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Major, Minor and Trace Elements in Surficial Sediments from the Open Adriatic Sea: A Regional Geochemical Study

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Abstract

The concentrations and distributions of major (Al, Ca, Fe, K, Mg), minor (Mn, P, Ti), and trace elements (Ag, As, Ba, Be, Co, Cr, Cu, Ag, La, Ni, Pb, Sc, Sr, Th, U, V, Zn, Zr), in the surficial sea bottom sediments were studied in an attempt to establish their distribution in the Adriatic Sea. Results indicate that major, minor and several trace elements are strongly related to the catchment geology, their distribution being essentially controlled by the type of sediments. However, the majority of trace elements are believed to have been introduced into the Adriatic from the riverine inflows that are also affected by the impact of industrial, mining and urban wastes. Other sources of these elements are located along the coast. The highest concentrations for several trace elements were thus recorded from the coastal ecosystems and from the most polluted Albanian and Italian rivers. The concentrations of trace elements generally decrease with distance from the coast. The regional distribution patterns are influenced by the counter-clockwise system of the Adriatic Sea currents which carry these elements away from the riverine inflows. Correlation analysis indicates that the trace elements are largely associated with the clay minerals, Fe and P contents rather than with the Mn concentrations. Magnesian minerals are suggested as the carrier for some trace elements (As, Co, Cr, Ni, Se and V) only in the southern Adriatic, which reflects their ophiolitic origin in the Albanian hinterland. Organic matter concentrations does not considerably influence the abundance and distribution of trace metals.

1. INTRODUCTION

The determination of element concentrations in the marine sediments is among the first steps in the quantification of the natural and anthropogenic contribution to marine ecosystems. The Adriatic as a modern epicontinental sea is situated between the northeastern Italian coast and the southwestern coasts of Slovenia, Croatia, Yugoslavia and Albania. It is especially subjected to pollution due to its enclosed character. In general, the sources of major, minor and trace elements in the surficial sediments from the Adriatic are expected to be a combination of natural weathering, run-off and riverine inflows affected by anthropogenic impact - industrial, mining and urban wastes as well as the atmospheric inputs.

Although the studies of element contents in the Adriatic sediments date back more than 20 years, the available data and publications are mostly limited and patchy. Most of the studies were on trace metal concentrations in sediments from selected coastal areas of the Adriatic (STEFANINI, 1971; MAJORI et al., 1979; DONAZZOLO et al., 1979, 1981, 1983, 1984; STEGNAR et al., 1981; JURAČIĆ & PRAVDIĆ, 1983; ZVONARIĆ & STEGNAR, 1987; FRASCARI et al., 1988; GIORDANI et al., 1989; PROHIĆ & JURAČIĆ, 1989; FAGANELI et al., 1991; VDOVIĆ et al., 1991; FERRARA & MASSERTI, 1992; VDOVIĆ & JURAČIĆ, 1993; CORREGGIARI et al., 1994; SONDI et al., 1994). The only, but preliminary data set of some major, minor and trace elements (Fe, Mn, P, Cu, Cr, Ni, Pb and Zn) from analysis of the surficial part of sea-bottom sediment samples that cover the whole Adriatic was reported by PAUL & MEISCHNER (1976). Their data showed that all heavy metal concentrations found can be attributed to natural sedimentological processes and are not necessarily to be interpreted as indicators of pollution. However, later studies showed that some of them can hardly be explained by natural processes alone (PAUL & MEISCHNER, unpubl.).

The present study was conducted in order to determine the total concentrations of major, minor and trace elements in the sediments in an attempt to establish the pattern of their enrichment over the whole Adriatic, and thus to complete the previous investigations of PAUL & MEISCHNER (1976). Determination of the distribution and concentrations particularly of the trace elements, which are potentially toxic contaminants, is of great importance for further environmental pollution studies, as means of identifying the principal pollution sources and their influence on the Adriatic Sea through time. The results from this regional survey will also complete the general picture of the distribution of sediments and other geochemical variables (organic carbon, total nitrogen and phosphorus contents) in the Adriatic as studied by FAGANELI et al. (1994).

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Fig. 1 Map of the Adriatic Sea showing sites of sediment sampling.

2. HYDROLOGICAL AND GEOLOGICAL SETTING

The Adriatic is a relatively shallow elongated continental margin sea extending for approximately 800 km in a NW-SE direction with a width of between 100-200 km. Its special character is conferred by the girdle of Alpine age mountains. The axes of two chains mark its edges, the Apennines separating it from the western Mediterranean, and the Dinaric mountains separating it from the Eastern Alps and the Pannonian basin (see CELET, 1977, and references therein).

The Adriatic Sea is morphologically divided into three separate areas (Fig. 1). The deepest one is the southern basin, subcircular bathyal basin more than 1200 m deep separated from the Ionian Sea by an 800 m deep sill. The central basin is relatively shallow with a maximum depth of approximately 275 m in the Jabuka Pit. It is separated from the southern basin by the Palagruža sill approximately 130 m deep extending in the Split - Monte Gargano direction. The third submarine high located between the Jabuka Pit and the northern Adriatic separates the central basin from the broad and level northern shelf characterized by decreasing depth from 130 m to a few metres, averaging about 30 m. The most important characteristic of the Adriatic is the general anti-clockwise circulation of the Adriatic waters which is mostly affected by the elongated shape of the sea, the continental climatic conditions and the morphological features of the sea bottom. From the Ionian Sea, water of high salinity enters the Adriatic and spreads by general circulation along the eastern coast. The low salinity water generated in the northern Adriatic, due to the inflows of the river Po and other local rivers travels along the Italian coast. The riverine influence is more strongly expressed along the western coast and to a lesser extent along the eastern coast which is affected by Albanian and Dalmatian riverine inflows as well as by submarine springs. A comprehensive description of the hydrological characteristics of the Adriatic Sea was given by BULJAN & ZORE-ARMANDA (1976).

The exposed lithologies of the eastern and western drainage areas are mostly sedimentary rocks of different ages ranging from the Upper Palaeozoic to the Holocene. Geologically, the eastern coast of the Adriatic is a part of the High Karst Platform and the Dalmatian zone with predominantly carbonate lithologies. Near the Albanian border sediments of the Budva-Cukali zone outcrop containing tuffs and porphyries. Along the Albanian coast sedimentary rocks of the Ionian zone of predominantly clastic character are exposed. Part of the catchment area of the Albanian rivers, which drain into the Adriatic, especially that of the river Drini (the largest) is composed of mineralized ultrabasic, basic and metamorphic rocks of the Dinaride ophiolite zone. In the northern and western part of the Italian coastal zone outcrops are mostly composed of continental and marine sediments of post Middle Pliocene age, while in the southern part Mesozoic-Cenozoic neritic carbonates prevail. The drainage area of the river Po and other northern Italian rivers is also the source of weathered material of metamorphic and predominantly acid to intermediate igneous rocks, as well as carbonates. The

Element Units	Al %	Ca %	Fe %	Ti %	K %	Mg %	C org. %	P %	Ba ppm	Mn ppm	Sr ppm	Ag ppm	As ppm	Be ppm
Location														
v1	5.11	9.68	2.55	0.24	1.69	2.11	0.92	0.05	227	572	339	1	7	2.1
v2	5.38	10.3	2.77	0.25	1.74	1.88	1.18	0.05	214	577	411	0.5	1	2.2
v3	5.7	8.82	2.99	0.26	1.77	2.09	0.64	0.05	247	2050	427	0.9	15	2.3
v4	5.07	12.6	2.86	0.25	1.59	2.23	1.36	0.06	269	1140	578	0.7	1	2.3
v5	6.31	6.46	4.18	0.31	2.01	3.1	1.34	0.05	274	682	316	0.7	12	2.5
v6	4.18	13.7	2.72	0.2	1.35	2.41	1.15	0.05	213	1410	664	0.9	17	1.9
v7	5.34	10.5	3.02	0.25	1,76	2.42	0.55	0.07	336	1280	530	0.8	9	2.7
v27	4.75	10.7	2.64	0.23	1.45	2.01	0.96	0.04	204	1030	485	0.9	9	1.9
v28	5.97	6.33	3.84	0.27	1.85	2.67	1.06	0.05	242	1570	290	1.2	19	2.3
v32	4.7	9.16	2.98	0.24	1.38	2.63	0.8	0.05	223	717	332	1.3	9	1.9
v34	3.96	14.5	2.04	0.19	1.12	1.79	1.07	0.04	153	845	608	1.2	1	1.6

