in the samples collected north and south of the 45th parallel (just south of the Po River delta). The gross beta radioactivity values have been given by Schreiber *et al.*[40]

This work was mainly in connection with the effects on the marine environment of nuclear bomb tests in the 1950s and '60s; it has not been continued on such a scale until recent times. Albertazzi *et al.*[21] reported Cs-137 distribution in sediments of the area in front of the Po delta. Activities in superficial samples range from 46 to 611 pCi/kg (dw) at the date of collection (1977 and 1979). The values are strongly dependent on the grain size composition of the samples. The higher value, found in a sediment core, is 862 pCi/kg (dw); the maximum values found at depth in cores should represent sediment portions deposited in the year 1963 (maximum fallout of bomb-derived radionuclides). The core was collected in 1978 in a zone of rapid sedimentation just in front of the main branch of the delta (Po della Pila). Some Cs-137 reference data are summarized in TABLE 3 and compared with values found in the Northern Adriatic.

Profiles of excess Pb-210 activity in function of the depth in the sediment cores have been determined so that the sedimentation rates in the same area can be studied in detail (we can derive some very useful informations also from Cs-137 depth profiles). Because of the strong dilution due to the high suspended load of

TABLE 3. Comparison of Cs-137 Activities in Sediments of Different Areas

Areas	Reference	Range (pCi/kg)
Atlantic sediment waste dumpsites	Bowen and Livingston,[65] 1980	6.3 ± 2.2–145 ± 4
Hudson estuary	Bopp *et al.*,[32] 1981	1158 ± 21
Pacific sediment waste dumpsites	Bowen and Livingston,[65] 1980	18 ± 7–110 ± 10
Oyster Creek	Olsen,[66] 1980	320 ± 33–1510 ± 53
Tyrrhenian Sea (near Tiber River)	Frignani *et al.*,[67] 1984	5 ± 10–394 ± 23
Mar Ligure	Delfanti *et al.*,[68] 1986	55–441
Gulf of Taranto	Delfanti *et al.*,[68] 1986	27–337
Northern Adriatic Sea	Albertazzi *et al.*,[21] 1986	46–611

the river the Pb-210 activities are less than 10 dpm/g (dw). The first data show apparent sedimentation rates up to a few cm/year.[21,40]

Recently in Italy people have been very concerned because of the radionuclide contamination due to the accident in the nuclear power plant of Chernobyl (Soviet Union). Since the background levels of Cs-137 before the accident are known on the basis of the cited studies and of the Adriatic Saving Cooperation Project between Italian and Jugoslavian scientists, we think it would not be difficult to quantify this new contamination event in terms of sediment pollution. It will be more difficult to assess the risk for the Adriatic ecosystem.

TRACE METALS

General Biological Aspects and Chemical Associations in Sediments

The metal pollution problems in the Mediterranean Sea are chiefly due to the high quantities of agricultural and domestic sewage and the virtually total absence of control on toxic components. Among the rivers entering the Mediterranean, the Rhône, Po and Tiber discharge by far the highest contaminant load, which originates from both industrial and municipal inputs.[41]

The influence of the metal pollution on mortality,[42–44] cell movement, cell growth and cell contents is usually related to metal ion activities. In natural systems, difficulties arise because the composition of the media may not be known and, in particular, information is rarely available on the concentration and complexing capacity of individual organic compounds.[45] Studies of benthic detritivores and filter-feeders suggest that the extent of trace metal uptake might be controlled more by the availability of metal on particle surfaces than by the availability of metal in solution.[46,47]

Since, as said, the availability of trace metals for metabolic processes is closely related to their chemical species (both in solution and in particulate matter), the type of chemical association between metals and particulate matter has become of interest within the framework of sediment investigations of especially polluted marine coastal regions. Furthermore, the suspended and settled particulate matter provides a trace metal reservoir characterized by low availability but high local concentrations.

