

Geochemistry of recent sediments in the Lagoon of Venice

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ABSTRACT. — Geochemical researches have been carried out on bottom sediments subdivided in two levels (0-2 cm; 3-10 cm) from an area of the Lagoon of Venice.

The samples have been analysed for the following major, minor and trace elements Al, Fe, Ca, Mg, Na, K, Mn, P, Cr, Cu, Zn, Pb, Cd in order to define their concentration and their pathways in the two layers.

The top sediments differ from deeper ones for some significant elements such as Al, K, Fe, Mg and P, Zn, Pb, Cd.

To evaluate the anthropogenic contribution, the heavy metals contents detected in two levels were discussed and compared with similar data reported in literature, following various criteria employed for this purpose. So a relevant man's influence has been determined for Pb, Cu, Cd and P, produced in particular in recent years up to 1970. Exceptionally high pollution also affecting top sediments was recorded for Zn.

Correlation between minor and trace elements were of particular interest.

Cluster analysis of all the variables produced three geochemical associations: silicate, carbonate, chalcophile metals.

Rearrangement of samples in function of geochemical composition has identified three groups of sediments in both levels. Each group has a peculiar geochemical composition and is located in a specific environment.

Key words: geochemistry, trace elements, bottom sediments, pollution, Lagoon of Venice.

RIASSUNTO. — Sono state condotte ricerche sulla composizione geochimica di sedimenti di fondo in un'area della Laguna Veneta, distinti in due livelli (0-2 cm e 3-10 cm).

Sono stati esaminati i seguenti elementi maggiori Al, Fe, Ca, Mg, Na, K, minori e in tracce Mn, P, Cr, Cu, Zn, Pb e Cd allo scopo di definire la loro concentrazione e il loro comportamento geochimico nei due livelli.

Il velo superficiale differisce dal sedimento sottostante per contenuto di elementi maggiori e minori. Le differenze più significative sono riferibili a Al, K, Fe, Mg e P, Zn, Pb, Cd.

I valori di metalli pesanti osservati nei due livelli vengono discussi e confrontati con analoghi dati riportati in letteratura, per identificare, secondo diversi criteri comunemente usati a questo scopo, un eventuale arricchimento legato ad attività umane. Si è così rilevata una chiara influenza antropica, verificatasi soprattutto negli anni passati, per quanto riguarda Pb, Cu, Cd e P. Inquinamento eccezionalmente elevato è stato registrato per lo Zn, che interessa anche il velo superficiale.

Lo studio delle correlazioni tra elementi è risultato particolarmente interessante per quanto riguarda gli elementi minori e in tracce.

L'analisi cluster delle variabili ha identificato tre associazioni geochimiche dei silicati, carbonati e metalli calcofili.

La classificazione dei campioni in funzione della composizione geochimica complessiva ha messo in evidenza tre gruppi di sedimenti in entrambi i livelli, con caratteristiche geochimiche proprie e localizzati in aree specifiche.

Parole chiave: geochimica, elementi in traccia, sedimenti superficiali, inquinamento, Laguna di Venezia.

Introduction

It is an interesting problem to investigate the geochemistry of bottom sediments. In such sedimentary environment geochemical differentiation may occur due to several physico-chemical processes affecting the surface materials. The first centimetres of sediments can be submitted, with respect to

sediments below, to different potential-redox conditions and can interact with dissolved elements in the overlying water rather than with pore water, supported by resuspension of particles with consequent phenomena of release and adsorption.

The top and deeper sediments may also naturally differ from textural and mineralogical composition, in the case of deposition by gravitational settling. Therefore the surface materials are finer and enriched in clay minerals with respect to deeper ones. These properties, which play an important role in the surface interactions, may influence the geochemical differentiation. Consequently in this study we decided to consider two levels in the bottom sediments separately.

An area in the sedimentation basin of the Lagoon of Venice between Porto Marghera industrial zone and the city was selected as a case study. The textural characters of the bottom sediments in this area have been already determined (BARILLARI and ROSSO, 1975; BARILLARI, 1978; BARILLARI et al., 1981; MENEGAZZO VITTURI and MOLINAROLI, 1984). Clay silts and silty clays are the most common sediments, particularly enriched in clay fraction along the translagoon bridge. Coarser materials silty sands, sandy silts, loam occur only in restricted zones where channels enter the lagoon.

This environment has very peculiar characteristics. In fact in this century changes in input of minor and trace elements occurred with an anthropogenic contribution to natural level, due to wastes from the Porto Marghera industrial zone directly discharged into the Lagoon for several decades up to 1970.

These input changes may have been recorded by the bottom sediments and may have influenced the geochemical difference between top and deeper materials. Furthermore the Lagoon of Venice is a shallow basin with an average depth of 0.6 m and therefore the surface layer may have been frequently subject to resuspension processes, due to tidal currents, wind storms and boat transit (ALBEROTANZA and ZANDONELLA, 1982). The resuspension tends to increase the mobility of some elements, producing differences in

concentration and behaviour in the two layers. As a result of all these above mentioned considerations it is thought particularly significant to investigate the lagoonal sediments by geochemical approach.

Experimental

Sampling and Preservation

Sediments were sampled in the Lagoon of Venice at stations shown in Fig. 1. The stations are located in an area constantly submerged; only few stations at S W along the translagoon bridge can emerge during exceptionally ebb-tide. Twenty five bottom sediments were collected with a corer in summer 1977. Almost undisturbed cores 8 cm diameter, 10 cm depth can be obtained with this sampler. The top sediments (0-2 cm, A layer) was removed from the bottom (3-10 cm, B layer) with a spatula.

The samples were air-dried at room temperature. The dry samples were homogenized in an agate mortar and stored in plastic bags.

Geochemical analyses

The sediments were sieved by 0.5 mm A.S.T.M. sieve in order to eliminate shell debris, and washed by distilled water.

Representative sub-samples obtained by a mechanical sample divider for each core (A and B layer) were powdered. To estimate the total amounts of elements in sediments the samples were dissolved, using the digestion procedure of SHAPIRO and BRANNOCK (1962) slightly modified, consisting in an acid mixture of 450 ml conc. HF, 175 ml of conc. H₂SO₄ and 40 ml of conc. HNO₃.

Aluminium, Ca, Mg, Fe, Mn, Cr, and Zn contents were determined by absorption, and Na and K by emission in flame on a Perkin Elmer 4000 atomic spectrometer.

Copper, Pb and Cd were analysed on a Perkin Elmer 603 spectrometer coupled with a graphite furnace HGA 500. Phosphorus was determined photometrically using a Pye Unicam SP 6 spectrophotometer.