Element Units	Co ppm	Cr ppm	Cu ppm	Hg ppb	La ppm	Ni ppm	Pb ppm	Sc ppm	Th ppm	U ppm	V ppm	Zn ppm	Zr ppm
Location													
v1	10	54	21.8	70	27.9	50	8	9.5	8	2.5	91	66	42.1
v2	12	55	37.3	77	28.8	56	13	10.3	8.1	3	95	74	49.9
v3	20	119	40.1	71	28.5	105	11	11.3	8.2	1.9	110	79	52.2
v4	18	113	44.3	115	26.6	117	10	10.9	7.6	1.8	101	73	52.3
v5	25	246	42.7	86	25.9	264	11	15.9	8.1	2.5	142	97	47.2
v6	20	144	24.1	69	23.3	154	11	10.1	6.6	1.5	88	63	40.8
v7	23	62	44.9	70	25.5	129	18	11.1	8	1.9	107	79	53.9
v27	17	53	31.9	108	25.2	99	10	9.9	7	1.8	94	71	46
v28	24	199	36.6	149	25.5	211	17	14.6	7.4	1.9	128	101	43.9
v32	18	97	24.2	418	24.3	170	5	11.3	6.8	2	94	75	37.3
v34	13	65	34.1	235	22.3	49	11	7.4	6.1	1.6	76	58	41.5

Table 1 Total elemental concentrations in surficial sediments from the southern Adriatic (C org. - FAGANELI et al., 1991, 1994), n=11.

variety of the source areas and thus the variety of the origin of the exposed rocks have resulted in various mineral and elemental associations in the sediments of the Adriatic Sea (PIGORINI, 1967, 1968).

3. MATERIALS AND METHODS

Thirty-five surficial sediment samples were collected during two trans-Adriatic cruises of the research vessel "Andrija Mohorovičić" in March and July 1975. The sample sites were chosen to be representative of the whole Adriatic Sea (Fig. 1). Samples were collected with a gravity core sampler according to MEISCHNER & RUMOHR (1974) with a plastic liner of 4 cm diameter down to a depth of 30 cm. Only the top 5 cm was used for the purpose of this study. In the laboratory, the sediment samples were dried at 50°C for 48 hours. Before further analysis the dried sediment samples were homogenized by grinding. Major, minor and trace elements (Al, Ca, Fe, K, Mg, Mn, Ti, P, Ag, As, Ba, Be, Bi, Cd, Co, Cr, Cu, La, Mo, Ni, Pb, Sb, Sc, Sn, Sr, Th, U, V, Zn, Zr and W) were, after decomposition with $HF/HNO_3/HClO_4$, determined by Inductively Coupled Plasma (ICP) Spectrometry. Concentrations of Cd, Bi, Mo, Sb, Sn and W were generally lower than the detection limit of ICP analysis (1, 3, 1, 5, 10 and 10 ppm, respectively). Hg was analysed separately according to procedures described by HATCH & OTTO (1968). Analytical blanks were run with the samples, and a marine sediment reference standard MAG-1 (US National Bureau of Standards) was used to check the accuracy of the analytical procedure. Geochemical analyses were carried out at the ACTLAB Activation Laboratories Ltd., Ontario, Canada. Analytical precision was generally better than 10% at the 95% confidence level. This was indicated by results of duplicate measurements for 7 samples.

4. RESULTS AND DISCUSSION

The concentrations of analyzed elements are summarized in Tables 1-4. Correlation matrices were also calculated to aid the interpretation of data. Critical values of correlation coefficients are $r_{0.05;\,9} = 0.601$ (samples from the southern and central Adriatic) and $r_{0.05;\,11} = 0.553$ (samples from the northern Adriatic). The regional distributions of major, minor and trace elements in the Adriatic Sea as indicated by the total analysis of surficial sea-bottom sediments are shown in Figs. 2-4.

Element	Al	Ca	Fe	Ti	K	Mg	C org.	P	Ba	Mn	Sr	Ag	As	Be
Units	%	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm
Location														
v8	5.58	9.02	2.79	0.25	1.84	1.79	0.89	0.06	231	764	411	0.5	10	2.3
v9	3.26	15.9	2.27	0.14	1.31	1.49	1.04	0.04	212	538	888	0.7	32	1.6
v10	4.61	11.5	2.63	0.21	1.51	2.2	0.82	0.05	207	898	583	1.2	6	2
v11	4.9	10.5	3.07	0.23	1.54	2.48	0.77	0.05	204	825	534	0.9	9	2
v12	2.77	15.2	2.28	0.14	0.83	3.24	1.41	0.03	117	600	545	0.6	17	1.1
v13	5.44	9.71	3.1	0.23	1.71	2.26	0.99	0.05	213	3760	495	1.3	6	2.2
v17	5.08	11.1	2.81	0.22	1.67	2.07	1.33	0.05	205	1490	535	0.9	1	2.3
v30	4.75	11.1	2.63	0.21	1.52	2.16	0.78	0.05	207	1140	552	0.7	1	2
v31	5.12	11.3	3.16	0.24	1.47	2.37	0.74	0.05	203	2100	595	0.9	13	2.1
v71	2.27	19.2	1.66	0.11	0.74	3.08	0.9	0.03	109	644	669	0.8	19	1
v73	4.1	13.6	2.37	0.19	1.34	2.36	0.8	0.04	187	616	621	0.6	1	2.2

Element	Co	Cr	Cu	Hg	La	Ni	Pb	Sc	Th	U	V	Zn	Zr
Units	ppm	ppm	ppm	ppb	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Location													
v8	11	94	29.6	132	27.6	60	14	10.6	7.8	2.3	116	83	47.2
v9	11	39	22.4	63	20.8	49	11	6.4	5.7	1.9	82	44	33.7
v10	17	127	23.9	217	25	124	9	10.3	7.4	2.5	86	82	42.1
v11	19	165	32.6	89	25.5	173	12	11.8	7.3	2.5	106	93	41.4
v12	14	127	16	86	13.5	108	9	7.8	3.7	1.2	68	44	21.8
v13	22	139	32.3	78	24	140	14	11.8	7	1.8	105	95	44.2
v17	19	116	32.7	79	24.3	115	12	10.6	7.1	2	97	84	43.5
v30	17	111	24.2	229	24.1	106	10	10	6.8	1.8	86	84	41.3
v31	23	150	30.8	220	24.1	155	13	11.7	6.9	1.7	103	91	45.8
v71	10	76	9.8	20	14.6	66	13	5.7	3.9	1.2	50	38	20.2
v73	15	122	17.2	253	21.7	125	7	9	7.1	3.7	78	61	46.7

Table 2 Total elemental concentrations in surficial sediments from the central Adriatic (C org. - FAGANELI et al., 1991, 1994), n=11.