The bonding of metals in aquatic sediment can be the result of the following mechanisms: (1) transport and deposition on particles (minerals, organic residues, waste materials); (2) sorption and cation exchange; (3) formation of metal hydroxides and carbonates; (4) solubilization by the combined processes of complexation and reduction; (5) incorporation into the sediment by mechanisms of adsorption, flocculation, polymerization, and precipitation.[48]

The various organic and inorganic phases are closely interrelated: clay minerals, carbonates and other suspended materials form the nucleation centers for the deposition of Fe/Mn hydroxides.[49] Humic acids are increasingly adsorbed to clay minerals at higher salinity.[50] There is also a characteristic relationship between Fe, Mn and P with both river water (dissolved) and seawater (partly flocculated) organic substances.[51]

Trace Metal Distribution

The Adriatic Sea, as explained before, is particularly susceptible to pollution, especially that from the industrial centers in the northern part of the region.

Naeve[41] reported concentrations of certain heavy metals (e.g., Hg) in water and edible organisms at or above the acceptable safety levels. Data of Grancini *et al.*[52] from the northern Italian Adriatic coast from Trieste to Ravenna indicate significantly higher values of Ag, Co, Sb and Zn compared to the data from open-sea water samples; similar findings on sediment samples[52] suggest that this increase is related to the waste input from rivers. Significant anthropogenic effects, mainly for Zn concentrations, were found in the Kvarner region (Rjieka) of the Jugoslavian Adriatic Sea.[53,54]

A distribution study of some elements was done by Stefanini[55] in an area from Trieste to Venezia and by Paul and Meischner[56] in the whole basin. Their results confirm that the concentration of trace elements in the marine sediments is essentially dependent on their mineralogical composition, on the size of the deposited particulate matter, on the biological activity occurring at the sea bottom, and finally on the lithological nature of the sediment.

Most of the recent studies in the Northern Adriatic Sea sediments can be summarized from the papers of the Marine Biology Institute and University of Venice, and the Marine Geology Institute in Bologna.[3,4,15,24,34,57,58,59]

River Fluxes

Provini *et al.*[60] indicated a mean annual particle discharge of 8.4×10^6 t/year over a period of 18 months; over the same period they calculated a total metal flux for Cu, Cr and Pb of, on average, 760, 970 and 1080 t/year, respectively.[61] Other estimates for the amounts of heavy metals entering the sea from the Po River give over 2500 tons of Zn, 89 of Ni, and 65 of Hg.[25] Guerzoni *et al.*[20] estimated that the total annual natural metal fluxes from the Po are about one-third of the present-day fluxes.

Lagoons

In the studied region, other than the typical riverine and marine depositional environments, there are many others such as lagoons (Marano, Venezia, Po delta) and subtidal marshes (''Piallasse'' near Ravenna, the saltmarsh of Cervia). Those environments collect in particular the fine-grained sediments and are heavily polluted from inorganic and organic wastes (industrial and agricultural discharges). Donazzolo *et al.*[57] reported that the source of trace metals (especially Hg, Pb, Co, Cu, Zn and Cd) in the sediments of the Venice Lagoon is the Marghera industrial zone. High organic carbon levels were found in the southwest part of the lagoon. Guerzoni *et al.*[3] found that deltaic lagoons did not show the maximal concentration among the studied metals (Cd, Co, Cr, Cu, Mn, Zn) except for Pb. Anconelli *et al.*[62] studied Ravenna saltmarshes and found extremely high levels of Hg and high values of Pb, Zn and Cu, indicating industrial pollution due to direct dumping of petrochemical wastes. Majori *et al.*[63] and Frascari *et al.*[4] studied Marano Lagoon and Cervia saltmarshes, and published other data. TABLE 4 summarizes the available data on confined environments in the studied area.