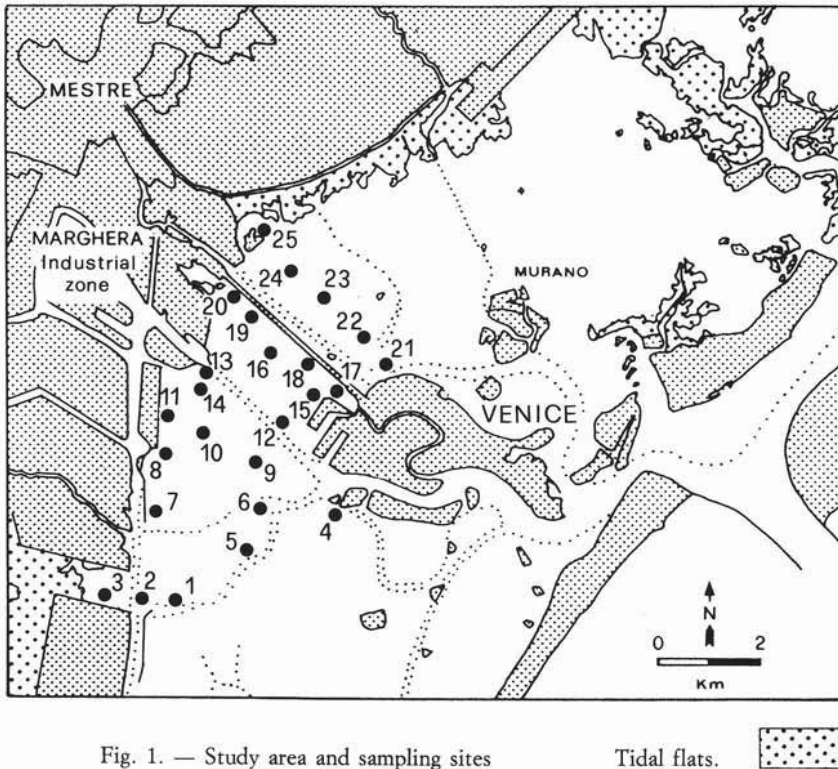


Fig. 1. — Study area and sampling sites

Tidal flats.



Standard reference materials

All analytical methods were checked for accuracy by analysis of the following international standard samples Marine sediment BCSS-1 (NRC, Canada); Estuarine sediment 1646 (NBS, Washington); Soil sample 5 (IAEA, Wien).

Organic matter content

The total organic matter was determined gravimetrically by weighing the samples before and after treatment with 20 vol. H_2O_2 and heating at 450 °C for 2 hours. The weight loss was assumed to represent the approximate content of organic matter; these estimations are as more approximate as higher the contents in clay minerals, colloids and hydroxides are.

Statistics

All the chemical data (14 variables on 25

samples of both A and B layers) were evaluated statistically. Correlation coefficients were calculated between all element pairs separately for A and B sediments, and the matrix of these correlation coefficients was then used in hierarchical cluster analysis programs.

Results and discussion

Elemental abundances and areal and vertical distribution

Results obtained for all A and B samples are given for selected major, minor and trace elements in Table 1, whereas the concentration ranges are illustrated in the relative frequency histograms of Fig. 2.

We can observe that among major elements Ca is the most abundant except for one sample. Its values generally increase from the inner border of the Lagoon toward the middle

TABLE 1

Elemental concentrations, mean values (\bar{x}), standard deviations (σ) and relative coefficients of variation (c) in sediments (A and B layer)

Sample	Al	Fe	Ca	Mg	Na	K	Mn	P	Cr	Cu	Zn	Pb	Cd	Org. ^(*) matt. %
	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%
1 A	4.41	1.85	14.74	4.05	1.22	1.62	379	491	67	53	687	39	1.11	8.14
1 B	6.22	2.43	14.15	4.48	1.09	3.08	398	1311	48	94	1384	77	1.70	4.05
2 A	4.79	1.73	12.67	2.90	0.84	1.26	379	285	42	13	150	19	0.68	1.47
2 B	6.42	2.31	14.42	4.60	0.99	3.16	445	1003	54	30	185	33	0.70	5.52
3 A	4.65	1.50	12.11	3.02	1.12	1.38	357	351	17	13	302	22	0.42	1.59
3 B	6.10	1.91	11.92	4.09	1.28	3.15	377	1020	43	34	481	49	1.20	3.38
4 A	4.35	1.83	14.83	3.86	1.02	1.12	335	359	76	48	506	52	0.94	7.73
4 B	5.41	2.17	17.18	5.24	1.08	2.58	347	1077	60	64	690	74	1.80	2.06
5 A	4.22	1.73	16.38	3.45	0.96	1.13	332	366	42	53	475	35	0.81	5.93
5 B	5.61	2.16	17.50	5.01	0.89	2.55	363	1148	54	62	764	86	1.80	5.29
6 A	4.27	1.69	16.39	3.73	0.86	1.09	349	352	50	48	487	38	0.99	4.78
6 B	5.57	2.17	17.56	4.74	0.86	2.46	413	958	60	37	235	33	1.10	2.46
7 A	4.87	2.03	13.02	2.96	1.23	1.50	430	520	34	38	369	46	0.44	6.75
7 B	7.24	2.67	14.07	3.84	1.20	3.78	465	1199	60	32	161	33	0.80	9.13
8 A	4.84	2.11	11.25	3.23	1.26	1.56	367	388	42	80	866	47	1.56	4.16
8 B	9.60	3.94	5.59	3.12	1.98	5.75	400	1284	94	47	400	71	1.10	6.68
9 A	4.38	1.93	16.09	2.64	0.93	0.92	426	580	42	48	659	43	0.81	3.24
9 B	6.56	2.54	16.97	4.44	1.21	3.05	402	1344	60	62	700	66	1.50	5.66
10 A	4.70	2.13	13.02	3.10	1.18	1.37	382	594	59	92	8710	62	1.78	8.24
10 B	5.52	2.29	15.54	4.96	1.15	2.81	376	1165	65	130	2170	149	3.20	5.82
11 A	5.50	2.65	15.61	2.72	0.94	1.69	373	638	80	77	487	57	0.50	6.66
11 B	6.62	2.78	12.89	3.81	0.99	3.33	472	1682	71	116	884	70	1.50	2.20
12 A	4.45	1.49	16.13	3.23	0.96	1.04	313	351	59	38	347	25	0.76	6.97
12 B	4.90	1.80	19.08	4.80	1.01	2.34	353	1022	54	54	674	116	1.80	3.21
13 A	4.47	1.53	12.50	2.98	0.93	1.26	379	440	34	23	337	30	0.32	3.11
13 B	5.80	1.76	13.30	4.08	1.08	2.96	329	778	60	43	339	33	0.80	1.56
14 A	4.56	1.73	12.47	3.04	1.18	1.54	455	425	25	38	560	34	0.99	4.94
14 B	6.07	2.07	16.56	4.17	1.17	3.24	346	890	48	48	630	33	1.50	4.17
15 A	3.91	1.43	17.38	3.77	0.83	0.92	310	315	50	40	370	30	0.84	3.64
15 B	6.16	2.38	17.68	4.60	0.86	2.88	408	1003	60	37	222	62	1.10	6.51
16 A	4.75	2.08	15.13	3.54	1.00	1.30	423	396	59	48	305	33	1.31	4.06
16 B	5.85	2.30	16.85	4.43	1.04	2.79	412	907	54	43	606	41	1.30	5.20
17 A	4.47	1.90	15.38	3.72	1.21	1.25	367	388	67	43	458	37	0.50	9.09
17 B	5.97	2.33	16.83	5.03	1.02	2.81	382	1091	60	62	756	94	1.30	7.73
18 A	4.58	2.01	14.18	3.50	0.97	1.22	364	432	46	62	866	48	0.90	6.12
18 B	6.23	2.39	16.44	5.03	1.20	2.89	372	1257	65	86	1280	78	2.10	2.46
19 A	4.82	2.35	13.35	3.23	1.16	1.45	411	506	59	87	1580	48	1.43	7.14
19 B	6.50	2.69	15.14	4.50	1.12	3.19	425	1020	65	64	1308	78	1.50	7.23
20 A	5.19	3.15	12.70	3.23	1.24	1.62	417	513	76	241	10137	77	2.92	9.96
20 B	6.69	3.02	14.96	4.66	1.16	3.43	508	1019	65	88	1960	86	2.00	3.27
21 A	4.41	1.86	15.35	3.83	0.98	1.21	395	403	67	28	252	27	0.59	9.93
21 B	5.65	2.17	17.25	5.23	1.23	2.56	406	1371	54	43	274	66	2.60	3.59
22 A	4.16	1.70	16.60	3.80	0.93	1.07	342	381	67	28	250	30	0.55	5.98
22 B	5.22	2.06	18.61	4.94	1.07	2.39	333	1123	60	43	300	70	1.20	7.28
23 A	4.90	2.29	13.96	3.60	1.29	1.49	442	577	55	43	546	45	0.6	4.31
23 B	5.88	2.28	18.51	4.82	1.24	2.82	389	1379	54	59	764	49	1.90	3.90
24 A	4.62	2.18	14.12	3.37	1.66	1.35	382	432	76	57	1223	44	1.78	5.12
24 B	6.01	2.35	16.26	4.78	1.25	2.91	389	1043	60	73	1268	62	2.30	7.59
25 A	4.87	2.02	18.46	3.01	0.80	1.42	442	476	55	62	560	46	1.65	2.38
25 B	5.99	2.31	17.95	4.06	1.04	3.07	435	1189	43	45	382	45	1.30	4.53
\bar{x} A	4.62	1.96	14.55	3.34	1.07	1.31	382	438	54	56	1260	41	1.01	5.66
\bar{x} B	6.15	2.37	15.73	4.54	1.12	3.04	398	1131	59	60	753	66	1.56	4.82
σ A	0.34	0.38	1.83	0.39	0.19	0.22	41	93	17	44	2486	13	0.59	2.43
σ B	0.88	0.44	2.82	0.50	0.21	0.66	44	194	10	26	538	28	0.58	2.06
c A	7.3	19.6	12.6	11.6	18.3	16.6	11	21	31	78	197	32	58.6	42.9
c B	14.3	18.4	18.0	11.1	18.9	21.7	11	17	17	43	71	42	37.2	42.8

