Heavy metals in sediments of the Venice Lagoon

Heavy metals
Sediments
Transport mechanisms
Venice Lagoon
Métaux lourds
Sédiments
Mécanismes de transport
Lagune de Venise

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Received 17/12/82, in revised form 1/7/83, accepted 1/8/83.

ABSTRACT

The horizontal distributions (ppm/dry weight) of Hg, Pb, Zn, Cd, Cu, Fe, Ni, Co and Cr in the sediments of the Venice Lagoon indicate that the source of these metals is the Marghera industrial zone. The highest concentrations of Hg (3.46 ppm), Pb (164 ppm), Co (199.8 ppm), Cu (180 ppm), Zn (3 000 ppm) and Cd (20.8 ppm) are found in the lagoon area between Venice and the Marghera industrial area. While Hg seems to be transported mainly in association with particles, soluble species of Fe, Zn and Cu presumably responsible for the high concentrations in the south-western part of the lagoon, where high organic carbon levels have also been observed. Chromium does not originate from local industries, but enters the lagoon from the sea, transported by tidal currents. Quantitative estimates of the antropogenic heavy metals in the upper 10 cm of the lagoon sediments are: Hg, 35 t; Cd, 200 t; Pb, 1 300 t; Cu, 1 600 t; Zn, 16 500 t; Fe, 600 000 t; Ni, 240 t; Co, 550 t; Cr, 480 t.

Oceanol. Acta, 1984, **7**, 1, 25-32.

RÉSUMÉ

Métaux lourds dans les sédiments de la lagune de Venise

On reporte les concentrations (ppm/poids sec) de Hg, Cd, Pb, Ni, Co, Cu, Zn, Cr et Fe dans les sédiments de la lagune de Venise. La distribution de ces éléments montre des panaches de diffusion dérivants de la zone industrielle de Marghera et s'étendant vers le centre de la lagune. On a trouvé des concentrations très élevées de Hg (3,46 ppm), Pb (164 ppm), Co (199,8 ppm), Cu (180 ppm), Zn (3 000 ppm) et Cd (20,8 ppm) dans la partie de la lagune entre la ville de Venise et la zone industrielle de Marghera. Tandis que Hg semble être transporté principalement associé aux particules solides, les espèces solubles de Fe, Zn et Cu sont probablement responsables des concentrations élevées dans la zone sud-ouest de la lagune, où l'on observe aussi des hautes teneurs en carbone organique. On remarque enfin que le Cr ne provient pas des fabriques locales, mais il entre dans la lagune de la mer charrié par les courants de marée. Une estimation quantitative indique que les pollutions métalliques stockées dans les dix premiers centimètres des sédiments sont : Hg, 35 t ; Cd, 200 t ; Pb, 1 300 t ; Cu, 1 600 t ; Zn, 16 500 t ; Fe, 600 000 t ; Ni, 240 t ; Co, 550 t ; Cr, 480 t.

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INTRODUCTION

The adverse effects of toxic elements from industrial or domestic wastes, discharged in embayments or lagoons where hydrological conditions do not allow for dilution and dispersion of pollutants, have been of growing concern to the scientific community in recent years (FAO, 1972). Related to this are heavy metals introduced into the Venice Lagoon during past decades from the Marghera industrial area. Bound mainly to the sediments, they are partially remobilized to the overlying water by chemical and biological reactions (Bruchman, Iverson, 1975; Ederfield, Hepworth, 1975). Physical processes such as sediment resuspension due to waves (Cavaleri, 1980) and dredging operations are also responsible for mobilizing these elements.

A precise knowledge of the heavy metals distribution in the sediments seems to be very important in the assessment of their impact on the lagoon biota and the evaluation of their spatial and temporal differences.

On this basis, the effects of lagoon pollution from industrial and domestic sewage treatment plants can be evaluated. These plants are now under construction. An incompletely known environmental impact may be the narrowing of the port entrances between the sea and the lagoon to eliminate or at least to reduce the tidal storms which raise water levels in the historical centre of Venice.

A further aim of our research is to study the transport mechanisms of toxic substances at the sediment-water interface in the Lagoon of Venice, and to assess the importance of sedimentation as a pollution source, in comparison with other sources of these species.

As preliminary results, we report here: the horizontal distribution of Hg, Cd, Pb, Cu, Zn, Fe, Ni, Cr and Co, together with some information on the origin of these heavy metals and on the transport pathways inside the lagoon and to the Adriatic Sea.

STUDY AREA AND ANALYTICAL PROCEDURES

The Lagoon of Venice (Fig. 1) has an area of some 550 km^2 and is connected to the Adriatic Sea by the port entrances of Lido, Malamocco and Chioggia. Three hydrographic sub-basins may be defined, with surface areas of 276, 162 and 110 km^2, respectively (Ghetti, 1974). Daily water exchange between the sea and the lagoon is about 3×10^8 m^3. The lagoon has an average depth of ~0.6 m and a salinity in the range 28-36‰. Many natural channels cross the entire area. Two main artificial canals, i.e.: Vittorio Emanuele (~4 km long and 10-12 m deep) and Malamocco-Marghera (~15 km long and 12-14 m deep) were dredged in 1926 and 1978, respectively, in order to allow the passage of large vessels to the industrial zone of Marghera (Fig. 1). At present, some 28 000 persons are employed in steel, chemical and other industries. Agricultural drainage (a maximum of 650 m^3/sec. of fresh water from 2 000 km^2 of heavily cultivated land) enters the lagoon at twenty points (small rivers, channels or pumping stations) located along the inner border (Cavazzoni, 1973). In addition to industrial and agricultural wastes, the lagoon has received for several decades urban wastes from Venice (90 000 inhabitants) and Mestre (200 000 inhabitants).