4.1. MAJOR ELEMENTS

The concentrations of Al and K in the surficial sediments range from 2.27 to 6.31% and from 0.74-2.01%, respectively (Tables 1-4). The areal distribution of Al and K contents (Fig. 2) and a strong correlation between the K and Al concentrations (r = 0.97 southern Adriatic, 0.96 central Adriatic and 0.99 northern Adriatic) suggest that the two elements are related in their mode of deposition. Both of these elements enter into the composition of clay minerals, which comprise 13-54% of the surficial sediments (FAGANELI et al., 1994) and of feldspars, pyroxenes and amphiboles. The Al and K concentrations are thus primarily a function of clay mineral content. The highest concentrations of Al (4.75-6.31%) and K (1.12-2.01%) were found in sediments from the southern Adriatic and the Jabuka Pit as well as along the Italian coast, while the lowest (2.27-4.11%) and (0.74-1.47%) were restricted to the Dalmatian coast and Istria. These observations agree favourably with the data on clay mineral content in surficial sediments reported by FAGANELI et al. (1994). The geographic distribution pattern of Al and K also correlates with the sediment type (mostly pelitic clayey silt and silt) that originated from the river Po and other Italian rivers, carrying the suspended sediment which is transported by the marine current along the Italian coast. Another area of higher clay content coincides with the dominantly pelitic silty sediments, which probably originate in the Albanian riverine inflows.

The concentrations of Fe range from 1.27-4.18%. Since clay minerals carry more iron than sand grains, this element is principally associated with the silt-clay fraction. This is supported by a strong correlation of Fe with Al and K (r = 0.85, 0.79 southern Adriatic, 0.90, 0.81 central Adriatic and 0.95, 0.93 northern Adriatic). Iron is also present in sulphide form as authigenic pyrite (up to 5%), which indicates reducing conditions in the surficial sediments (FAGANELI et al., 1994). In the oxic environment an important role of scavenging heavy metals seems to be played by the Fe oxides/hydroxides (WALDICHUK, 1985; ARAKEL & HONGJUN, 1992). The regional distribution of Fe is similar to that of Al and K (Fig. 2), maximum enrichment occurring in the southeastern part of the southern Adriatic, and could be attributed to the basic volcanics in Albania.

The concentrations of Ca and Mg range from 6.33-19.20% and from 0.91-3.58%, respectively. The highest concentration levels of Ca (9.31-19.20%) and Mg (3.05-3.58%) were found in the northern Adriatic - Venetian province (BRAMBATI et al., 1973) and in the central Adriatic, mostly along the Dalmatian coast.

Element Units	Al %	Ca %	Fe %	Ti %	K %	Mg %	C org. %	P %	Ba ppm	Mn ppm	Sr ppm	Ag ppm	As ppm	Be ppm
Location														
v14	5.82	8.71	2.91	0.27	1.93	1.92	0.84	0.05	228	681	350	0.7	1	2.3
v15	5.25	8.76	2.59	0.24	1.71	2.22	0.94	0.05	247	669	359	1.3	4	2
v16	3.61	10.3	1.3	0.15	1.15	2.05	0.8	0.03	195	398	384	0.5	1	1.4
v26	2.77	14.8	1.27	0.15	0.9	3.58	1.06	0.03	117	305	587	1	4	1.1
v29	2.98	13.2	1.48	0.3	0.78	2.21	0.81	0.05	136	543	681	0.6	1	1
v33	3.19	15.5	1.66	0.24	0.92	2.06	0.78	0.05	146	542	883	0.7	1	1.3
v50	4.47	10.6	2.3	0.23	1.38	1.19	1.05	0.04	190	407	318	0.9	3	1.6
v59	5.47	7.69	2.99	0.27	1.8	1.49	1.06	0.05	169	330	226	0.9	7	1.4
v60	4.11	7.37	2.29	0.22	1.22	0.91	1.47	0.05	169	330	226	0.9	7	1.4
v64	3.17	14.2	1.58	0.17	1.02	3.06	1.08	0.03	119	323	518	0.8	1	1.2
v65	5.92	9.31	3.13	0.3	2	3.05	1.6	0.06	259	593	273	1.2	1	2.4
v70	3.7	14.7	1.79	0.21	1.06	1.05	0.7	0.03	155	242	773	0.9	9	1.7
v72	4.53	8.12	1.9	0.19	1.46	1.78	1.4	0.04	237	440	345	0.6	1	1.7

Element Units	Co ppm	Cr ppm	Cu ppm	Hg ppb	La ppm	Ni ppm	Pb ppm	Sc ppm	Th ppm	U ppm	V ppm	Zn ppm	Zr ppm
Location													
v14	11	87	23.9	112	27.5	56	7	11.2	7.9	2.3	117	86	43.3
v15	10	87	17.2	1230	30.2	53	14	9.9	8.9	2.6	92	89	32.3
v16	4	40	22.2	119	15.5	21	7	5.1	5.3	2.7	48	51	24.4
v26	5	43	9.6	270	18.2	25	14	5.4	5.3	2.7	48	51	24.4
v29	4	50	4.1	85	43.2	19	7	6.8	12	3.9	39	29	16.6
v33	6	67	11.6	795	35.6	37	10	7	9.3	2.7	47	48	18.9
v50	8	84	24.3	323	22.7	55	20	9	6.6	2.3	92	81	43.7
v59	11	116	33.4	312	25.3	86	20	11.4	7.3	2.5	123	116	51.5
v60	7	82	29.6	429	20.6	53	26	7.7	5.8	2.7	73	102	41.6
v64	5	40	11.4	409	20.2	36	18	6.2	5.9	2.5	65	61	26.4
v65	12	129	32.6	610	28.7	68	51	11.8	8.7	3.2	112	167	47.5
v70	5	73	15	339	25.2	34	27	6.9	7.3	3.4	70	64	48.1
v72	8	70	7.1	99	23.7	39	8	7.2	6.6	2.4	57	49	18.2

Table 3 Total elemental concentrations in surficial sediments from the northern Adriatic (C org. - FAGANELI et al., 1991, 1994), n=11.

They probably suggest the enrichment of sediments with predominantly detrital calcite and dolomite carried into the basin from the land and/or reworking of Pleistocene dolomite sands carried in by northern Italian rivers, when the northern Adriatic shelf was dry during glacial periods. The X-ray diffraction patterns showed peaks corresponding to dolomite, supporting the chemical measurements. Lack of correlation of Ca with Mg contents in the northern and central Adriatic also confirms these observations. Relatively high levels of Mg (2.01-3.10%) and low concentrations of Ca (6.33-13.7%) in the southern Adriatic along the Albanian and Montenegro coast can be attributed to the weathering of basic and ultrabasic igneous rock in the drainage area of the Albanian rivers. Positive correlation of Mg with Al, K and Fe (r = 0.87) and negative correlation with Ca (r = -0.64) probably indicate the presence of montmorillonite and other aluminosilicates containing Mg. However, low concentrations of Ca (8.71-10.30%) and Mg (1.79-2.22%) are generally restricted to the Italian coast where the sediments have the lowest carbonate content (FAGANELI et al., 1994). The regional distribution of Ca and Mg is shown in Fig. 2.

The correlation analysis reveals a strong association of Ca and Sr (r = 0.92 southern Adriatic, 0.69 central Adriatic and 0.91 northern Adriatic), and a negative or absence of correlation with virtually all other metals present. Ca being an obvious indicator for carbonate minerals, its negative correlation with trace metals confirms the important role of clay minerals as the carrier phase.

The positive correlation of Ca with As might indicate the presence of calcium arsenate ($Ca_3(AsO_4)_2$) in the central Adriatic (maximum depth 273 m). The seawater down to 200 m depth is supersaturated with respect to calcite, and $Ca_3(AsO_4)_2$ may be more stable than $Mn_3(AsO_4)_2$ (SADIQ, 1990). In the southern Adriatic with a maximum depth of about 1200 m the formation of $Mn_3(AsO_4)_2$ is more probable.