(*) Approximate values due to the presence of clay minerals, colloids and hydroxides.

of the basin. The Mg contents show a similar behaviour, whereas Al and K present an opposite distribution, reaching their maxima in proximity of the land. Also the Fe and Mn higher concentrations were determined in the inner stations but this was observed only for B samples. In fact the top sediments (A layer) present a different areal distribution with a iron rich zone along the translagoon bridge. As regards Na the values are quite uniform.

Average concentration of selected minor and trace elements in relative order of abundance is for surface sediments $Zn > P > Cu > Cr > Pb > Cd$ and for deeper ones $P > Zn > Pb > Cu > Cr > Cd$.

Phosphorus shows very wide range and reaches exceptionally high contents (> 1300 ppm) in B layer (samples 1,9,11,21,23). Zinc concentrations are extremely variable from 150 to 10137 ppm. The maxima were measured in A layer (samples 20 and 10). The maximum of Cu was also detected at station 20 (A layer), relatively high levels were found along the bridge too. On the contrary the maximum of Pb (> 100 ppm) was determined in deeper sediments (10 and 12 samples). Cadmium values over 2 ppm were observed both in A and B layer. Chromium contents have little variation.

All sediments are rich in organic matter (1.47-9.96%), but its distribution is uneven.

Figure 3 illustrates the difference between the average geochemical composition of A and B layer. Furthermore the results presented in Tab. 1 and in Fig. 2 give some useful information on the behaviour of the elements as a function of depth.

In particular major elements such as Al, Fe, Mg and K have a distinct increase in deeper sediments. Surface materials (A samples) are generally characterized by lower concentrations of Ca in comparison with B samples. Only Na presents similar values on both levels.

As regards minor and trace elements different behaviour may occur. For example Cr and Mn present average concentration and similar range in both layers. Lead and Cd generally show lower values in surface materials even if locally very high contents may be measured in top sediments. A general increase upwards was observed for Zn. An op-

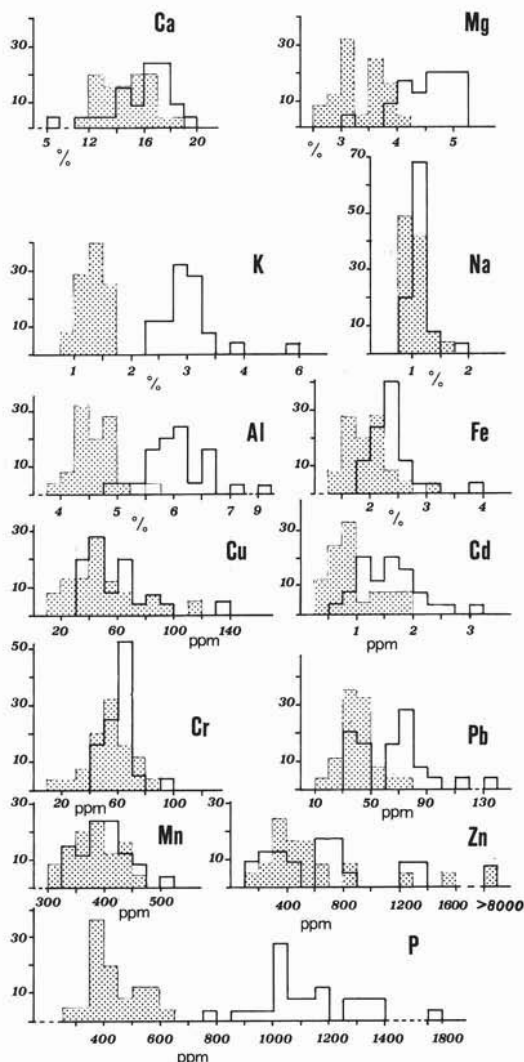


Fig. 2. — Frequency histograms of elements in A layer (dotted histogram) and in B layer (blank histogram).

posite trend was remarked for P, which is always enriched downward.

