

## **Trace Metal Contamination in Marine and Riverine Sediments around San Rossore Park (Italy).**

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### ABSTRACT

Surficial sediments collected in 1984 and 1985 in the marine coastal belt and in the final stretch of rivers flowing in the San Rossore zone were analyzed for ten trace elements using atomic absorption spectrophotometry.

Inter-element relationships as well as those with grain size and organic carbon contents were examined before interpreting the data obtained. The results indicate that rivers flowing in this area and especially the river Morto, are subject to anthropogenic input of Cr, Cd, Hg, Pb, Cu and Zn.

The remobilization of several elements in the estuarine zone and their possible involvement in the deterioration processes of coastal vegetation of the San Rossore park, are discussed.

### **Introduction**

The presidential farm of San Rossore is a natural park of about 5,000 Ha, covered by pine forest (*Pinus pinea* and *Pinus pinaster*) and broadleaf woods (alders, oaks, white poplars and ash-trees). The park lies between the Arno and the Serchio rivers, the Tyrrhenian Sea and the suburbs of Pisa (Fig. 1). The two rivers receive the sewage, which has undergone little treatment, from the most industrialized and densely populated areas of Tuscany. Moreover, the Morto river, a canal built in 1939, flows through the middle of the park after receiving industrial and urban waste waters.

In this area westerly winds prevail and the south-westerly one (libeccio) is dominant, while proximal and distal drifts flow consistently northwards (Rapetti and Vittorini, 1983). Thus a large portion of pollutants carried by the rivers is pushed towards the

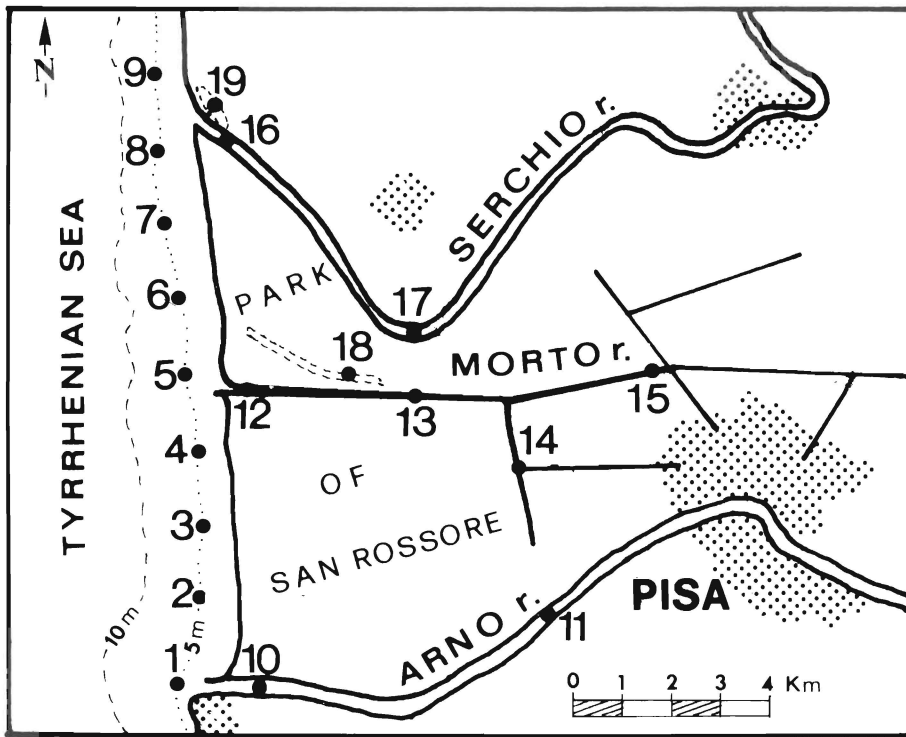


Fig. 1 Study area and sampling locations.