Sediment samples were collected in 1976, 1977 and 1978 with a stainless steel modified Van Veen grab sampler at stations shown in Figure 1. They were placed in sealed glass containers, immediately transported to the laboratory and air-dried in aluminium dishes at room temperature. The dry samples were subsequently homogenized in an agate mortar and stored in airtight glass jars. The chemicals used for analyses were reagent grade.

Sediment samples analyzed for heavy metals except Hg were digested with HNO_3 8 N for 2 hours, following the procedure reported by Carmody *et al.* (1973) and finally analyzed using a Perkin Elmer Model 5000 atomic absorption spectrophotometer in a flame mode. Instrument settings were as recommended in the instruction manual (Perkin Elmer Corp., 1979) and background correction was used in all determinations. For the determination of Hg, the sediment samples were digested in an Erlenmeyer flask for 2 h at 60°C

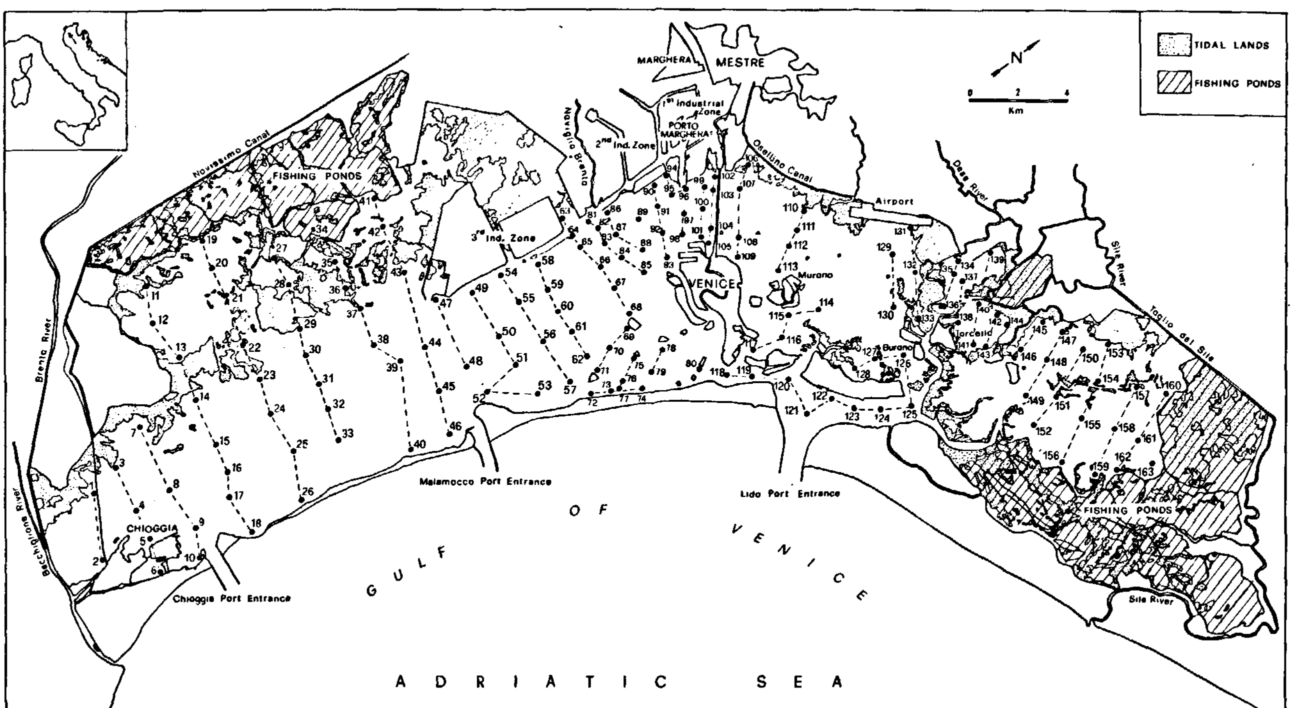


Figure 1
Venice Lagoon and location of sampling sites.

with conc. H_2SO_4, HNO_3, HCl and further addition of a 5% solution of $KMnO_4$ and $K_2S_2O_8$ as proposed by Agemian and Chau (1976), and analyzed with the same instrument in the flameless mode.

The extraction efficiencies and precision of our measurements agree with earlier published reports (Donazzolo *et al.*, 1981).

RESULTS AND DISCUSSION

The textural and mineralogical composition of the surface sediments in the entire Lagoon of Venice have been already reported (Barillari, Rosso, 1976; Barillari, 1978, 1981; Hieke Merlin *et al.*, 1979; Zanettin, 1955). These authors have shown that according to the lithological classification of Shepard (1954), sandy silts (29%) and clayey silts (26%) are more abundant than silty sands (15%), sands (11%), silty clays (10%) and silts (9%). Sands were observed only in restricted areas near the three port entrances where tidal currents up to 2.69 m/sec. (Tosi, 1970) do not permit the settling of fine particles (Fig. 2). There is a general decrease of particle size from these areas towards the inner parts of the lagoon. In the entire lagoon, the average concentration of the pelitic fraction ($\varnothing < 63$ μm) is 67%, with a variation coefficient of 0.15. Pelite is present in high percentage (> 70%) in the largest part of the area studied (Fig. 2).

Carbonates are the most abundant minerals (average 46%, variation coefficient 0.15), with dolomite prevailing over calcite. Other identified minerals include quartz, clay minerals (illite, kaolinite and chlorite) and feldspars, but the percentages are not reported.