Anthropogenic contribution to the heavy metals contents of sediments

It is difficult to give a quantitative estimate of anthropogenic enrichment with heavy metals in sediments. In fact it is necessary to subtract the natural levels defined for each element from the measured concentrations and the difference may represent the contribution of human activities.

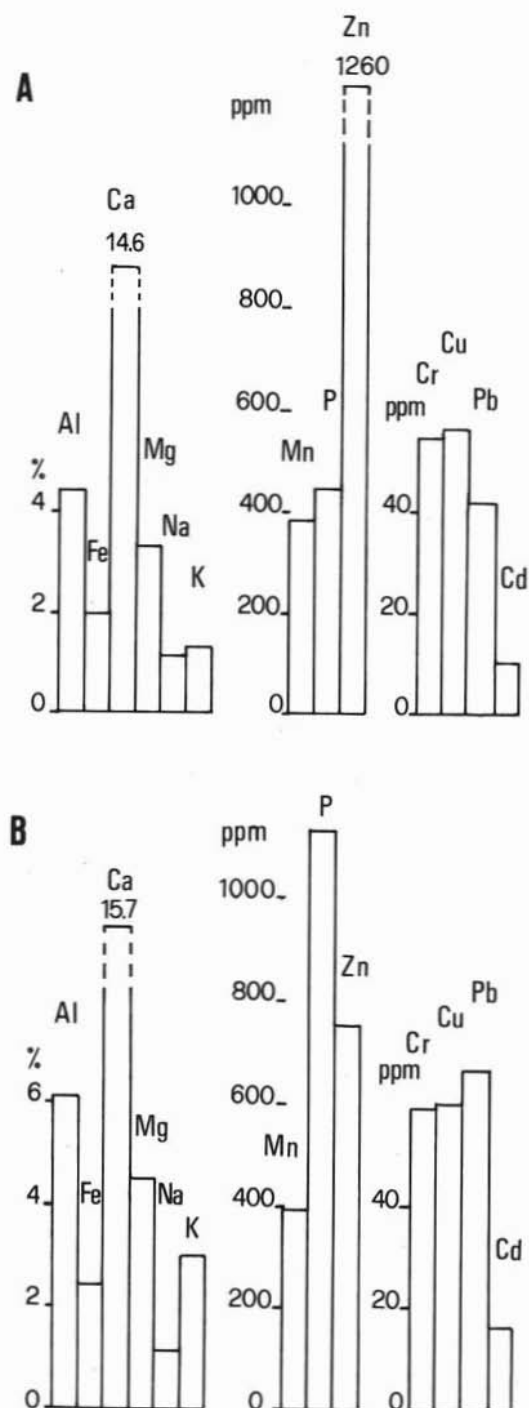


Fig. 3. — Average geochemical composition of A (top) and B (bottom) layer. The Cd graphic values correspond to real data multiplied by 10.

Various criteria exist to establish the comparative data for natural values. One of them is to consider as background the heavy metal contents determined in sediments deposited in the pre-industrial period. To this purpose we report in Tab. 2 the concentrations obtained from a core collected in the Northern basin of the Lagoon of Venice, and whose layers were dated by the Pb^{210} technique (DONAZZOLO et al., 1982). Unfortunately these concentrations were carried out by a different analytical procedure (AGEMIAN and CHAU, 1975), corresponding to a partial extraction and not to total digestion. The sediments now buried beneath later deposits, however have been subject to various physico-chemical processes and therefore may have lost part of the original heavy metal contents (BERNER, 1971). So such data represent minimum values (GROOT et al., 1976).

Another criterion employed is to consider as natural levels the average concentrations calculated from the analyses of sediments collected in a near zone, certainly not influenced by man. The values of BARILLARI et al. (1981) in this sense may correspond to background values for Cr, Pb and Cd. They resulted from the analyses of samples from the Southern lagoon, no directly subject to industrial contamination.

A third possibility is to use the element concentration mentioned in literature for average nearshore sediments, deep-sea clay. In Table 2 some mean heavy metal contents are reported together with the reference source of data. These average values exclude natural high concentration of some metals due to local mineralization in the drainage area of the rivers entering the basin under study. Furthermore the mineralogical composition of the investigated samples may differ from that of the reference sediments. In fact the abundance of major elements and the results on the essential minerals demonstrated that lagoonal materials are very rich in carbonates (MENEGAZZO VITTURI and MOLINAROLI, 1984). Therefore Table 2 gives also the mean values for carbonatic sediments as reference data.

In addition, the organic matter content is abundant in lagoonal sediments and because it is an excellent scavenger for several metals,

makes comparison with marine reference sediments unreliable because they are generally scarce in organic matter.

Also grain-size distribution influences the heavy metal concentration, since such elements are preferentially associated with the fine particles. Except for few samples, the studied sediments are pelites like the reference materials. Therefore the comparison is possible as regards that physical characteristic.

deeper layer. Zinc data well above natural abundances indicate heavy pollution, so human addition of this element is dominant on original values both in A and B layers.

These contaminants may have their origin in industrial wastes from sphalerite plant, which were discharged directly into the lagoon until a few years ago (BRAMBATI and MAROCCO, 1983). An additional input of Zn might originate from carbamate insecticides, wide-

TABLE 2

Mean heavy metal contents (in ppm) in investigated sediments compared with base-line levels

Sediments of the Lagoon of Venice		Cr	Cu	Zn	Pb	Cd	
Sediments from the study area	A layer	54	56	1260	41	1.01	
	B layer	59	60	753	66	1.56	
" Natural background concentrations " from a pelitic core		<u>1</u>	21*	15*	49*	23*	1.20*
Average values of sediments from " uncontaminated area "		<u>2</u>	48	—	—	25	0.51
<u>Base-line levels</u>							
Nearshore sediments		<u>3</u>	100	48	95	20	—
		<u>4</u>	60	35	110	22	—
Deep-sea sediments clay		<u>5</u>	90	250	165	80	0.42
Deep-sea sediments carbonate		<u>5</u>	11	30	35	9	0.0x
Mediterranean sediments		<u>6</u>	15	15	50	25	0.15
<u>Nonpolluted sediment range</u>		<u>7</u>	<25	<25	<90	<40	—
<u>Heavily polluted sediment range</u>		<u>7</u>	>75	>50	>200	>60	>6

* Data obtained from partial extraction (digestion with HNO₃ 8N)

Reference source of data: 1 DONAZZOLO et al., 1982 ; 2 BARILLARI et al., 1981 ; 3 WEDEPOHL, 1960 ; 4 WEDEPOHL, 1978 ; 5 TUREKIAN and WEDEPOHL, 1961 ; 6 WHITEHEAD et al., 1985 ; 7 PRATER and ANDERSON, 1977.