coastal zone of the park. The effects of pollution are dramatically shown by the serious deterioration of the coastal vegetation: in a 1 km-wide belt along the coastline the pine trees are almost all dead. Several studies since the outset of the deterioration process (Lapucci *et al.*, 1972; Gellini *et al.*, 1983) have found evidence for a close relationship between the damage to the vegetation and the pollution of the sea by anionic surfactants. As reported for other marine coastal areas (Pitman *et al.*, 1977; Dowden and Lambert-Marcia, 1979) surfactants are concentrated in the sea-spray, carried coastward by the wind and deposited on the leaves of trees. They damage the wax that protects the epicuticle and the pre-stomatal chamber (Bussotti *et al.*, 1984), causing a substantial increase in the uptake of phytotoxic substances from sea-spray or from the air. It is likely that certain trace metals can also exert a harmful effect in synergism with other pollutants. It is known that relatively low concentrations of Pb, Cd, Ni and other elements can inhibit photosynthesis and transpiration or interfere with mitochondrial respiration (Ormrod, 1984).

In the framework of a research project on the cause of deterioration in San Rossore park, the present study was undertaken to analyze trace elements in surficial sediments of the coastal zone and in the final stretches of the rivers flowing in this area. A high level of trace metals in the sediment would provide further reason to suspect their involvement in the degradation of the vegetation.

## Materials and Methods

Surficial sediments (top 3 cm) were collected three times in 1984 and once in 1985 at 19 stations (Fig. 1). Samples were stored frozen in PVC vessels and before analysis, subsamples were dried at 105°C to determine water content. For trace element determinations, sediments were digested with conc. HNO<sub>3</sub> at 120°C for 6 h in Teflon decomposition vessels. Analyses were performed by A.A.S. using the cold vapour stream for Hg, the air/acetylene flame for Cr, Cu, Zn, Ni, Co, Fe, Mn and the graphite furnace for Cd and Pb.

Five replicates of two samples were run and the coefficient of variation ranged from 3.9 to 12.3%, depending on the element. Using sediment subsamples, the percentage of sand (by wet sieving through a 63 µm sieve) and the percentage of organic carbon (following the procedure suggested by Gaudette *et al.*, 1974) were also determined.

## Results and Discussion

According to the environment of collection, samples show very different features: whereas marine sediments are oxidate sands with a low content of organic carbon; riverine and estuarine samples have very variable grain size, redox conditions and organic matter content. Thus it seems more difficult to interpret the results of sediment analysis summarized in Table 1.

Concentrations of trace elements are far higher in river sediments, especially in those of the Morto river and in those with the finest grain size. Their degree of pollution could be estimated assuming as background values those of samples 18 and 19, collected in the former bed of the Morto and in the former mouth of the Serchio respectively. Moreover, from a comparison with previous data on sandy and silty sediments analyzed with comparable procedures (Pearce and Yasso, 1973; Perkins *et al.*, 1973; Bargagli *et al.*, 1985) or assuming as anomalous values those  $> \bar{x} + 2s$  (where  $\bar{x}$  is the mean concentration of all samples and  $s$  is the standard deviation) (Chester *et al.*, 1985), several values (marked in Table 1 with an asterisk) are clearly polluted.