Barillari *et al.* (1982) reported that the relationships between trace elements and sediment properties in two sample areas located in the central and in the southern parts of the lagoon were the same. On the basis of these results, it seems reasonable to conclude that from the sedimentological point of view the Lagoon of Venice is a fairly homogeneous area.

Donazzolo *et al.* (1982) measured the following heavy metal concentrations from the one metre depth in a sediment core taken in the northern part of the lagoon: Hg, 0.1 ppm; Cd, 1.2 ppm; Pb, 23 ppm; Co, 17 ppm; Ni, 20 ppm; Cu, 15 ppm; Zn, 49 ppm; Fe, 7 500 ppm; Cr, 21 ppm. They discussed the possible use of these values to distinguish polluted from non polluted lagoon sediments. While concentrations of Hg, Cd, Ni, Co, Pb and Cr are in reasonable agreement with those based on data from over 100 different harbours (Prater, Anderson, 1977), the values for Cu, Zn and Fe are somewhat lower than those reported for non polluted sediments (25 ppm, 90 ppm and 17 500 ppm, respectively; *ibid*). However, lower backgrounds values have been observed in calcareous nearshore marine sediments for Zn and Fe (15.9-24.5 ppm and 856-4 290 ppm, respectively; Dossis, Warren, 1981). Furthermore, the average content of these elements in the earth crust carbonates is Cu: 4 ppm; Zn: 20 ppm; Fe: 3 000 ppm (Turekian, Wadepohl, 1961). If one considers that the average content of carbonates in the sediments of the Venice Lagoon is 46%, it seems quite reasonable to tentatively use the background values previously suggested for this area.

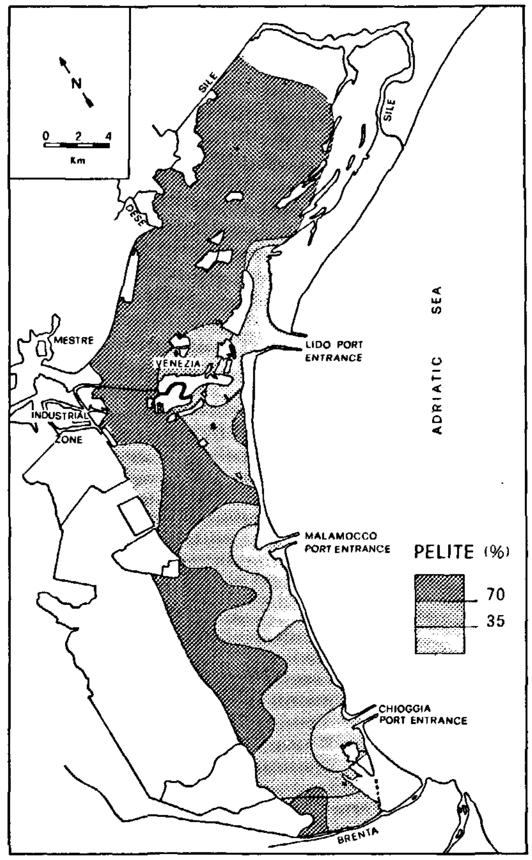


Figure 2
Areal distribution of pelitic fraction (< 63 μm). Drawn using data from Barillari, Rosso (1976), Barillari (1978; 1981).

To distinguish further between moderately and heavily polluted areas, the following indicative concentrations reported by Prater and Anderson (1977) seem to be useful: Hg, 1.0 ppm; Cd, 6.0 ppm; Pb, 60 ppm; Co, 50 ppm; Ni, 50 ppm; Cu, 50 ppm; Zn, 200 ppm; Fe, 25 000 ppm; Cr, 75 ppm.

The horizontal distribution of Hg, Cd, Pb, Ni, Cu, Fe, Zn and Cr, drawn using the above mentioned limits and the data reported in the Table, are shown in Figures 3 and 4. Very high values of Zn (up to 3 000 ppm), Pb (up to 164 ppm), Cd (up to 20.8 ppm), Hg (up to 3.46 ppm), Cu (up to 221 ppm) and Co (up to 99.8 ppm) are found in the stations nearest to the industries. For some elements, *e.g.* Cd and Cu, concentration gradients may be observed, originating from each canal connecting the industrial zone to the lagoon and extending SE towards the town of Venice. The northwestern part of the town is also surrounded by sediments heavily polluted by Hg, Pb, Cd, Cu, and Zn. This is in very good agreement with the results obtained (Alberotanza, Zandonella, 1982) by Landsat satellite observations, which show that highly turbid waters, originating in the industrial zone, surround the historical centre under different tidal conditions. The fact that the northern basin exchanges waters with the sea mainly through the Lido port entrance is certainly relevant to an understanding of this feature.