A proposal of sediment classification in nonpolluted, moderately and heavily polluted sediments was presented by PRATER and ANDERSON (1977). These Authors defined the ranges by evaluating chemical parameters on over a hundred different samples from harbors and on the basis of the mortality percentage of various species from bioassay in sediment sub-strate contaminated by industrial and municipal discharges.

Taking into account all these considerations and in comparison with the base-line level presented in Tab. 2, we conclude that studied samples have Cr concentrations close to natural background. The anthropogenic contribution appears to be significant with respect to Pb, Cu and Cd contents particularly in

ly used in the surrounding land. This last hypothesis suggested by DONAZZOLO et al. (1984) is supported by high values of phosphorus, tracer of agricultural pollution, even if in the investigated area P of municipal wastes origin cannot be excluded.

Inter-element correlations

To investigate the relationships between pairs of geochemical variables Table 3 contains linear correlation coefficients separately calculated for A and B samples and classified according to their level of significance. In Fig. 4 some graphic correlation diagrams are also presented.

Many element pairs showed strong correla-

TABLE 3
Correlation coefficients *r* between elemental concentration

	Al	Fe	Ca	Mg	Na	K	Mn	P	Cr	Cu	Zn	Pb	Cd	Org. matt.
Al		.78* .90*	-.40* -.83*	-.55* -.75*	.28 .76*	.80* .97*	.53* .43*	.59* .27	.18 .67*	.48* -.04	.34 -.06	.55* -.17	.32 -.30	.07 .31
Fe	.78* .90*		-.23 -.67*	-.20 -.53*	.41* .65*	.64* .85*	.48* .56*	.66* .40*	.51* .77*	.82* .21	.61* .19	.84* .09	.64* -.06	.42* .32
Ca	-.40* -.83*	-.23 -.67*		.31 .76*	-.53* -.72*	-.54* -.88*	-.27 -.22	-.10 -.15	.02 -.59*	.36 -.06	-.18 -.01	-.30 .09	-.15 .26	.02 -.06
Mg	-.55* -.75*	-.20 -.53*	.31 .76*		.06 -.51*	-.24 -.80*	-.38 -.31	-.39 -.11	.41* -.33	-.09 .17	-.13 .26	-.14 .39	-.03 .54*	.42* -.11
Na	.28 .76*	.41* .65*	-.53* -.72*	.06 -.51*		.51* .81*	.28 -.01	.28 .24	.18 .56*	.28 -.01	.29 .05	.35 .02	.37 .07	.30 .19
K	.80* .97*	.64* .85*	-.54* -.88*	-.24 -.80*	.51* .81*		.54* .34	.51* .20	.09 .65*	.42* -.03	.30 -.04	.47* -.13	.34 -.28	.18 .27
Mn	.53* .43*	.48* .56*	-.27 -.22	-.38 -.31	.28 -.01	.54* .34		.57* .31	-.14 .17	.21 .13	.16 .15	.30 -.14	.26 -.11	-.07 .14
P	.59* .27	.66* .40*	-.10 -.15	-.39 -.11	.28 .24	.51* .20	.57* .31		.24 .26	.40* .47*	.40* .12	.68* .22	.21 .29	.26 -.03
Cr	.18 .67*	.51* .77*	.02 -.59*	.41* -.33	.18 .56*	.09 .65*	-.14 .17	.24 .26		.42* .27	.28 .16	.46* .27	.36 .01	.63* .18
Cu	.48* -.04	.82* .21	.36 -.06	-.09 .17	.28 -.01	.42* -.03	.21 .13	.40* .47*	.42* .27		.83* .86*	.83* .69*	.84* .68*	.47* -.18
Zn	.34 -.06	.61* .19	-.18 -.01	-.13 .26	.29 .05	.30 -.04	.16 .15	.40* .12	.28 .16	.83* .86*		.72* .68*	.76* .71*	.45* -.05
Pb	.55* -.17	.84* .09	-.30 .09	-.14 .39	.35 .02	.47* -.13	.30 -.14	.68* .22	.46* .27	.83* .69*	.72* .68*		.67* .69*	.48* .07
Cd	.32 -.30	.64* -.06	-.15 .26	-.03 .54*	.37 .07	.34 -.28	.26 -.11	.21 .29	.36 .01	.84* .68*	.76* .71*	.67* .69*		.26 -.14
Org. matt.	.07 .31	.42* .32	.02 -.06	.42* -.11	.30 .19	.18 .27	-.07 .14	.26 -.03	.63* .18	.47* -.18	.45* -.05	.48* .07	.26 -.14	

* significance > 99.9%; * significance > 95%

The first line refers to A layer samples, the second one to B layer samples.

tions significant at the 95% and 99.9% confidence level.

Major-element correlations reflect the dominant mineralogy. For example in B sediments high positive coefficients were determined between Al and Fe (Fig. 4), Al-K, Fe-K and Al-Na. Such relations imply that these elements are the main components of silicates (micas, feldspars and clay minerals). The strong correlations observed between Fe-Cr, Fe-Mn (Fig. 4), Al-Cr, Al-Mn may indicate the occurrence of these minor elements in silicates due to their chemical affinity. The negative correlations between Al-Ca and Al-Mg indicate that Ca and Mg are preferentially present in other minerals than silicates. They are in fact associated with each other to con-

stitute the carbonates, which from mineralogical investigations included dolomite and calcite (MENEGAZZO VITTURI and MOLINAROLI, 1984).

Of particular interest are correlations with trace elements. For the chalcophile metals positive relations were found even if at difference level of significance.

The highest coefficients were calculated for pairs Zn-Cu and Zn-Cd, whereas Pb shows similar affinity for the metals Zn, Cu and Cd. Phosphorus is scarcely correlated with Cu and Fe. That last relation may suggest only a physical association of P on Fe-oxyhydroxides or chemical association to form Fe-phosphates such vivianite and strengite (BERNER, 1980; EMSLEY, 1980).

Such discussed correlations are relative to B samples. They are not always identical for A samples. For example in top sediments positive coefficients were observed not only between major and minor elements of silicates but also between such metals (Al, Fe, K, Mn, Cr) and the chalcophile elements Zn, Cu, Pb, Cd and also P. These correlations do not necessarily imply a geochemical association. In fact such correlations can result from close

physical processes or a combination of physical and chemical phenomena, occurring later and/or by man's influence. The significant coefficients determined between the pairs Al-P, Al-Cu, Al-Pb, Fe-P, Fe-Cu, Fe-Pb may suggest the accumulation of trace elements in phyllosilicates or Fe-minerals by adsorption mechanisms.