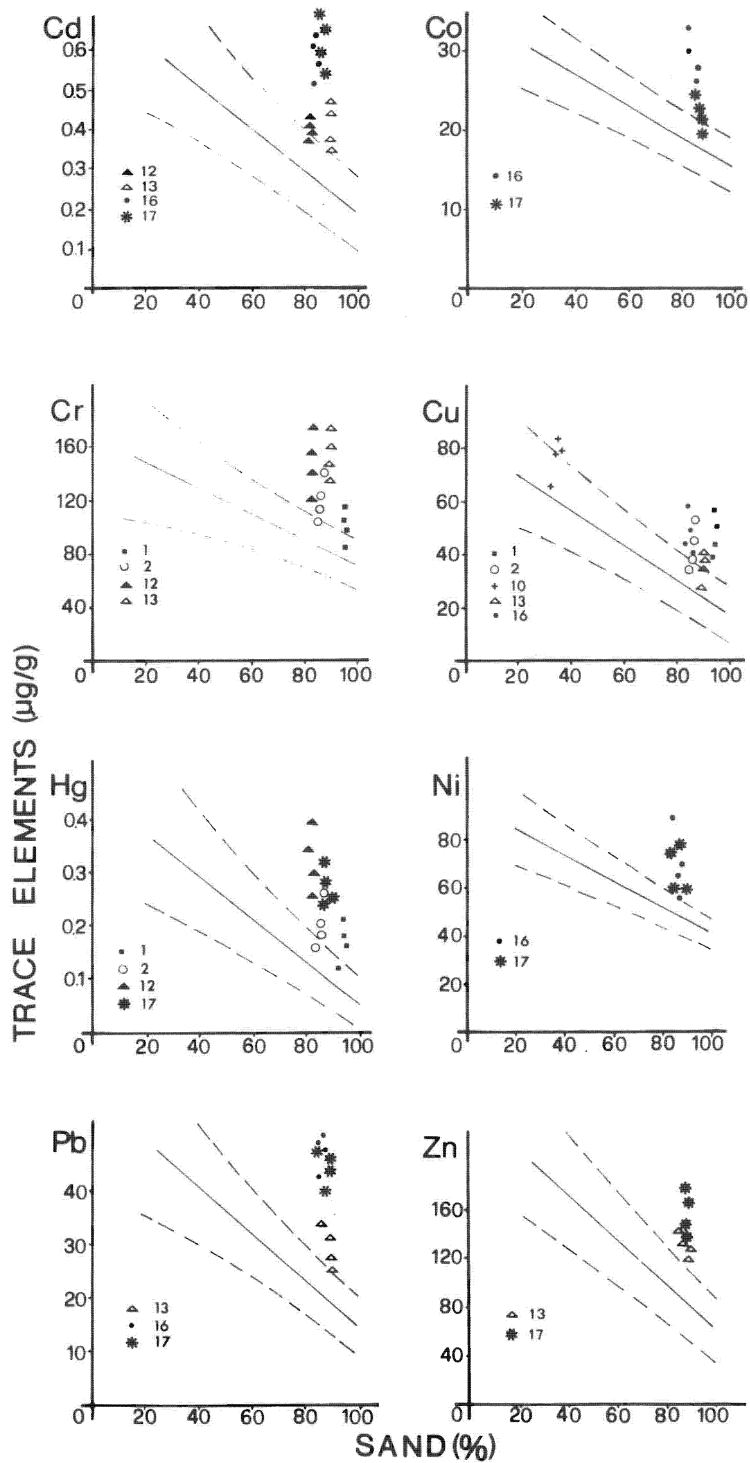
A correlation coefficient matrix for all the analyzed parameters was calculated (Table 2). At the 0.001 probability level very significant and positive correlations occur between Cd, Cu, Fe, Hg, Pb, Ni, and Zn, i.e. the metals dumped into the rivers, especially the Morto, in large quantities. Cr, which arises above all from the Arno, is related only with Fe, Cu, and Ni, moreover it is not correlated with organic carbon contents. Except for Mn, which tends to be incorporated into larger inorganic particles (Baldi and Bargagli, 1978; Forstner *et al.*, 1982) it is known that trace elements concentrations increase as sediment grain size decreases or that they may be associated to organic materials. Nevertheless, the significant relationship between many elements and the organic matter is probably also a consequence of the fact that organic rich sediments are finer in size (Bargagli and Baldi, 1983). Thus the percentage of sand exercises a determining influence on the concentrations of the other parameters. In fact, the coarse-grained quartz, feldspar and carbonate are rather chemically inert in comparison with clays, hydrates or organic substances. Hence, without a correction for grain size, a mutual comparison of metal data in marine and fluvial samples is impossible.

In order to reduce these effects the linear regression equations of each element vs. the sand content of samples was calculated and values above the 95% confidence belt of the regression line were considered polluted. Obviously, heavily contaminated

Table 1 Sand, organic carbon and trace elements in surficial sediments around the San Rossore park (average values±SD of analytical determinations performed in the four samples collected at each sampling point).