4.2. MINOR ELEMENTS

The concentrations of Mn range from 242 to 3760 ppm. The spatial distribution pattern of Mn concentrations shows a general tendency to increase in the deepest parts of the central and southern Adriatic (Fig. 2). The peak values of Mn were measured in the Jabuka Pit

Southern Adriatic

Element	Al	Ca	Fe	Ti	K	Mg	C org.	P	Ba	Mn	Sr	Ag	As	Be
Units	%	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm
Mean	5.13	10.25	2.96	0.24	1.61	2.3	1	0.05	237	1079	453	0.9	9.1	2.2
Min.	3.96	6.33	2.04	0.19	1.12	1.79	0.55	0.04	153	572	290	0.5	1	1.6
Max.	6.31	14.5	4.18	0.31	2.01	3.1	1.36	0.07	336	2050	664	1.3	19	2.7

Element	Co	Cr	Cu	Hg	La	Ni	Pb	Sc	Th	U	V	Zn	Zr
Units	ppm	ppm	ppm	ppb	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Mean	18	110	34.7	133	25.8	128	11	11.1	7.4	2	102	76	46.1
Min.	10	53	21.8	69	22.3	49	5	7.4	6.1	1.5	76	58	37.3
Max.	25	246	44.9	419	28.8	264	18	15.9	8.2	3	142	101	53.9

Central Adriatic

Element	Al	Ca	Fe	Ti	K	Mg	C org.	P	Ba	Mn	Sr	Ag	As	Be
Units	%	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm
Mean	4.35	12.56	2.62	0.2	1.41	2.32	0.95	0.05	190	1216	584	0.8	10.5	1.9
Min.	2.27	9.02	1.66	0.11	0.74	1.49	0.74	0.03	109	538	411	0.4	1	1
Max.	5.58	19.2	3.16	0.25	1.84	3.24	1.41	0.06	231	3760	886	1.3	32	2.3

Element	Co	Cr	Cu	Hg	La	Ni	Pb	Sc	Th	U	V	Zn	Zr
Units	ppm	ppm	ppm	ppb	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Mean	16	115	24.7	133	22.3	111	11	9.6	6.4	2.1	89	73	38.9
Min.	10	39	9.8	20	13.5	49	7	5.7	3.7	1.2	50	38	20.2
Max.	23	165	32.7	253	27.6	173	14	11.8	7.8	3.7	116	95	47.2

Northern Adriatic

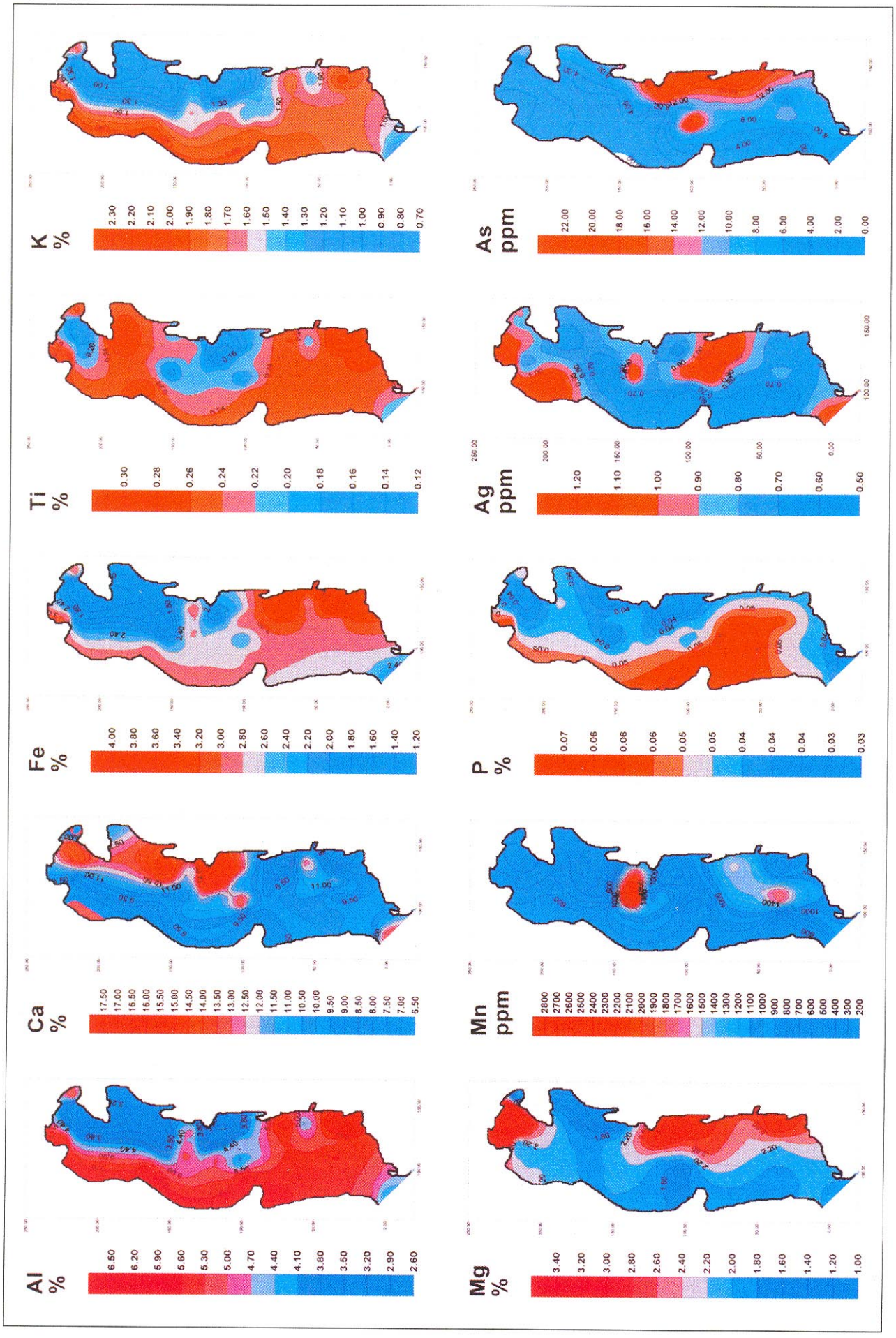
Element	Al	Ca	Fe	Ti	K	Mg	C org.	P	Ba	Mn	Sr	Ag	As	Be
Units	%	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm
Mean	4.23	11.02	2.09	0.23	1.33	2.04	1.05	0.04	184	462	460	0.8	3.5	1.6
Min.	2.77	7.37	1.27	0.15	0.78	0.91	0.7	0.03	117	242	226	0.5	1	1
Max.	5.92	15.5	3.13	0.3	2	3.58	1.6	0.06	259	681	883	1.3	11	2.4

Element	Co	Cr	Cu	Hg	La	Ni	Pb	Sc	Th	U	V	Zn	Zr
Units	ppm	ppm	ppm	ppb	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Mean	7	74	18.6	395	25.9	45	18	8.1	7.4	2.7	75	75	32.8
Min.	4	40	4.1	85	15.5	19	7	5.1	4.5	1.6	39	29	13.5
Max.	12	129	33.4	1230	43.2	86	51	11.8	12	3.9	123	167	51.5

Table 4 Medium, minimum and maximum concentrations of chemical elements in surficial sediments from the Adriatic (C org.- FAGANELI et al., 1991, 1994).