As regards the relation between metals and organic matter, significant coefficients (> 95%) were remarked only in surface samples for elements Zn, Pb, Cu, Fe, Mg due to its well known capacity to accommodate them. A

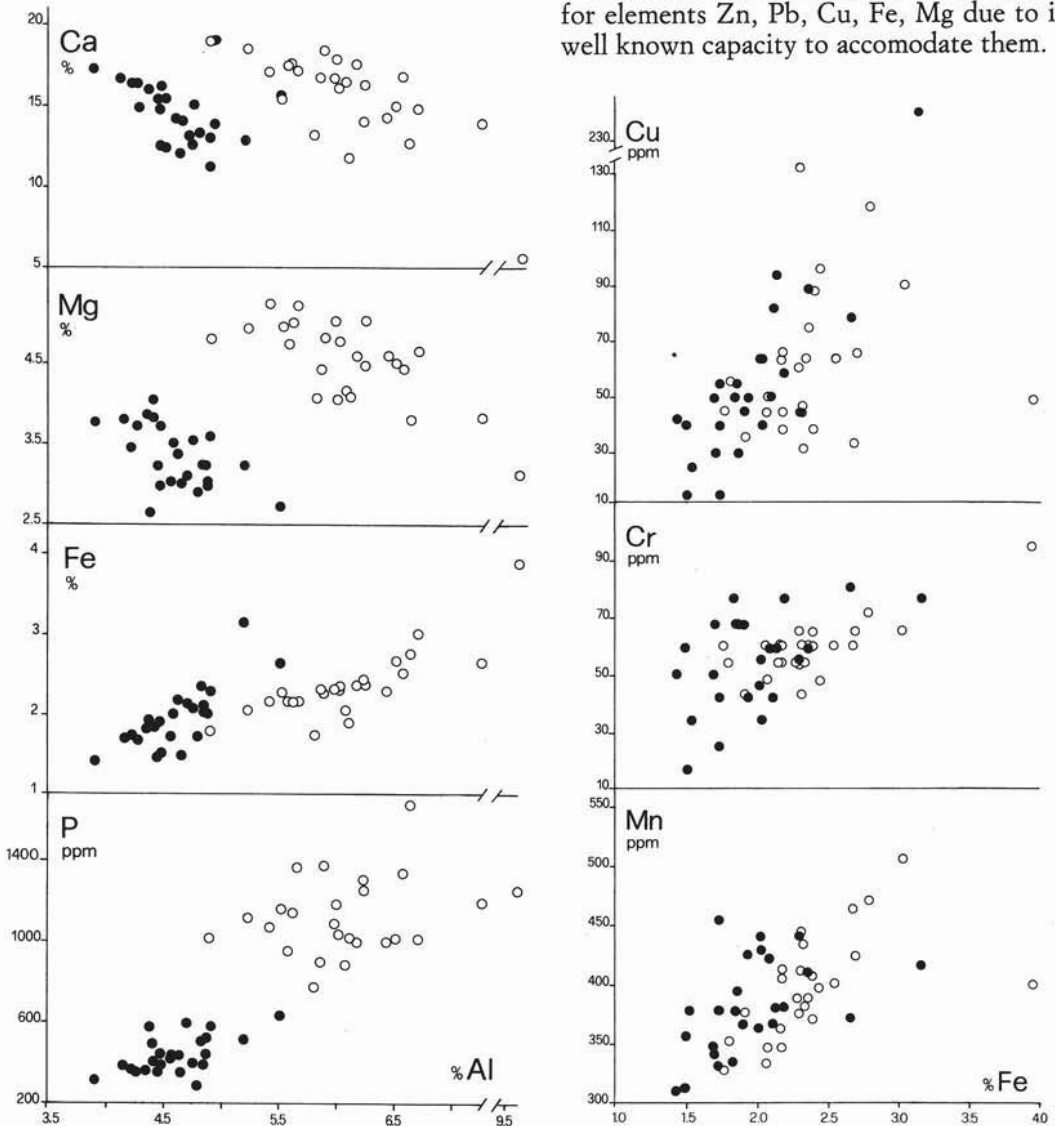


Fig. 4. — Correlation diagrams. Relationships of Ca, Mg, Fe and P versus Al (• A samples, ○ B samples). Relationships of Cu, Cr, Mn versus Fe (• A samples, ○ B samples).

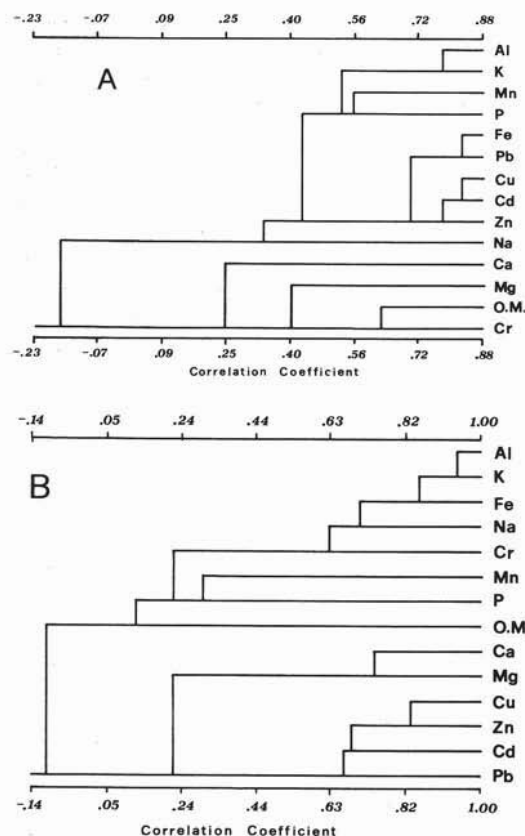


Fig. 5. — Dendrograms showing the clustering of elements in A and B layer.

preferential association was observed for Cr. A similar relation has been also determined in estuarine and lagoonal sediments (JURAČIĆ et al., 1986; BARILLARI et al., 1981).

Geochemical associations

By clustering the geochemical variables in 25 samples separately for A and B level the dendrograms of Fig. 5 were produced. The values plotted on the horizontal axis are the correlation coefficients used as a similarity measure.

The dendrogram relative to B layer suggests the geochemical associations:

- silicate (Al, K, Fe, Na) and as minor elements associated Cr, Mn, P;
- carbonate (Ca, Mg);
- chalcophile metals (Cu, Zn, Cd, Pb).