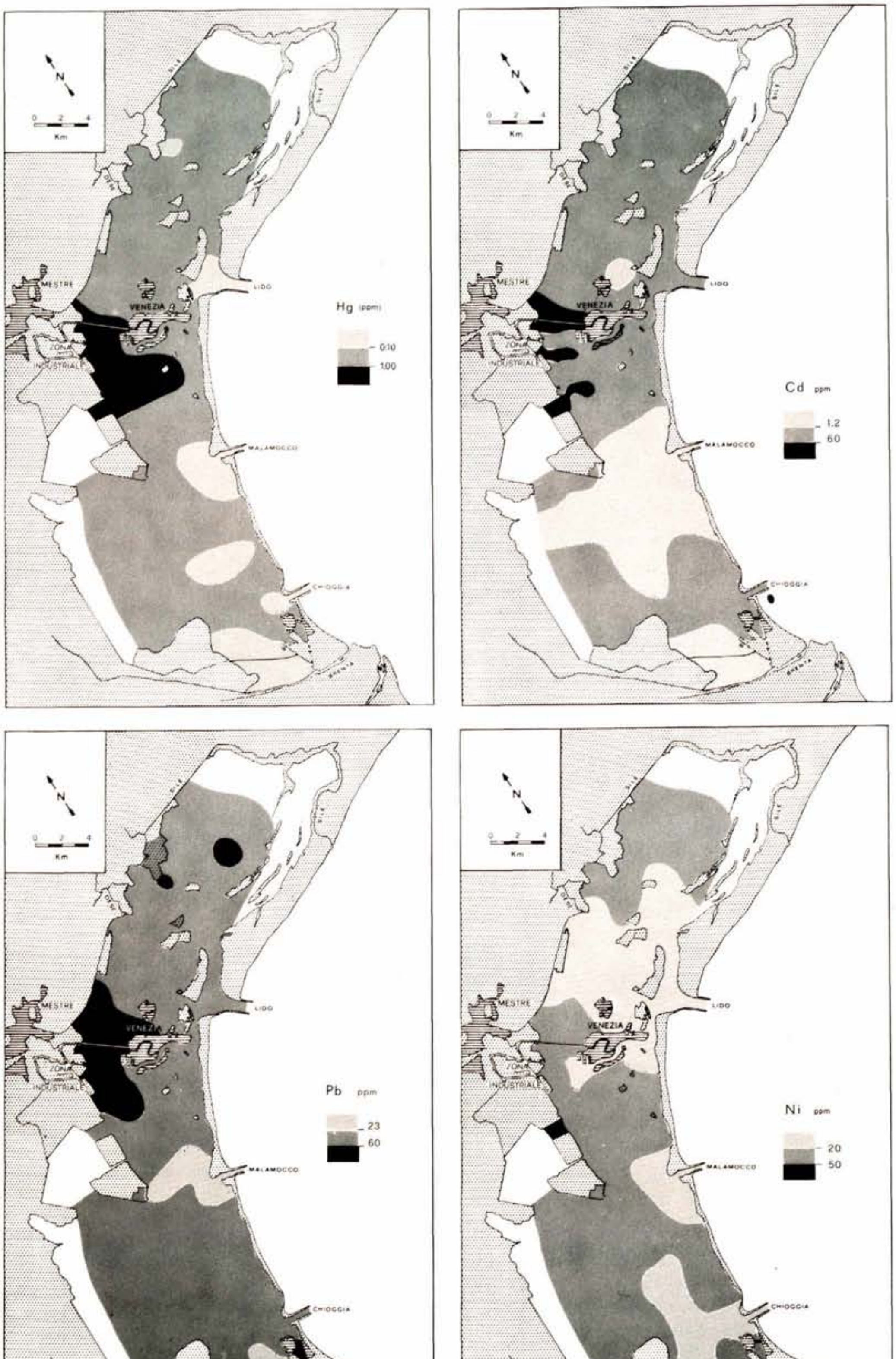
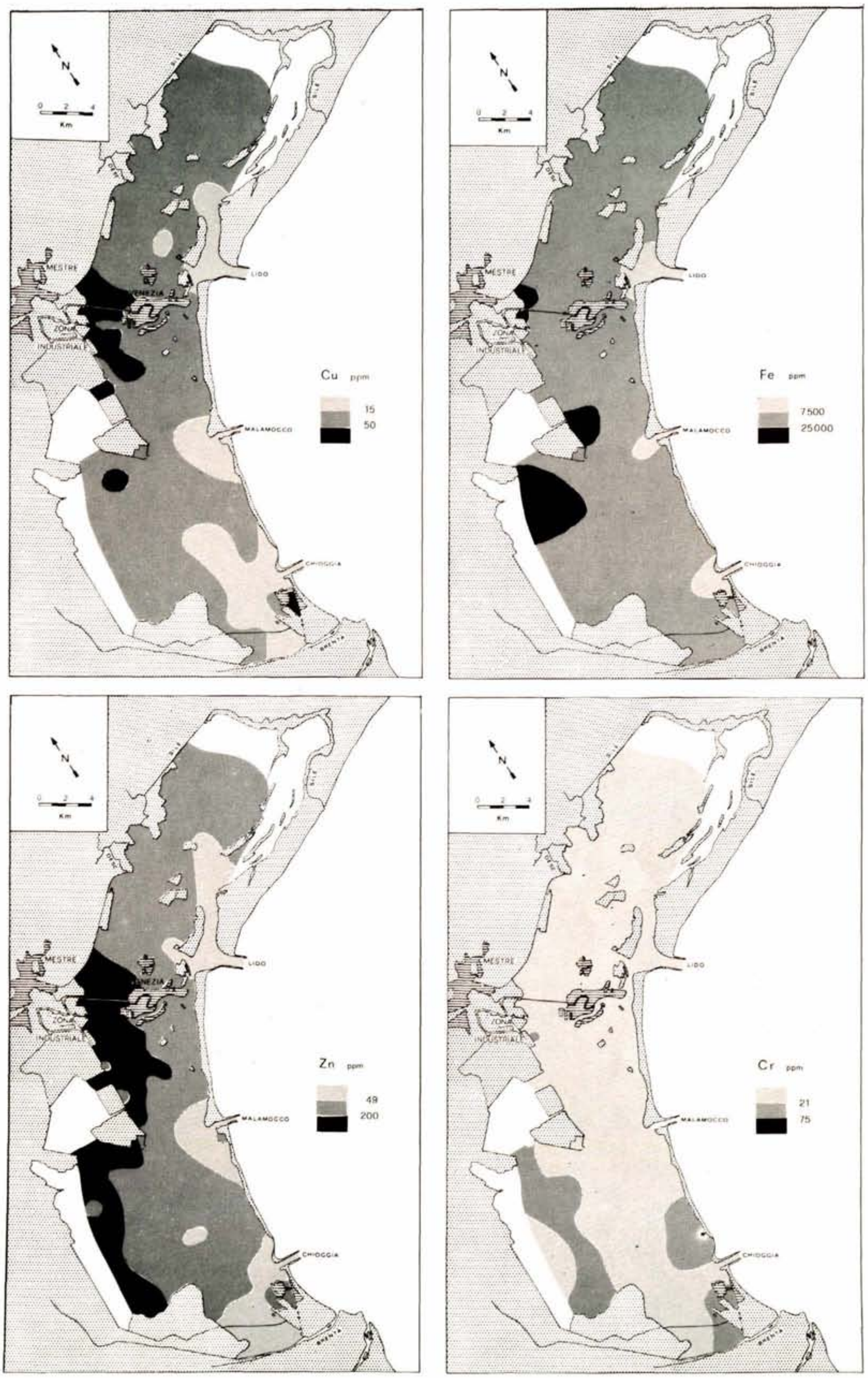