(central Adriatic) and in the southern Adriatic (572-2050 ppm), while the lowest Mn concentrations (242-681 ppm) are restricted to the northern Adriatic. These values are close to those reported by PAUL & MEISCHNER (1976). As the rock-forming ferromagnesium minerals contain considerable amount of Mn (1000-4000 ppm, WEDEPOHL, 1978), much of the Mn accumulation in the southern Adriatic can be derived from the detrital material from the Albanian hinterland. The suspected main source of Mn concentrations in the Jabuka Pit is probably the submarine weathering of basaltic rocks of the islands Jabuka and Svetac. Contamination from the manganese processing plant located in the Šibenik Bay may also result in very high concentrations of Mn in this basin. The obvious concentration of Mn in the closed depression of the sea bottom is a clear indication of diagenetic redistribution as already discussed by PAUL & MEISCHNER (1976).

Fig. 2 Regional distribution of Al, Ca, Fe, Ti, K, Mg, Mn, P, Ag and As in the surficial bottom-sea sediments of the Adriatic Sea.


Al %
6.50 6.20 5.90 5.60 5.30 5.00 4.70 4.40 4.10 3.80 3.50 3.20 2.90 2.60
Ca %
17.50 17.00 16.50 16.00 15.50 15.00 14.50 14.00 13.50 13.00 12.50 12.00 11.50 11.00 10.50 10.00 9.50 9.00 8.50 8.00 7.50 7.00 6.50
Fe %
4.00 3.80 3.60 3.40 3.20 3.00 2.80 2.60 2.40 2.20 2.00 1.80 1.60 1.40 1.20
Ti %
0.30 0.28 0.26 0.24 0.22 0.20 0.18 0.16 0.14 0.12
K %
2.30 2.20 2.10 2.00 1.90 1.80 1.70 1.60 1.50 1.40 1.30 1.20 1.10 1.00 0.90 0.80 0.70
Mg %
3.40 3.20 3.00 2.80 2.60 2.40 2.20 2.00 1.80 1.60 1.40 1.20 1.00
Mn ppm
2800 2700 2600 2500 2400 2300 2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200
P %
0.07 0.06 0.06 0.06 0.05 0.05 0.04 0.04 0.04 0.03 0.03
Ag ppm
1.20 1.10 1.00 0.90 0.80 0.70 0.60 0.50
As ppm
22.00 20.00 18.00 16.00 14.00 12.00 10.00 8.00 6.00 4.00 2.00 0.00

The total P concentrations vary from 0.03-0.07% and are within the range quoted for the Adriatic by various authors (BRAMBATI et al., 1973; PAUL & MEISCHNER, 1976; FAGANELI et al., 1994). P is substantially enriched in the southern Adriatic, with higher levels along the Italian coast south of Monte Gargano and in the deepest part of the southern Adriatic (Fig. 2). P may be present in marine sediments either as detrital inorganic phosphate minerals, or phosphate ions in association with various sediment compounds, for example alumino-silicate minerals, ferric oxides, manganese oxides and organic matter (BELTAGY et al., 1983). P is also contained in carbonate lattices. A considerable variability of correlation of P with Al, K, Fe and Mn (no correlation in southern Adriatic, appreciable - r = 0.95, 0.96, 0.80, 0.36 in central Adriatic, and moderate correlation - r = 0.62, 0.56, 0.73, 0.78 in northern Adriatic) indicate different chemical combinations of this element. No correlation in the southern Adriatic suggests that the clay minerals and Mn and Fe oxides/hydroxides are not important as the carrier phase. Higher correlation in the central Adriatic may have resulted due to the close association between clay minerals and P, and between P and Fe. In this area P also shows a high affinity towards iron which probably suggests the importance of iron oxides in the removal of phosphate ions from sea water (BERNER, 1980).

In the northern Adriatic the most important bounded phases for P are the Mn and Fe oxides, and clay minerals. The absence of a statistically significant correlation of P with C org. most probably limits the role of organic matter as a carrier phase of P.

The concentrations of Ti range from 0.11-0.31%. The highest values (0.20-0.31%) were recorded in the southern Adriatic along the eastern coast, and could be attributed to the weathering of mafic rocks of the Albanian hinterland. Slightly lower Ti (0.15-0.30%) occurs in the northern Adriatic, where this element is slightly enriched in the vicinity of some industrial and urban centres and where it decreases with distance from it. The lowest Ti concentrations are restricted to the central Adriatic, mostly along the Dalmatian coast.

The Ba concentrations range from 109-336 ppm. The highest concentrations (230-336 ppm) were found along the Italian coast and in the deepest part of the southern Adriatic. The correlation between the concentrations of Ba with K and Al (r = 0.69, 0.62 southern Adriatic, 0.95, 0.85 central Adriatic and 0.88, 0.88 northern Adriatic) confirm the importance of the aluminosilicate minerals as the main carrier phase for Ba. Due to the nearly identical ion size Ba occurs in a number of silicate structures as the most important substitution for K. Barium may also be associated with iron-manganese oxyhydroxides (DE LANGE et al., 1990; DYMOND et al., 1992). This is confirmed by the positive correlation of Ba with Fe and Mn. However, a considerable variability of correlation (r = 0.25, 0.56 southern Adriatic, 0.32, 0.73 central Adriatic, 0.63, 0.73 northern Adriatic) suggests a variable relationship between Ba, Fe and Mn.

The organic carbon contents range from 0.5-1.4% (FAGANELI et al., 1994). The majority of organic matter originates from both marine and terrestrial sources. The fate of organic matter due to its low concentrations seems to be unimportant with respect to the processes for the removal and fixation of the metals in the surficial sediments of the open Adriatic. This is confirmed by the low correlation ($0.29 \leq r \leq 0.63$) of C org. with several elements (Al, Fe, Co, Sr, Cu, Pb, Se, V and Zn) in the northern Adriatic. Similar correlation between C org. and Cr was also observed in the southern Adriatic, while in the central Adriatic there was virtually no correlation of C org. and the trace metal contents of the sediments. Such low correlation most probably suggests that these metals may be concentrated to a lesser degree on organic matter probably by ion exchange complexing and chelation or adsorbed on fine grained sediments associated with a higher C org. content.

4.3. TRACE ELEMENTS

4.3.1. Southern Adriatic Sea

The highest concentrations of most trace elements, such as Be (2.7 ppm), Co (25 ppm), Cu (44.9 ppm), Cr (246 ppm), Ni (264 ppm), Sc (15.9 ppm), Th (8.2 ppm), V (142 ppm) and Zr (53.9 ppm) are found in the southern Adriatic (Table 1). Sediments from this area also exhibit high concentrations of As (1-19 ppm), La (22.3-28.8 ppm), Hg (69-418 ppb), Pb (5-18 ppm) and Zn (58-101 ppm) and rather low concentrations of Ag (0.5-1.3 ppm), Sr (290-664 ppm) and U (1.5-3 ppm).

Several trace elements, among them Co, Cr, Cu, Ni, Sc, V and Zn, are strongly related to the catchment geology, with the greatest concentrations occuring in inshore sediments along the Albanian, Montenegro and southern Dalmatian coasts. This area also coincides with the dominantly pelitic silty sediments, originated from the Albanian riverine inputs. In the drainage area of the Albanian rivers the mineralized mafic, ultramafic and other igneous as well as metamorphic rocks are exposed which are the main source of these elements in the southern Adriatic. A significant correlation of Fe, Ti, Co, Cr, Ni, Sc, V and Zn with each other (correlation coefficient $0.62 \leq r \leq 1$) and Mg (correlation coefficient $0.66 \leq r \leq 0.96$) indicate the close link of these elements with the Albanian ophiolite outcrops and the river Drini inflow. This is also confirmed by the peak elemental concentrations of Al, Fe, K, Mg, Ti, Co, Cr, Ni, Sc and V, as well as by the high concentration levels of Cu (42.7 ppm) and Zn (97 ppm) close to the mouth of the river Drini (sampling point 5). Additional support to these observations has come from the heavy mineral accumulations (chromite, titanomagnetite, ilmenite and rutile) found in the offshore sands of the southern Montenegro coast (JANKOVIĆ, 1967). Other sources of these elements are probably of anthropogenic origin. Albanian rivers also receive discharges from mining activities (Cr, Ni, Cu) and industry. In the eastern part of the southern Adriatic the regional trends of Al, Fe,

K, Ti, Co, Cr, Ni, Sc, V, Zn and partly As, Cu and Mg show common features (Figs. 2-4). The highest levels of most of these elements occur in the vicinity of the river Drini inflow, and then trend towards northwest along the coast, and further west between Dubrovnik and Monte Gargano, following the northeastern bottom contours of the basin. This distribution results from the other Albanian riverine inflows and is further controlled by the roughly anti-clockwise water circulation system of the Adriatic. Higher current velocities occur near the shore, and there is little circulation in the centre of the basin. The metal level mostly decreases in the seaward direction. The only exception is Cu with a peak in the central part of the basin.