The dendrogram obtained for A layer shows differences on geochemical behaviour for some elements. Calcium is less related to Mg, and Cr and Na are not clearly associated to any geochemical group. The chalcophile metals are associated to Fe, which is not related to silicate association. Such association agrees with preliminary results from mineralogical investigations on heavy minerals in bottom sediments of this area (FRIZZO et al., 1986). Pyrite and other Fe-sulphides have been recognized; in particular the occurrence

TABLE 4
Average elemental concentrations of the three geochemical groups in A and B layer

Group		●	▲	□	●	▲	□		
		1	2	3	1	2	3		
Al %	A	4.52	4.59	4.79	P ppm	A	443	397	477
	B	5.89	6.48	6.19		B	1122	1141	1136
Fe %	A	1.88	1.78	2.32	Cr ppm	A	56	46	60
	B	2.19	2.50	2.53		B	56	61	61
Ca %	A	15.65	13.91	13.10	Cu ppm	A	49	27	103
	B	16.14	15.39	15.41		B	59	39	89
Mg %	A	3.40	3.29	3.28	Zn ppm	A	512	281	3897
	B	4.54	4.39	4.73		B	662	270	1562
Na %	A	1.02	1.00	1.24	Pb ppm	A	40	30	54
	B	1.09	1.15	1.16		B	65	52	88
K %	A	1.27	1.28	1.43	Cd ppm	A	0.87	0.61	1.73
	B	2.87	3.26	3.05		B	1.49	1.24	2.13
Mn ppm	A	377	386	387	Org. matt. %	A	5.65	4.70	6.80
	B	379	413	411		B	4.03	5.71	5.07

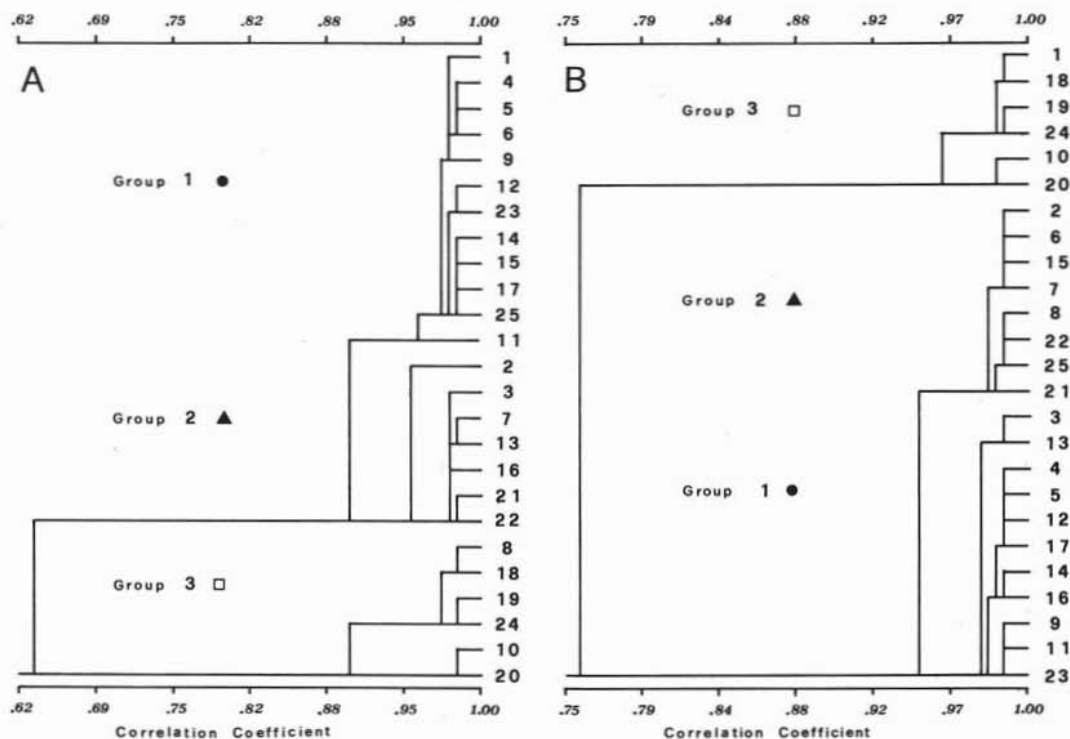


Fig. 6. — Dendrograms showing the clustering of samples according to their geochemical composition in A and B layer.

of pyrite also in the reactive framboidal form may contain the chalcophile metals (PATTERSON et al., 1986).

Geochemical groups of sediments

In the attempt to identify different groups of samples with similar geochemical composition, cluster analysis was employed using the correlation coefficient between all pairs of samples from the same level.

Three groups of sediments were produced, according to the clustering sequence represented in the dendrograms of Fig. 6. The most numerous is group 1 ($n = 12$ and $n = 11$ for A and B level). Group 2 assembles 7 and 8 samples in A and B layer respectively. These two groups were strictly associated by the aggregation procedure. The third group 3 is quite distinct from the above mentioned.

The differences among the average geochemical composition of each group in the

two layers are visualised in Tab. 4 and in Fig. 7. Examining the data one can observe that sediments of group 1 in both levels show higher concentration of Ca, Mg, Cu, Zn, Pb, Cd and lower concentration of Al, K, Mn than group 2. The behaviour of Fe, Na, P, Cr is different in A and B samples.

Group 3 has the highest contents of Fe as well as of trace elements Cr, Cu, Zn, Pb, Cd in both levels.

The spatial distribution of the groups is displayed in the maps of Fig. 8.

The sediments of group 2 located in proximity to the inner border of the lagoon correspond to rather coarse sediments (BARILLARI, 1978; MENEGAZZO VITTURI and MOLINAROLI, 1984) and therefore have no capacity to accumulate heavy metals. The samples of group 1 are on the contrary pelitic (BARILLARI, 1978; MENEGAZZO VITTURI and MOLINAROLI, 1984) so can more easily interact with trace elements. The samples of group 3 are placed along the translagoon bridge and