Figure 3
Distributions of Hg, Cd, Pb and Ni in the sediments

Most of the lagoon is polluted by Hg, Pb, Cd, Cu, Zn and Fe. Only in few small zones are these elements within their natural backgrounds. The area at the extreme southern part of the lagoon, SW of the town of Chioggia, is so far from industries and from the main tidal water streams that it has no yet been affected by industrial pollutants. The low concentrations of heavy metals near the three port entrances are due to the low percentage of pelitic fraction present in these sediments (Barillari, 1978; 1981; Barillari, Rosso, 1976). Here the strong water currents do not permit the settling of fine particulates and therefore of pollutants.

Biweekly field measurements were carried out by the authors over a period of one year at 9 stations inside the industrial canals and at 11 stations in the nearby lagoon, where high levels of heavy metals are present in the surface sediments. It was found that in this area, the water is characterized by relatively low redox potentials

Figure 4
Distributions of Cu, Fe, Zn, and Cr in the sediments.



(—100 to +200 mV) and a wide pH range (6.0 to 8.7). While in this condition most heavy metals exist in soluble forms, mercury, which originated from a chlor-alkali plant, can be present mainly as element or insoluble compounds such as HgS or HgO. The formation of the soluble complexes $HgCl_3^-$, $HgCl_4^{2-}$ or $HgCl_3Br^{2-}$, as observed in sea water by Dyrssen and Wedborg (1974), may be prevented by the low salinity (0.5-15 $^0/_{00}$) of the water in the industrial canals. As a consequence, this element has a low residence time in the water body and is readily scavenged by the suspended particulates and by the sediments as previously reported (Cranston, Buckley, 1972).

Other heavy metals, such as Pb, Zn, Fe and Cu, which can be present in the lagoon water as several soluble species (Kester, 1975), have higher residence times in water and can therefore be displaced by tidal currents farther from their emission point. On this basis, it can

Table
Heavy metal contents (in ppm)