In the western part of the southern Adriatic trace element values maintain relatively low levels. Silver, As, Co, Cr, Cu, Ni, Sc, V and Zn concentrations are lower than those reported for the eastern part of the basin. The exceptions are Ba, Be, La, Th, U and Zr which are enriched along the western part of the southern Adriatic. The highest concentrations of As (19 ppm), Hg (149 ppb), Pb (18 ppm) and Zn (101 ppm) were measured in the northern part of this basin.

The lack of any significant correlation between trace metals and organic carbon content most probably indicates that metals in the southern Adriatic are primarily associated with inorganic matter. The most consistent observation is an enrichment of several trace elements in clay minerals, Fe sulphides, and/or Fe and Mn oxide/hydroxides. Clay minerals are characterized by a large surface area per unit mass, and this is considered to be the major reason for enrichment of trace metals on clays (PANDARINATH & NARAYANA, 1992). This seems to be confirmed by a strong correlation of Be, La, Sc, Th, V, Zn ($0.79 \leq r \leq 0.96$) with Al and K. Alternatively, the correlation of Fe with Co, Cr, Ni, Sc, V and Zn ($0.79 \leq r \leq 1$) indicates that these metals may also be present in association with pyrite and/or partly as pure metal sulphide phases. DYRSSEN (1985) pointed out the possible role of precipitating Fe sulphides and/or Fe oxides/hydroxides as a scavenger for trace elements. If the detrital fraction is considered, it is quite clear that the trace metals are also present in the heavy mineral fraction. Correlation of Fe, Ti, Co, Cr, Ni, Sc, V and Zn with Mg ($0.66 \leq r \leq 0.96$) suggests that their presence in the lattice of Mg-bearing minerals also might be an important factor controlling their distribution.

4.3.2. Central Adriatic Sea

In the central Adriatic, the highest concentrations were measured only for As (32 ppm) and Sr (888 ppm) (Table 2). Surficial sediment contents of Ba (109-231 ppm), Be (1.0-2.3 ppm), Co (10-23 ppm), Cu (9.8-32.7 ppm), Hg (20-253 ppb), La (13.5-27.6 ppm), Ni (49-173 ppm), Sc (5.7-11.8 ppm), Th (3.7-7.8 ppm), V (50-116 ppm), Zn (38-95 ppm) and Zr (20.2-47.2 ppm) are generally lower when compared with the southern Adriatic, and the Ag (0.5-1.3 ppm), Pb (7-14 ppm) and U (1.2-3.7 ppm) contents are similar.

The main sources of trace metal accumulation in the central Adriatic are inflowing currents from the southern Adriatic and the outflowing currents along the Italian coast, as well as the impact of agricultural, touristic, domestic and industrial wastes discharged both directly and via rivers. The regional distribution (Figs. 2-4) indicates that Ag, As, Co, Cr, Cu, Ni, Sc, V and Zn enter from the southern Adriatic by the prevalent currents and follow the bottom contours of the basin. Good correlation of the elements suggests similarities in their sources and post depositional behaviour. In fact, the distribution of Cu, Sc, V and Zn show that these elements have at least two sources, the southern Adriatic basin and the Italian mainland.

The high Ba, Be and Zr concentrations are restricted along the Italian coast and they decrease in an offshore direction. Their distribution patterns are similar, and are generally related to the areal distribution of clay minerals.

Mercury, La, Th and U are introduced in the central Adriatic mostly from sources in the northern Adriatic and the Italian mainland. The highest concentrations of Hg found in the northern and western part of the basin probably originated variously from human (industrial and mining activities) and natural sources (Hg mineralization in the drainage area of the Soča - Isonzo river). The distribution pattern of La and Th is characterized by a slightly higher content in the northern and western part of the basin followed by a seaward decrease, while higher U concentrations were observed in the northern and southern part (Fig. 4). The distribution patterns of these elements are slightly different. The possible sources of La, Th and U probably include their natural content in clay minerals and industrial wastes.

Lead showed an areal distribution completely different from the other metals (Fig. 3). Higher concentrations were found along the Dalmatian and Italian coastal areas. The metal level decreased seawards, indicating that there is an anthropogenic input of Pb to the study area. The major sources are supposed to be industrial and domestic wastes.

It is interesting to compare offshore sediments with sediments taken from the coastal area of the central Adriatic in the vicinity of the industrial and urban centres such as Zadar, Šibenik, Split and Ploče (ZVONARIĆ & STEGNAR, 1987; PROHIĆ & JURAČIĆ, 1989). Such comparisons show that trace metal concentrations of As (9.7-11.8 ppm), Cu (21.8-49 ppm), Hg (210-110 ppb) and Zn (90.5-182.6 ppm) are systematically higher than those from the offshore, suggesting the influence of industrial and urban effluents on the heavy metal contents in the coastal area. In the Kaštela Bay (near Split), which is one of the most polluted areas in the central Adriatic due to the discharge of the large quantities of untreated domestic and industrial wastes the situation is even worse. The highest concentrations in surficial sediments from this bay measured by VUKADIN et al. (1982) are as follows: As - 28.0 ppm, Co - 10.0 ppm, Cu - 550 ppm; Hg - 4390 ppb and

Pb - 1275 ppm. By comparison with a few published data from Italian coastal areas of the central Adriatic (GIORDANI et al., 1989), metal concentrations shown in this study also indicate an increased loading of trace metals to the Italian coastal ecosystems.

Lack of significant correlation between organic carbon and trace metals indicates that the interaction between organic matter and trace metals is not an important process for the removal and fixation of the metals in the central Adriatic.

The high correlations of Ba, Be, Cu, La, Sc, Th, V, Zn and Zr with Al ($0.85 \leq r \leq 0.98$) and K ($0.80 \leq r \leq 0.96$) indicate the close association of these elements with the clay mineralogy. On the other hand very strong correlation ($0.73 \leq r \leq 0.96$) between the Fe content and Ti, Ba, Co, Cu, La, Sc, Th, V, Zn and Zr concentrations show that some of the investigated trace metals occur in the form of metal sulphides in the anoxic environment probably, in association with authigenic pyrite and/or partly as pure metal sulphide phases. In the oxic environment the Fe oxides/hydroxides seem to have an important role in precipitating heavy metals. It is known that Fe and Mn oxyhydroxides are very effective scavengers for heavy metals (JENNE, 1968; TAYLOR et al., 1983; ARAKEL & HONGJUN, 1992). Incrustations of Mn oxides/hydroxides on mollusc shells from the Jabuka Pit suggest a diagenetic redistribution of this element in the surficial sediments as already discussed by PAUL & MEISCHNER (1976). At the sediment water interface dissolved Mn^{2+} diffuses into the overlying water, which due to mixing and precipitation of MnO_2 by dissolved O_2 maintains low Mn^{2+} concentrations. This mechanism which is active over the whole basin, may explain the formation of Mn coatings on mollusk shell fragments which are slightly enriched in Ag, Co, Cu, Ni, Pb and Zn (DOLENEC & FAGANELI, 1996).