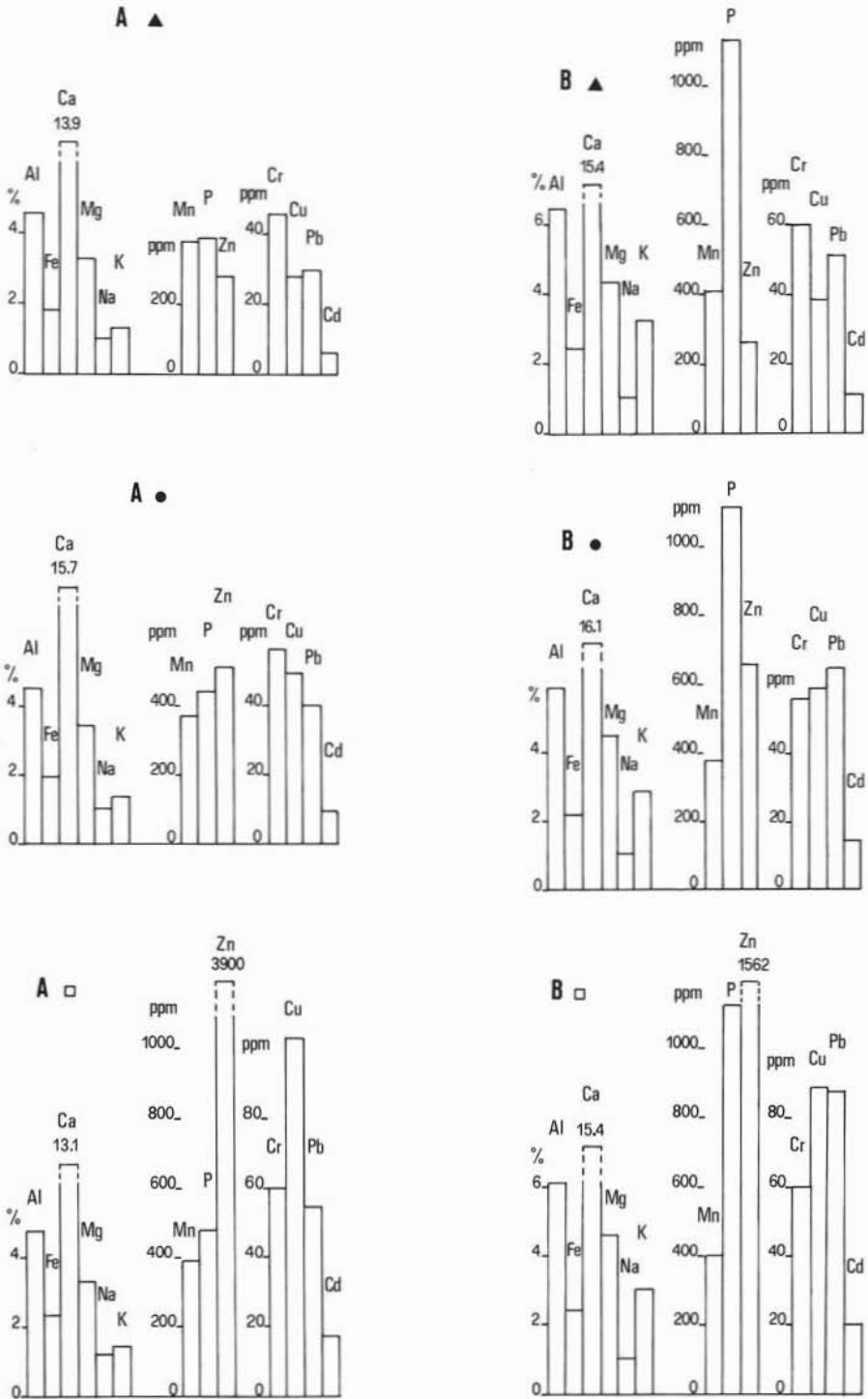


Fig. 7. — Average composition of geochemical groups in A and B layer. The Cd graphic values correspond to real data multiplied by 10.

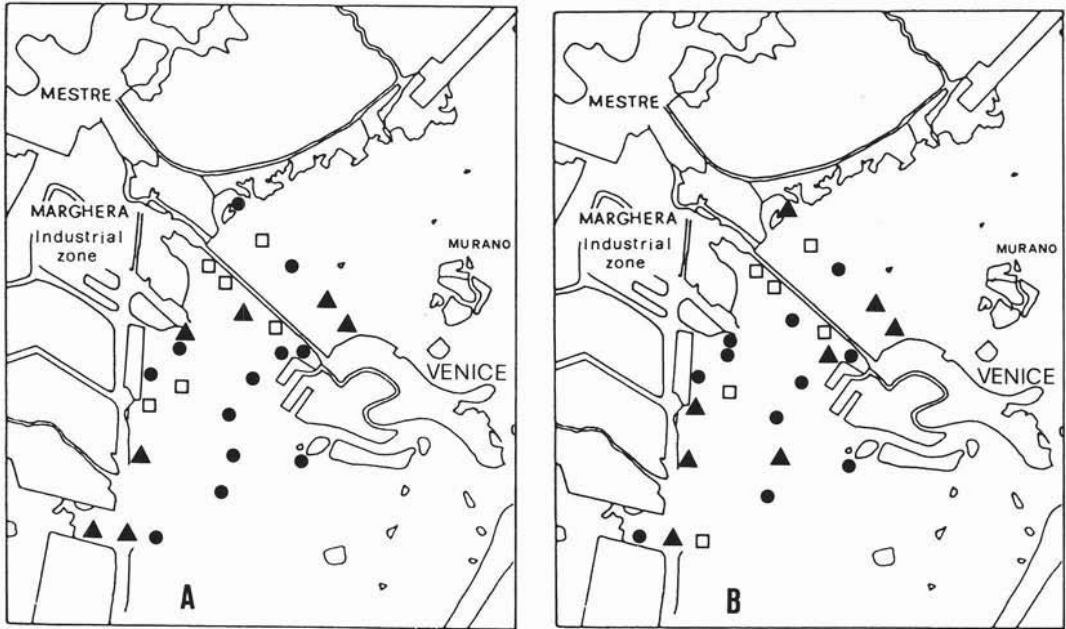


Fig. 8. — Samples distribution identified according to geochemical group.

correspond to pelitic sediments more influenced by human activities.

Conclusions

In summary it can be concluded that:

- from research on geochemical composition of bottom sediments in the Lagoon of Venice it was possible to ascertain that surface level differs from deeper level as regards the content of major, minor and trace elements;

- the examined major elements Al, Fe, Ca, Mg and K have an increase in deeper sediments in comparison with top sediments. Among major elements Ca was detected as the most plentiful;

- the geochemical behaviour of minor and trace elements in function of depth resulted different for each element. Chromium and Mn present similar range in both layers. Systematically P, generally Pb and Cd are accumulated in deeper sediments. An opposite trend was observed for Zn;

- the comparison between the contents of investigated samples and the data reported in literature allowed the demonstration that Pb, Cu, Cd and P are enriched in the deeper

layer by anthropogenic contribution in particular in recent years up to 1970. Human addition is also dominant for Zn in modern surface sediments;

- coefficients of correlation between major elements give information about the main minerals of sediments, which resulted constituted by Ca and Mg carbonates and silicates as feldspars and phyllosilicates;

- of particular interest were relations between minor and trace and major elements, not always identical in the two levels studied. In addition to obvious relationships between pairs of chalcophile metals, in top sediments a positive correlation between these metals and silicates was observed. These relations may be due to physico-chemical processes, not excluding an anthropic influence;

- the inter-element correlations among all the geochemical variables by cluster analyses has identified three geochemical associations: silicate, carbonate, chalcophile metals. In A layer the iron is not related to silicate association, but links with the chalcophile elements;

- the rearrangement of samples in function of their geochemical composition produc-

ed three groups of sediments for each layer. Nearly all samples were included in two similar groups, but with a different capacity to interact with trace elements. A third group of samples is clearly distinct and corresponds to heavily polluted sediments by various man activities.

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