St.	Sand	Org.C %	Fe	Cd	Co	Cr	Cu	Hg µg/g	Mn	Ni	Pb	Zn
1	93.6±1.8	0.20±0.04	1.96±0.21	0.18±0.06	21.2±5.6	98.6±16.6	46.9±7.5	0.17±0.04	562±115	52.4±12.3	12.2±3.2	77.2±13.4
2	85.1±1.4	0.21±0.04	1.98±0.25	0.34±0.06	20.4±4.9	120 ±19	39.8±9.4	0.18±0.06	727±84	50.4±14.3	14.2±4.1	81.6±15.9
3	87.5±1.9	0.40±0.10	1.53±0.18	0.14±0.05	17.5±4.0	72.9±13.2	18.1±3.5	0.10±0.02	590±77	46.9±10.6	15.5±4.2	55.0±17.5
4	93.6±1.0	0.19±0.04	1.92±0.27	0.06±0.02	17.9±3.7	67.6±12.4	10.4±2.4	0.09±0.02	516±83	42.3±4.9	15.8±5.6	67.6±23.1
5	96.8±1.3	0.21±0.04	1.36±0.19	0.07±0.02	14.0±3.8	64.4±15.4	14.6±2.2	0.05±0.02	598±101	31.9±8.4	10.2±3.6	49.7±13.2
6	97.6±2.3	0.11±0.04	1.40±0.12	0.05±0.01	9.1±1.6	47.5±10.9	16.8±2.7	0.06±0.02	533±112	35.5±7.9	12.2±4.5	43.2±11.3
7	95.4±1.9	0.17±0.05	1.79±0.23	0.07±0.03	14.1±2.6	62.7±16.5	18.7±4.8	0.08±0.02	514±98	37.1±8.6	11.8±3.7	44.4±12.2
8	90.8±2.2	0.19±0.04	1.73±0.33	0.09±0.02	15.8±3.5	73.7±15.9	18.1±5.4	0.11±0.03	612±111	39.4±9.2	13.6±2.8	50.9±13.6
9	98.2±1.1	0.09±0.01	1.45±0.25	0.08±0.02	13.3±1.9	56.3±15.6	15.1±5.3	0.09±0.02	504±61	39.7±10.6	7.9±2.4	41.5±11.5
10	32.5±2.9	1.80±0.38	3.30±0.91	0.36±0.13	20.2±4.9	263 ±63*	70.0±26.4	0.29±0.08	484±73	61.6±18.0	34.2±12.5	150 ±20
11	31.5±2.7	2.37±0.50	3.49±0.43	0.64±0.23	32.1±9.4	248 ±42*	66.6±14.4	0.34±0.10	890±112	83.8±16.9	50.2±9.9	217 ±22
12	81.4±1.7	1.08±0.15	2.18±0.41	0.30±0.11	17.9±6.0	141 ±33	32.1±11.2	0.32±0.09	607±146	56.4±17.1	19.6±5.7	108 ±28
13	86.8±2.6	1.40±0.08	2.53±0.56	0.38±0.09	20.5±3.0	152 ±24	32.6±12.5	2.51±0.45*	341±62	61.5±15.4	30.7±9.6	122 ±24
14	39.1±3.7	7.83±1.06*	3.83±0.53*	2.40±0.47*	32.1±4.7	140 ±15	107 ±19*	32.8±4.6*	474±76	74.4±16.2	144 ±28*	710 ±103*
15	32.4±3.3	5.71±1.77	3.15±0.42	2.60±0.84*	28.5±4.2	122 ±22	122 ±21*	68.5±15.8*	604±97	79.7±8.8	216 ±24*	428 ±75*
16	85.2±1.9	0.64±0.22	2.16±0.58	0.61±0.11	28.8±6.8	82.6±15.1	42.5±12.4	0.16±0.05	783±189	64.8±20.2	50.2±14.6	90.5±11.4
17	85.6±2.1	0.71±0.15	2.23±0.20	0.62±0.12	20.5±3.7	96.7±13.5	19.9±3.5	0.28±0.05	802±121	63.4±14.7	50.4±13.2	156 ±35
18	74.7±2.6	5.80±1.34	1.84±0.38	0.26±0.07	11.7±4.3	60.0±13.7	20.1±5.3	0.12±0.04	1433±431	52.3±16.7	19.3±5.9	71.5±16.4
19	97.7±2.1	0.07±0.02	1.11±0.22	0.07±0.02	12.0±2.9	50.3±17.6	8.3±2.1	0.04±0.01	797±116	30.5±7.2	7.9±1.7	37.0±12.8

\* Values clearly anomalous ( above the mean concentration of all samples  $\bar{x}+2s$  ,where s is the SD).