Sample No.	Hg	Pb	Cd	Ni	Co	Cu	Zn	Cr	Fe
1	<0.10	29.6	1.00	20.0	12.2	17.0	46.8	10.2	17250
2	<0.10	14.6	0.60	31.0	7.4	10.0	32.0	29.6	14860
3	<0.10	25.0	1.00	16.2	11.0	12.0	44.2	10.0	13240
4	0.13	23.0	1.00	25.0	9.6	12.8	46.0	16.8	11860
5	0.31	31.8	1.40	24.0	6.8	28.0	102.0	33.8	13000
6	0.63	65.4	2.00	33.8	19.2	62.0	198.0	31.2	16000
7	0.16	30.4	1.40	21.0	9.0	19.8	98.4	16.4	17600
8	0.18	26.6	1.40	19.8	8.4	13.6	60.0	17.8	9500
9	<0.10	36.4	1.40	15.4	8.0	5.2	28.0	12.4	4940
10	0.26	27.0	1.40	17.2	7.8	11.8	48.6	15.4	7320
11	0.54	57.6	2.00	30.6	15.2	34.2	228.0	24.0	21600
12	0.57	84.8	1.80	33.8	14.4	37.2	202.5	31.0	22800
13	0.27	34.0	1.40	25.0	12.0	22.2	126.0	20.0	20000
14	0.20	33.0	1.20	27.4	13.6	25.6	76.0	17.8	22000
15	0.17	25.6	1.20	16.8	9.0	11.2	58.0	13.4	9540
16	0.29	28.4	1.20	24.0	9.0	15.6	64.9	26.2	13400
17	0.38	26.8	1.20	34.0	9.2	16.0	68.0	35.2	13400
18	0.26	24.6	1.20	24.2	8.4	7.4	44.1	21.4	7700
19	0.37	52.6	2.00	34.4	30.2	27.4	156.0	16.0	15000
20	0.21	42.4	2.00	24.0	14.8	22.8	222.0	16.8	15800
21	0.19	44.8	1.40	28.6	13.2	26.0	134.0	22.8	18000
22	0.49	50.6	1.00	30.8	11.8	28.2	88.7	24.6	22800
23	<0.10	24.6	0.60	15.4	7.0	10.0	38.0	13.6	9440
24	<0.10	28.0	1.60	14.0	11.4	8.0	54.6	9.2	5880
25	0.10	35.0	1.40	29.4	12.0	17.2	88.0	22.2	13200
26	0.12	33.8	1.20	25.2	11.8	14.6	82.0	23.8	10800
27	0.23	47.6	2.20	35.2	22.8	33.8	202.8	21.8	16800
28	0.19	26.2	1.40	25.2	11.8	15.6	152.0	3.8	10000
29	0.10	20.0	0.61	17.6	10.8	25.4	79.4	7.8	16670
30	0.74	27.3	1.02	27.1	14.8	27.3	133.5	17.9	22860
31	0.80	27.3	1.02	26.5	16.7	28.6	129.4	19.6	22860
32	0.37	25.4	0.71	21.2	14.8	17.3	66.5	14.7	14290
33	0.80	22.4	0.91	27.6	17.7	21.4	95.9	18.9	22380
34	0.46	41.8	1.02	32.3	21.7	41.4	121.8	24.2	29520
35	0.55	32.7	0.91	32.3	18.7	36.4	203.5	26.0	30950
36	0.31	27.3	0.51	36.5	17.7	31.4	94.7	22.5	30480
37	0.35	20.0	0.61	21.8	14.8	22.7	83.5	8.4	19050
38	0.82	27.3	0.71	29.4	16.7	27.7	69.4	22.5	25240
39	0.53	27.3	0.71	27.6	15.8	20.4	57.1	22.5	21900
40	<0.10	29.1	0.81	16.5	17.7	10.4	47.6	12.3	10140
41	0.44	32.7	1.52	30.6	24.6	47.7	364.7	22.5	27140
42	0.31	29.1	1.02	28.8	18.7	76.4	184.7	19.6	25710
43	0.64	34.5	1.93	26.5	16.7	40.0	264.7	20.0	22380
44	0.32	27.3	0.71	30.0	18.7	27.7	58.8	19.3	22860
45	<0.10	21.8	0.91	12.3	14.8	7.7	34.7	9.1	6720
46	<0.10	21.8	0.91	16.5	15.8	11.4	50.6	12.6	10190
47	0.12	21.8	0.71	23.5	13.8	23.2	94.1	14.7	20950
48	<0.10	23.6	1.02	15.9	17.7	10.9	39.4	10.5	9310
49	0.25	27.3	1.02	30.6	19.7	36.4	164.1	18.9	28090
50	0.12	23.6	0.81	22.3	15.8	20.0	76.5	15.4	19520
51	0.34	21.8	0.91	25.3	14.8	24.1	108.2	20.7	22380
52	0.14	20.0	1.02	14.7	16.7	10.9	46.5	10.5	9420
53	0.33	29.1	1.02	22.9	18.7	18.7	87.1	14.4	16660
54	0.72	36.4	2.13	29.4	23.6	46.8	282.3	21.0	26190
55	0.31	25.4	1.32	30.0	16.7	29.5	110.6	20.0	27140
56	0.20	40.6	1.60	24.0	17.6	19.6	58.0	12.4	15880
57	0.50	50.6	2.40	26.0	21.0	26.2	130.8	14.4	15800
58	0.30	43.6	1.60	24.0	19.6	23.4	108.0	13.4	19560
59	0.33	51.8	2.80	27.2	27.0	32.0	240.0	14.6	19440
60	0.51	45.2	1.60	27.6	18.6	23.0	64.7	15.4	18560
61	0.91	51.0	3.40	23.0	22.0	29.0	220.0	13.6	14360
62	0.40	48.4	3.00	23.4	23.4	26.0	146.0	12.4	13840
63	1.92	58.4	9.40	92.8	181.0	71.8	680.0	12.4	15200
64	1.72	40.2	1.00	18.4	17.8	22.4	112.4	12.4	16400
65	1.56	98.4	5.80	21.4	41.2	87.0	900.2	15.6	18400
66	2.20	102.2	12.60	25.2	55.6	97.2	960.0	17.8	17400
67	1.28	52.8	1.80	26.8	19.2	31.2	202.0	15.0	17600
68	1.06	50.6	1.80	22.0	17.8	26.2	158.6	13.2	14000
69	1.00	46.2	2.00	24.0	20.0	25.0	88.0	12.8	15440
70	1.08	47.6	1.80	26.8	19.8	27.8	74.5	13.8	16320
71	0.54	41.6	1.80	28.0	28.0	21.4	48.0	9.8	12520
72	0.66	52.6	2.40	19.0	19.8	21.4	100.0	10.0	11680
73	0.66	48.2	2.20	23.2	19.6	23.6	108.0	12.0	14520
74	0.78	47.0	2.00	21.6	19.2	22.0	78.9	11.4	12840
75	1.09	50.6	1.60	22.6	18.2	24.0	86.0	12.6	15400
76	0.98	51.2	3.00	21.8	21.2	30.2	260.8	14.0	14480
77	0.91	48.2	2.40	19.2	21.0	20.8	134.8	10.2	10920
78	0.85	49.8	2.80	21.4	20.0	25.8	140.4	11.6	12720
79	0.98	48.0	1.80	29.4	27.2	25.0	68.2	12.4	15000
80	0.30	44.0	2.40	17.2	18.8	15.0	70.0	7.8	8800
81	1.50	48.6	1.20	21.2	17.2	33.8	120.0	13.2	16600
82	2.23	82.8	7.20	23.8	30.8	72.4	540.0	16.6	18800