The most striking feature is the negative or lack of correlation between Mg and the trace metals. A possible explanation is that minerals containing Mg in the central Adriatic do not play any role as a carrier phase and/or in the removal of trace metals from the seawater. They are mostly restricted to the southern Adriatic with low carbonate sediments.

Another characteristic is the high correlation coefficients between Al, K, Fe, Ti, Ba, Cu, La, Sc, Th, V, Zn, Zr and P ($0.80 \leq r \leq 0.96$), which also suggest that these elements may be related to similar input sources and/or have similar geochemical affinities. Chemical analysis of Fe-Mn oxides from different marine environments indicate the presence of a high phosphorus content in association with these oxides (MANHEIN, 1965). BERNER (1973) also suggested the importance of iron oxides in the removal of phosphate ions from seawater. Thus the geochemical associations between Fe and P in the central Adriatic seems to be evident. A relatively close association of P with Ti, Ba, Co, Cu, La, Sc, Th, V, Zn and Zr may have resulted indirectly due to the close association between iron and phosphorous on the one hand and between iron and these elements on the other. Another possibility is, that phosphorous bearing material may act as an adsorption agent, perhaps as a hydrated ionic species. Mercury is regarded as associated mostly with Al, K, Fe, Ti, Be, Co and Cu.

4.3.3. Northern Adriatic Sea

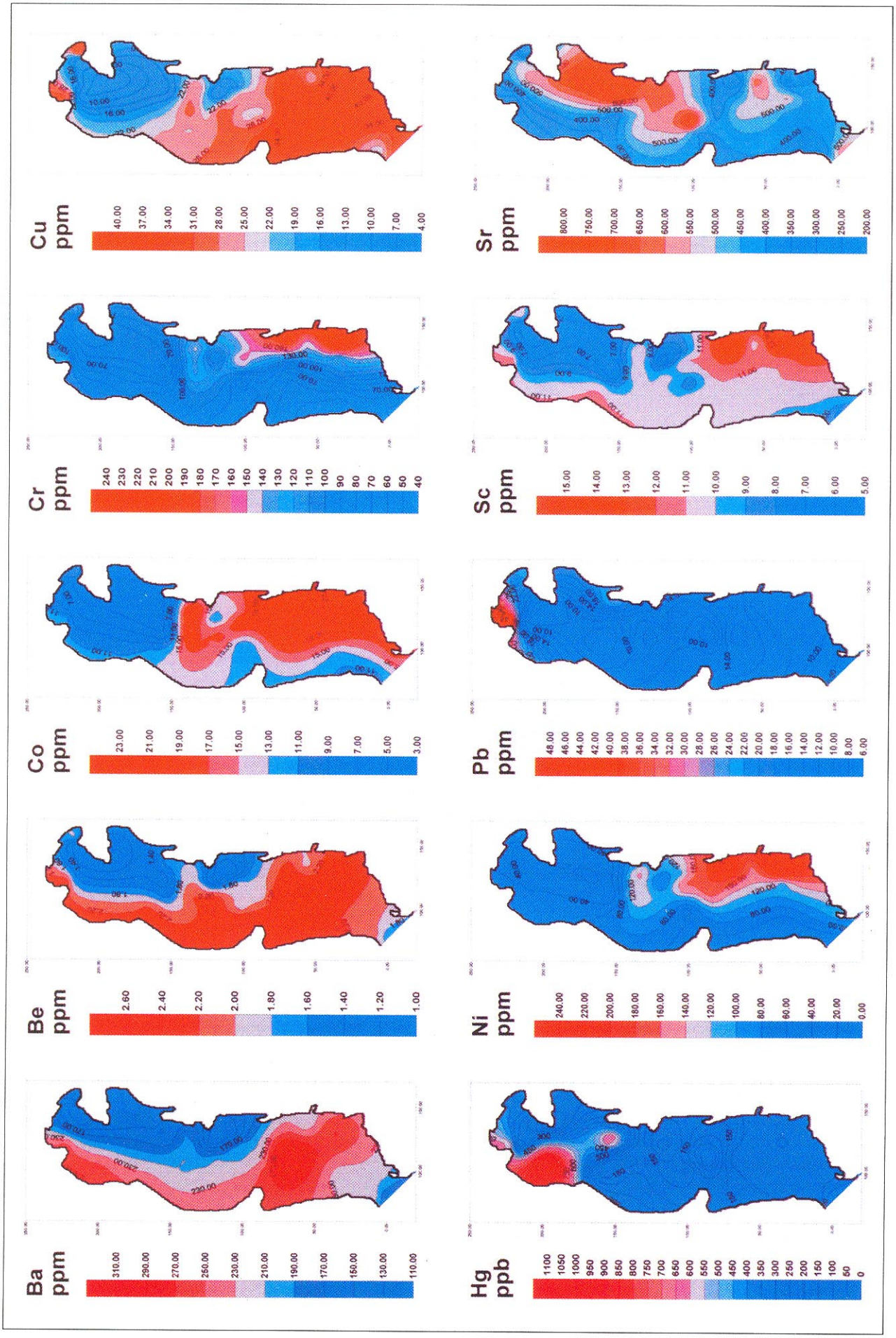
In the northern Adriatic the highest concentrations were measured for Hg (1230 ppb), La (43.2 ppm), Pb (51 ppm), Zn (167 ppm), Th (12 ppm) and U (3.9 ppm) (Table 3). The concentrations of As (1-11 ppm), Ba (117-259 ppm), Be (1-2.4 ppm), Co (4-12 ppm), Cr (40-129 ppm), Cu (4.1-33.4 ppm), Ni (19-86 ppm), Sc (5.1-11.8 ppm), V (39-123 ppm) and Zr (13.5-51.5 ppm) are generally lower than those measured in the southern and central Adriatic, while the Ag (0.5-1.3 ppm) content is similar to that over the whole Adriatic. The regional distribution of these elements is shown in Figs. 2-4.

The northern Adriatic is exposed to pollution due to the inflows of the river Po and other northern Italian (Isonzo, Tagliamento, Livenza, Piave, Brenta, Adige, Reno, etc.) and local Slovenian (Dragonja, Rižana) and Croatian (Mirna, Raša) rivers along which agricultural and industrial as well as mining activities take place. The trace metals are also introduced variously from industry (power plants, oil refineries, chlor-alkaline and other chemical plants of various types, glass factories, the leather industry, and other miscellaneous industrial zones), port areas, urban and touristic centres located along the coast.

The highest concentrations of heavy metals are generally found along the Italian coastal area. These areas are adjacent to the largest concentrations of Italian industry and are thus subject to the highest pollution. The lowest trace metal concentrations were restricted to the sediments along the Istrian and partly along the northern Dalmatian coast. Trace metal distribution in the northern Adriatic shows a general tendency to decrease towards the open sea. Regional trends of heavy metals in the sediments reflect inputs of pollutants via rivers, directly into the sea as well as from the atmosphere.

Silver was reported to be highest in the vicinity and to the south of the mouth of the river Po. Ba, Be, Co, Cr, Cu, Ni, Sc, V and Zr concentrations are elevated along the Italian coast and in the Gulf of Trieste. Pollution of sediments by As seems to be restricted to the inner district of the Gulf of Trieste and along the southeastern Dalmatian coast. Apart from these areas, As concentration levels are largely uniform. The most

Fig. 3 Regional distribution of Ba, Be, Co, Cr, Cu, Hg, Ni, Pb, Sc and Sr in the surficial bottom-sea sediments of the Adriatic Sea.