**Fig. 2** Trace element concentrations as function of % of sand. Samples above the 95% confidence belts of regression lines (broken lines) are indicated.

Table 2 Sand, organic carbon and interelement correlation coefficients  
 ( n=76; if  $r > 0.35$  , $P < 0.001$ )

	Sand	Org.C	Fe	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb
Org.C	-0.71										
Fe	-0.83	0.61									
Cd	-0.70	0.79	0.65								
Co	-0.61	0.40	0.22	0.23							
Cr	-0.75	0.24	0.72	0.25	0.11						
Cu	-0.84	0.70	0.60	0.23	0.66	0.56					
Hg	-0.57	0.67	0.47	0.89	0.41	0.09	0.74				
Mn	-0.08	0.26	-0.07	-0.08	0.07	-0.08	-0.12	-0.11			
Ni	-0.66	0.47	0.67	0.60	0.64	0.54	0.64	0.44	0.04		
Pb	-0.70	0.74	0.51	0.96	0.59	0.23	0.83	0.94	-0.07	0.59	
Zn	-0.73	0.81	0.70	0.91	0.64	0.35	0.83	0.73	-0.12	0.56	0.84

samples (marked in Table 1 with an asterisk) were excluded from calculations and are not reported in Figure 2. Following this procedure, less contaminated samples were displayed and more information on the metal distribution and on the pollution sources may be achieved.

Surficial sediments of the Morto river are polluted by almost all the analyzed metals. Those of the Serchio are slightly contaminated by Cd, Co, Ni, Pb, and Zn, while in those of the Arno particularly high is the Cr content. The contamination of this river by Cr was first reported by Taponeco and Giaconi (1969), who ascribed it to the chrome plating and tanning industries; our data indicate that this pollution probably continues or at least, that sediment constitutes a sink for the metal dumped in the past. Downstream from rivers metal concentrations decrease considerably; this fact, which has already been reported from other estuaries (DeGroot *et al.*, 1971; Forstner and Wittmann, 1983) has been explained by remobilization processes which occur in the passage from fresh to marine water and by mixing between the more polluted riverborne materials and the sea-derived particles. Marine sediments are slightly contaminated by Cr, Cu, and Hg only near the mouth of the Arno (st.1 and st.2); all the others do not seem to be affected by the Morto or Serchio input. Blundo *et al.* (1984) too, in a physico-chemical investigation on the coastal water of this area did not find evidence of inputs in front of these two rivers. This fact was ascribed, in the case of the Morto, to the small amount of water that it conveys (mean flow rate 1.2m<sup>3</sup>/s) and, in that of the Serchio, to its satisfactory water quality. In agreement with our results, the above mentioned authors, found that 4-5 km from the mouth of the Arno (mean flow rate 1.2m<sup>3</sup>/s) concentrations of nutrients and surfactants in seawater had typical Mediterranean coastal water values.

Although surficial marine sediments are almost uncontaminated, probably some trace elements are involved in the deterioration processes of coastal vegetation. In fact in the river-sea mixing zone significant quantities of phytotoxic metals such as Pb, Cd or Cu are transferred from suspended materials and from sediments (Salomons and Eysink, 1979) to estuarine waters. In the San Rossore coastal area the occurrence of these processes seems confirmed by the highest concentrations of heavy metals found (in the framework of the same research project) at the mouth of the three rivers by Betti *et al.* (1985).

Considering that these rivers, besides trace elements convey to the sea large amounts of surfactants (Gellini *et al.*, 1981) and that metals are 'stripped' very effectively from seawater polluted by surfactants (Kim and Zeitlin, 1971); it seems likely that heavy metals, as has been recognized (Lemlich, 1972; Mac Intyre, 1974), accumulate on spray drops. Moreover, the prevailing coastal drift and wind of this area support the transport and deposition of these pollutants on coastal vegetation.

Researches are in progress on the chemical composition of the coastal marine aerosol and on the metal content in pine needles collected both in the damaged coastal belt and inside the park.

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