Fine-Grained Sediments Off Shore

From Trieste to Chioggia, more than 200 sediment samples were classified, according to grain size, into homogeneous groups.[24] Three of them represent the

TABLE 4. Range of Values (mg/kg) in Three Confined Environments of the Studied Area

Lagoon	Cd	Cr	Cu	Hg	Pb	Zn
Venice[a]	0.6–20.8	6–34	5–180	<0.1–3.5	15–164	18–3000
Po delta[b]	1.2–1.6	47–85	46–65	0.3–0.6	59–81	156–210
Ravenna[c]	0.5–9.5		12–280	<0.1–245	12–122	19–303

[a] Donazzolo *et al.*,[57] 1984.
[b] Guerzoni *et al.*,[3,20] 1984 and 1986.
[c] Anconelli *et al.*,[62] 1980.

fraction of fine sediment more directly associated with sediment yield from the Isonzo, Tagliamento, Piave and Brenta rivers. They are composed of clayey-silt to sandy-silt and are abundant in clay minerals and poor in dolomite, with variable amount of calcite. These groups are distributed as follows: (1) Fine-grained sediments of the first identified area in the northern part can be divided in three geographical areas (i.e., between the Tagliamento and Piave rivers, the Lagoon of Marano, and the mouth of the Isonzo). High content of Hg is related to the cloroalkali plant located in Marano and the mining district of Idria. (2) In front of the Venice Lagoon fine sediments off shore show an anomalous quantity of Zn and Cd. (3) The Brenta-Po di Levante area presents an anomalous quantity of Cr, connected to leather industries centered long on the Brenta and Adige Rivers.

From Chioggia to Ancona, more than 120 samples were classified according to grain size, organic matter content, and trace metals. The pelitic geographical areas were essentially two: (1) The area between Chioggia and Ravenna is mainly influenced by the pelites coming from the Po River. The highest content of Zn and Pb (Cu, Cr) is found in the prodelta slope, in front of the main tributaries of the river. Carbonate fraction of the fine-grained sediments is due to almost the same amount of calcite and dolomite, with some differences in the central area of the delta, where a supply from the northern dolomite-rich sediments is evident. These fine materials coming from the northern part are mixed with Po sediments and are characterized by high Cd, V and Hg content. (2) In the area from Ravenna to the south, the pelitic sediments show lower levels of heavy metals with increasing distance from the Po and some local accumulations, especially Cr, in front of Destra Reno and Savio rivers. Inside the Ravenna's Channel (Porto Corsini) a high concentration of Hg was found, related to the industrial pollution due to direct dumping of petrochemical waste in the Ravenna saltmarshes.[62]

TABLE 5. Average and Range of Metal Data (mg/kg) of Surface Sediments in Front of the Po Delta and in Two Identified Subareas North and South of It

Area	Cd	Cr	Cu	Hg	Pb	Zn
Chioggia/TS	1.1	24	15	0.8	35	94
	<0.1–5.6	4–273	2–52	<0.1–16.9	5–96	2–870
Ancona/RA	0.5	44	17	0.2	30	71
	<0.1–1.2	16–74	1–48	<0.1–1.0	4–75	15–171
Po delta area	0.9	46	21	0.4	41	96
	0.2–1.8	13–97	1–66	<0.1–1.1	9–79	24–244

TABLE 6. Natural Background Values (mg/kg) from Preindustrial Fine-Grained Sediments

Element	Lagoon of Venice[a]	Po Delta and South[b]	Middle Adriatic Sea[d]	Unpolluted Area[d]
Cd	1.2	0.56	0.71	—
Co	17	—	12	—
Cr	21	25	45	<25
Cu	15	22	26	<25
Fe	7500	—	—	<17,000
Hg	0.1	0.12	0.30	—
Ni	20	35	50	<20
Pb	23	23	32	<40
Zn	49	70	89	<90

NOTE: The first two columns of this table are used as background levels for the Northern Adriatic Sea.

[a] Donazzolo *et al.*,[57] 1984.
[b] Guerzoni *et al.*,[3,20] 1984 and 1986.
[c] Selli *et al.*,[64] 1977.
[d] Prater *et al.*,[72] 1977.