83	3.42	90.6	5.80	25.2	36.2	65.2	600.2	16.2	16600
84	1.56	66.4	4.00	23.2	25.0	46.6	380.0	14.2	16000
85	1.80	68.0	4.80	23.0	22.2	50.8	400.0	13.8	15600
86	1.28	60.7	2.40	22.8	21.2	43.4	260.4	15.4	20600
87	1.57	74.4	3.00	25.8	29.4	52.6	380.0	16.8	19200
88	1.57	69.8	4.60	18.8	22.6	45.2	360.0	13.2	13200
89	1.57	73.8	3.40	24.0	27.0	52.6	400.0	16.2	18400
90	1.73	164.0	5.80	26.0	25.8	149.0	660.6	22.4	24000
91	3.02	106.4	8.60	47.2	88.2	103.6	960.0	17.0	18800
92	1.44	93.2	6.20	25.4	38.8	72.6	680.7	17.4	19000
93	0.69	49.0	2.60	15.0	19.2	20.4	220.0	9.0	10000
94	3.37	107.2	8.40	28.6	33.2	117.8	820.0	19.6	23600
95	2.00	76.8	5.80	20.2	26.8	59.8	580.5	14.2	16400
96	0.86	56.2	4.80	16.0	30.8	32.4	600.0	9.4	12400
97	1.25	65.0	2.40	23.8	19.8	39.4	220.2	13.2	17200
98	3.46	63.6	4.40	19.8	24.8	43.4	360.8	12.4	13000
99	2.19	110.4	13.80	26.8	91.0	171.0	2200.3	17.8	23400
100	1.83	85.4	7.60	24.0	51.2	79.0	900.0	15.2	16600
101	1.93	79.6	4.80	23.4	24.0	61.2	420.0	13.8	16400
102	2.10	123.0	20.80	27.6	99.8	221.0	3000.1	18.2	25600
103	1.72	97.8	10.40	25.6	48.0	96.8	960.0	15.6	19000
104	1.70	83.6	6.80	25.2	33.2	69.4	560.3	15.8	18200
105	2.50	86.6	7.20	25.2	28.4	71.8	540.0	15.4	17800
106	1.53	142.0	12.60	29.8	41.2	180.0	1760.0	21.0	24800
107	0.50	89.6	3.40	27.4	37.0	61.8	600.4	18.4	21000
108	0.68	64.4	2.20	23.0	20.4	40.0	260.0	14.0	15600
109	1.20	65.8	2.60	22.4	15.0	39.4	220.2	14.4	16800
110	0.24	876.0	1.60	10.6	22.2	14.0	158.4	6.0	9120
111	0.52	46.6	2.60	18.8	22.4	23.4	172.8	10.0	12320
112	0.78	55.4	2.20	23.8	21.4	30.0	164.0	13.2	16520
113	0.78	56.4	1.40	17.8	13.6	23.8	108.6	10.6	10600
114	1.01	37.6	1.00	17.2	15.0	15.8	38.2	9.6	10800
115	0.72	43.0	1.20	16.0	14.0	14.8	68.3	8.4	9920
116	0.50	44.4	2.20	16.8	15.8	20.6	170.0	8.6	9160
117	0.90	47.8	2.00	55.4	65.4	25.2	74.0	10.4	10640
118	0.47	45.8	2.00	16.4	19.0	17.2	52.0	8.0	8320
119	0.10	41.6	2.20	15.4	8.8	8.2	28.9	6.4	6200
120	0.10	40.0	2.00	13.8	20.2	6.2	18.0	6.0	5600
121	0.10	39.2	1.80	14.4	19.8	6.6	22.7	6.6	6440
122	0.73	41.0	1.80	16.6	19.0	12.2	36.0	8.4	8720
123	0.48	40.6	1.80	15.4	17.8	12.6	36.0	7.8	7960
124	0.31	40.2	2.00	15.6	18.8	10.2	28.5	7.4	7840
125	0.91	44.2	1.80	20.2	18.2	20.6	62.0	10.2	11400
126		43.0	1.80	19.6	17.0	18.8	58.0	10.4	11640
127		42.0	1.80	18.0	18.2	20.2	54.0	10.8	11640
128		47.6	2.20	17.2	18.2	19.6	72.6	9.6	10320
129	0.44	41.4	1.60	19.4	13.8	19.0	52.0	12.0	16940
130	0.70	45.8	1.80	18.4	14.4	24.4	92.9	12.6	16250
131	0.79	56.0	2.00	20.0	16.4	30.0	160.0	12.6	17250
132	0.33	41.0	1.80	18.0	14.2	21.8	64.0	10.8	15340
133	1.10	41.8	1.60	18.6	14.0	21.2	60.2	11.4	14780
134	0.62	38.6	1.40	17.2	11.2	33.8	86.4	10.8	15000
135	1.03	43.8	1.80	20.0	14.2	23.8	74.0	12.0	15020
136	0.84	45.8	1.80	21.8	13.6	24.4	74.5	14.2	15850
137	0.68	41.8	1.80	18.8	13.0	22.4	68.6	11.2	14330
138	0.91	45.4	1.80	50.2	67.0	27.0	64.0	13.0	15270
139	0.84	57.2	1.80	24.6	15.4	40.6	132.9	16.2	22340
140	0.42	50.2	1.80	23.2	14.4	32.0	86.7	15.4	17180
141	0.93	45.0	1.60	21.0	14.4	24.8	70.6	12.6	17230
142	0.34	58.8	1.60	25.4	13.6	34.2	106.0	18.0	19680
143	0.52	52.0	1.60	22.6	14.0	30.4	90.0	13.8	17560
144	0.52	70.2	1.60	24.4	14.8	33.4	100.2	17.4	21340
145	<0.10	50.6	1.40	24.0	10.8	31.2	90.0	14.6	19560
146	0.14	43.0	1.20	24.2	12.6	34.0	68.0	15.8	23630
147	0.40	44.8	1.20	17.4	11.0	21.0	60.0	8.2	14980
148	0.62	44.4	1.40	22.2	12.2	23.2	72.5	12.4	17820
149	0.50	31.2	1.40	13.6	11.2	11.6	34.0	7.6	9030
150	0.44	57.4	1.40	26.2	12.2	32.8	86.0	14.0	23450
151	0.49	43.8	1.40	22.4	13.8	23.6	74.3	12.6	16250
152	0.51	42.8	1.60	21.6	12.6	19.0	56.0	11.8	14780
153	0.35	40.0	1.00	27.2	11.8	24.4	76.4	14.8	25140
154	0.98	42.8	1.60	21.4	13.0	20.4	66.0	12.2	14980
155	0.44	118.2	1.60	21.2	12.8	23.4	70.0	11.8	15120
156	0.46	40.8	1.40	20.0	13.0	18.2	56.0	11.6	12750
157	0.79	42.6	1.60	20.0	13.0	20.2	74.2	10.8	12630
158	0.41	47.0	1.60	22.8	14.4	24.4	76.6	11.8	16730
159	0.22	41.8	1.40	24.6	14.4	19.6	50.0	12.8	17180
160	0.97	47.8	1.40	23.0	14.0	26.6	78.8	12.0	18150
161	0.12	37.8	1.60	24.6	21.6	15.0	40.1	10.4	12750
162	0.54	42.4	1.60	20.6	13.0	18.8	52.4	11.0	14660
163	0.26	45.6	1.60	21.4	14.8	17.8	46.0	10.4	14980