Background Levels

Natural background concentrations of fine-grained sediments have been proposed for the Lagoon of Venice, for the Po delta and south and for the Middle Adriatic Sea by Selli *et al.*,[64] Donazzolo *et al.*,[34] and Guerzoni *et al.*,[3,20] and are in good agreement with each other (TABLE 6 and FIG. 9). From these data a good estimate of the sediment contamination is possible and concentration factors (actual versus background) were calculated. FIGURES 10, 11, 12, and 13 show four examples of trace metal distribution in the whole basin, with some differences in the relative importance of sources. Looking at the distribution and in comparison with the calculated background levels of the area, peak concentration factors are

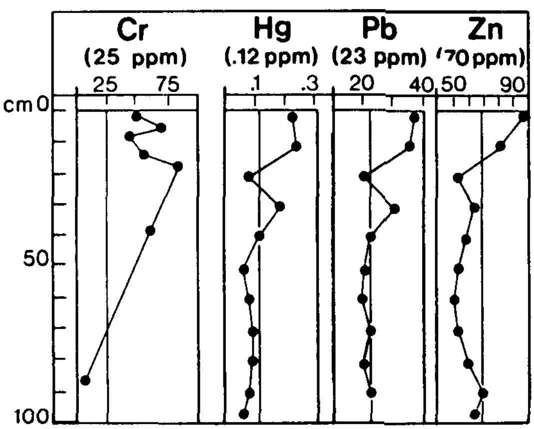

FIGURE 9. Concentration of trace metals with depth in one core used to calculate background levels (in brackets). (From Guerzoni *et al.*[3] Reprinted by permission.)

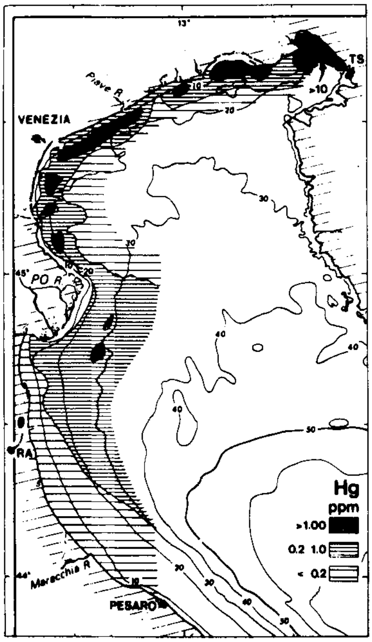

FIGURE 10. Distribution of Hg (mg/kg, dry weight) in surface sediments. (Redrawn from the work of Donazzolo *et al.*[15,57] and Guerzoni *et al.*[3])

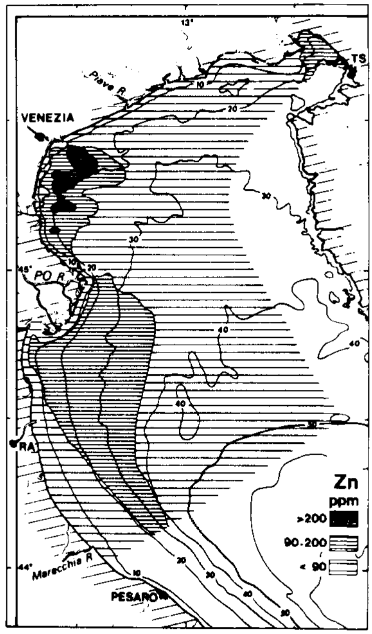

FIGURE 11. Distribution of Zn (mg/kg, dry weight) in surface sediments. (Redrawn from Donazzolo *et al.*[15,57] and Guerzoni *et al.*[3])

found in the northern part of the basin for Hg (five to ten times) and Zn (four times), in front of the Brenta, Adige and some small rivers to the south for Cr (two to four times), and in some spots to the north of the Po (Gulf of Trieste) and in its prodelta slope for Pb.

CONCLUSIONS

Even if the waters of the Northern Adriatic Sea are renewed completely in one year and the dissolved substances are transported southwards, toward the morphologic depressions or to the Eastern Mediterranean Sea, in some zones bottom sediments store a significant amount of pollutants which might partly be released to the overlying waters or contaminate the benthic fauna.