be understood that the high concentration area of Pb in the sediments extends to the central part of the lagoon (Fig. 3) crossing the watershed between the northern and central basins where water currents approach zero. Sediments with high levels of Zn, Fe and to a lesser degree Cu, are present along the southwestern border of the lagoon, where fish ponds have been exploited for centuries (Fig. 4). Since these elements were discharged into the lagoon from the early 1920s until a few years ago, it is not possible to assess the influence of the recently dredged Malamocco-Porto Marghera canal on their southward transport. The high content of organic carbon and therefore of humic substances observed in the sediments of this area (Favero *et al.,* 1980) may play a role in producing insoluble compounds with the heavy metals transported here from the industrial zone by tidal currents. However, Zn can also originate from carbamate insecticides, widely used in the adjoining land and reaching this area of the lagoon with the water runoff. This possibility is supported by the high concentration of total phosphorus of agricultural origin (>650 μgAt/g) observed in these sediments.

The amount of antropogenic heavy metals now present in the upper 10 cm of the lagoon sediments may be calculated from their areal distributions, assuming an average of 1.2 g of dry material for each cubic centimetre of natural sediment. The following values are thus obtained: Hg, 35 t; Cd, 200 t; Pb, 1 300 t; Cu, 1 600 t; Zn, 16 500 t; Fe, 600 000 t; Ni, 240 t; Co, 550 t; Cr, 480 t. The high burdens of Fe and Zn probably result from a zinc plant and iron works which have been operating for about 50 years in the first industrial zone. To the sphalerite used as raw material to produce elemental zinc, are mainly associated Cd, Pb, Cu and, to a lesser degree, Ni and Co. Relatively smaller lagoon areas are polluted by the last two elements. It should be pointed out that the above reported figures are undoubtedly lower than the total amounts of heavy metals discharged into the lagoon, since their concentrations in the canal sediments inside the industrial area have not been considered. Furthermore, the levels of these elements in the sediment layers below 10 cm and the amounts mobilized by wave action and transported as sediment suspension to the sea by tidal currents or removed with dredged materials, are not known.

A special case is that of Cr, which is found in moderate concentrations only in the sediments of the southern basin (Fig. 4). Its areal distribution does not suggest the Marghera industries as possible sources. It has been observed (Donazzolo *et al.,* 1981) that high levels of this element are present in the sea surface sediments in front of the Brenta river estuary, which flows into the Adriatic Sea some 5 km south of the Chioggia port entrance. Therefore, the possibility of Cr transport from the sea to the lagoon sediments by tidal currents cannot be excluded. As previously suggested for Zn, Fe and Cu, the moderate concentrations of Cr observed in the area near the fish ponds may perhaps be explained in terms of insoluble Cr complexes, which are formed in areas where the organic carbon content in the sediments is high and the water currents are low.

CONCLUSIONS

The horizontal distributions of the studied heavy metals, with the exception of chromium, indicate their common source in the area of Marghera, where industrial wastes have been directly discharged into the lagoon for several decades. Biological activity and physical processes such as tidal currents, wind waves and dredging of canals are responsible for their mobilization to larger lagoon areas, with the result that at present all three basins are to some extent contaminated. These pollutants, adsorbed to suspended particles in the water, have reached also the sea by way of the Lido and Malamocco entrances, where concentration gradients are clearly evident in the sediments (Donazzolo *et al.,* 1981).

Chromium does not originate in the industrial area. Its concentrations which are higher in the sea than in the lagoon sediments, indicate that it follows an opposite diffusion pathway, entering the lagoon southern basin through the Chioggia port entrance.

Acknowledgements

The authors are grateful to Capt. G. Piovan and to the crew of the R/V Umberto d'Ancona of the CNR for their valuable assistance in collecting the sediment samples. Thanks are also due to Mr. M. Pistolato for drawing the figures of this paper. Financial support from CNR (grants n. 80.1758.90 and 81.01248.90) is gratefully acknowledged.

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