The principal sediment pollution phenomena are located in the northern and northwestern coastal areas and the transport of part of the fine polluted matter north-northeast along the western coast can be clearly seen.

The highest pollutant accumulations are found in the prodelta zones of the rivers (off the shore of the Po delta at depths of more than 20 m) and in areas of low hydrodynamic energy (the northern part of the Emilia-Romagna coast, the Gulf of Trieste, and the lagoons).

Furthermore, the areas of direct discharge of solid wastes (dumping sites, Venice) show maximum concentrations of some pollutants. The pollution levels are not high in comparison to those of other polluted seas, with some exceptions: (a) nutrients along the Emilia-Romagna coasts, the delta and the lagoons; and (b) mercury on the extreme northern area and in the lagoons of Ravenna. Other elements such as Zn, Pb, Cu, show high value in small areas.

Other research is in progress to model the distribution of sediments, with related pollutants, and the water-pollutant interactions.

SUMMARY

The Po River and some other minor rivers transport toxic chemicals and nutrients from highly developed lands into the Northern Adriatic Sea. It is a shallow semi-enclosed basin with peculiar hydrodynamics, and the water circulation causes a surprisingly fast renewal of the water.

Many pollutants interact with particulate material, mainly silt and clay fractions, which settles in some areas along the northern and western coast of the basin, forming reservoirs with long-term and release potentials.

Some chemicals, such as toxic metals, chlorinated pesticides, PCBs, artificial radionuclides and nutrients, show their maximal concentrations in the prodelta

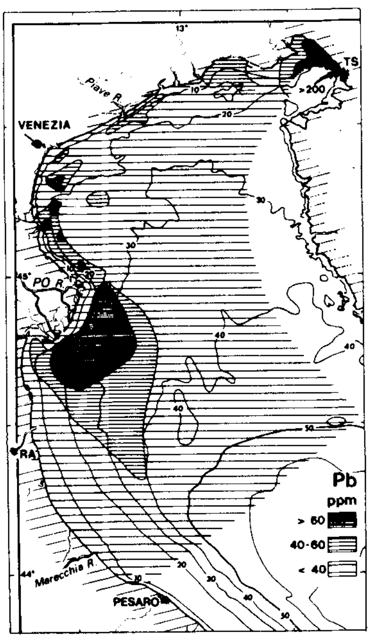

FIGURE 12. Distribution of Pb (mg/kg, dry weight) in surface sediments. (Redrawn from the work of Donazzolo *et al.*[15,57] and Guerzoni *et al.*[3])

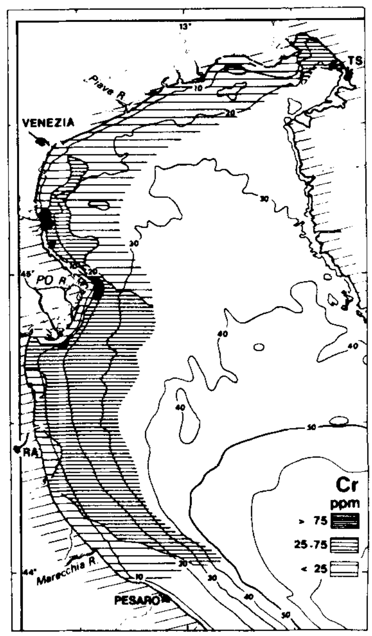

FIGURE 13. Distribution of Cr (mg/kg, dry weight) in surface sediments. (Redrawn from the work of Donazzolo *et al.*[15,57] and Guerzoni *et al.*[3])

areas off riverine mouths, in lagoons and inlets, and near particular waste discharges.

The concentrations of these chemicals in the Adriatic sediments are not high when compared to reference data of other marine coastal areas in the world. Most of the knowledge of the behavior of pollutants and particulate matter in the Adriatic is somewhat qualitative and semi-quantitative. A big effort is now needed to quantitate the sediment-pollutant interactions and the sediment distribution patterns.

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