Cu ppm
40.00 37.00 34.00 31.00 28.00 25.00 22.00 19.00 16.00 13.00 10.00 7.00 4.00
Sr ppm
800.00 750.00 700.00 650.00 600.00 550.00 500.00 450.00 400.00 350.00 300.00 250.00 200.00
Cr ppm
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40
Sc ppm
15.00 14.00 13.00 12.00 11.00 10.00 9.00 8.00 7.00 6.00 5.00
Co ppm
23.00 21.00 19.00 17.00 15.00 13.00 11.00 9.00 7.00 5.00 3.00
Pb ppm
48.00 46.00 44.00 42.00 40.00 38.00 36.00 34.00 32.00 30.00 28.00 26.00 24.00 22.00 20.00 18.00 16.00 14.00 12.00 10.00 8.00 6.00
Be ppm
2.60 2.40 2.20 2.00 1.80 1.60 1.40 1.20 1.00
Ni ppm
240.00 220.00 200.00 180.00 160.00 140.00 120.00 100.00 80.00 60.00 40.00 20.00 0.00
Ba ppm
310.00 290.00 270.00 250.00 230.00 210.00 190.00 170.00 150.00 130.00 110.00
Hg ppb
1100 1050 1000 950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0

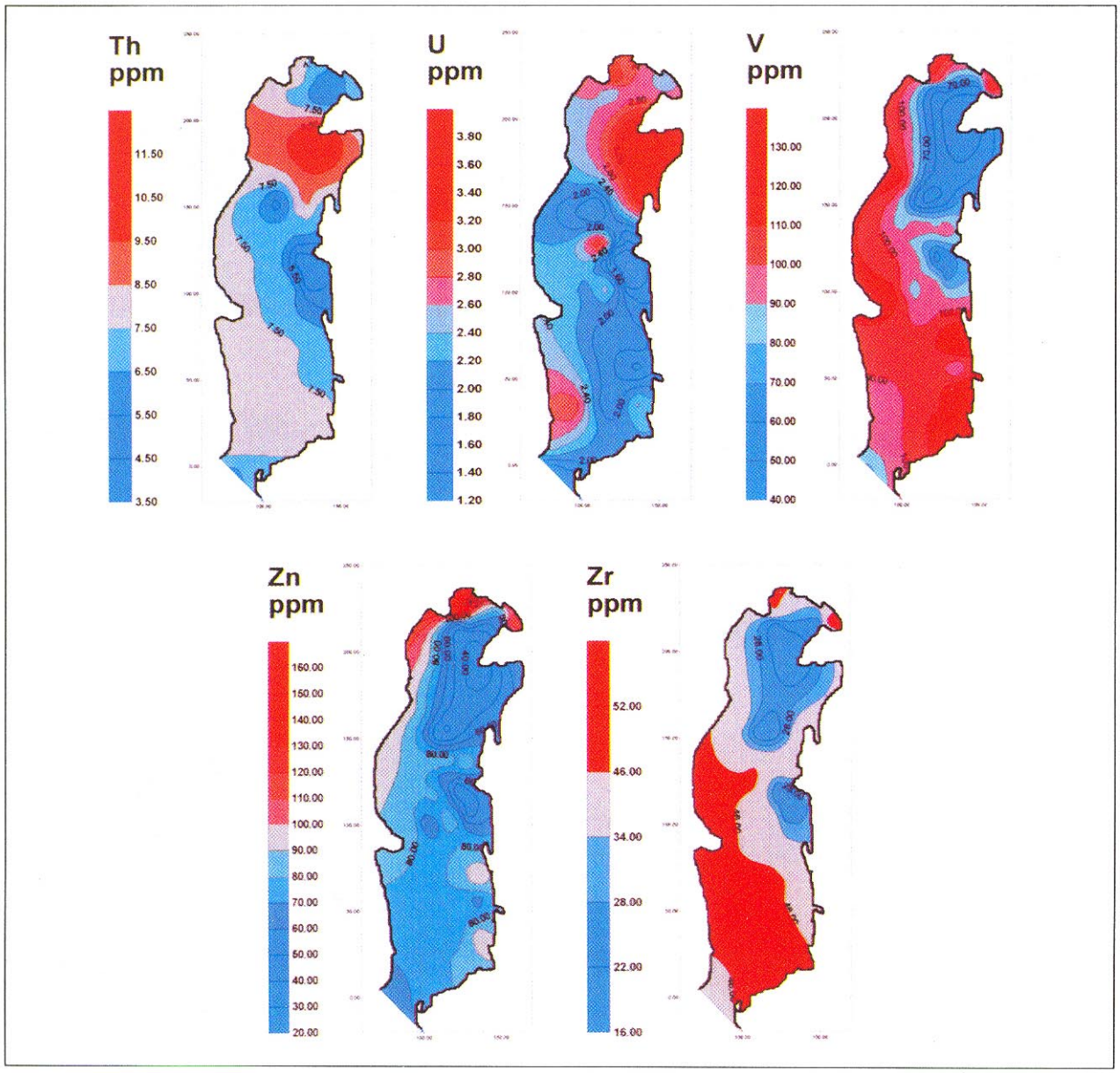


Fig. 4 Regional distribution of Th, U, V, Zn and Zr in the surficial bottom-sea sediments of the Adriatic Sea.

marked enrichment is that of Hg. The highest concentrations (1230 ppb) were measured offshore from the river Po, and are in good agreement with data reported by FERRARA & MASSERTI (1992). High concentrations of Hg were also found in the southern part of the Gulf of Trieste (312-429 ppb). These values are close to the concentrations observed in surficial sediments from this area by FAGANELI et al. (1991). However, the highest Hg contents in the Gulf of Trieste (25 ppm) were reported for the surficial sediments of the Isonzo River outflow (northern part of the gulf) which should be influenced by the Idrija Hg anomaly (DONAZZOLO et al., 1983). Another area of elevated Hg content (775 ppb) is the southeastern part of the basin. The main source of Hg contamination is the suspended riverine matter from the Isonzo and other polluted Italian rivers (FAGANELI et al., 1991; FERRARA & MASSERTI, 1992). The spatial distribution of the Hg content could be attributed to the prevalent marine currents that transport particulate matter towards the central Adriatic. Levels of Pb and Zn are notably high in the northern part of the northern Adriatic. The highest concentrations of both metals were measured offshore from the Po delta (51 ppm Pb, 157 ppm Zn) and in the Gulf of Trieste (26 ppm Pb, 116 ppm Zn). The data obtained agree with those found by GIORDANI et al. (1989), DONAZZOLO et al. (1983), and FAGANELI et al. (1991). Even higher concentrations of Pb and Zn were found for the Isonzo river delta (DONAZZOLO et al., 1983). Such elevated concentrations may result from the Raibl Pb-Zn mine waste dumped into the Isonzo river. The relatively high Pb and Zn concentrations (27 ppm Pb, 64 ppm Zn) were also characteristic for the southeastern part of the northern Adriatic. The Pb and Zn concentrations seem to have been introduced into the northern Adriatic from the coastal and hinterland

area and are strongly influenced by anthropogenic activities. Another probable source of Pb contamination are particles related to petroleum combustion along the coast which are transported by the rivers and through the atmosphere. La, Th and U are slightly enriched in the sediments south of Istria. This enrichment probably reflects the elevated concentrations of these elements in the uraniferous coal and associated carbonaceous shales from the Raša mine (eastern Istria). The mine imputs waste material into the Raša river, which flows directly into the sea.

Significant positive correlation of Ba, Be, Co, Cr, Ni, Sc, V and Zn ($0.78 \leq r \leq 0.96$) with Al and K may indicate a high degree of their association with clay minerals. On the other hand, the correlation coefficient of Co, Cr, Ni, Sc and V with Fe ($0.93 \leq r \leq 0.98$) suggest that these metals are also in close relation with Fe. As inferred from the positive correlation of Ag, Ba, Cu, Zn, Zr, Ti with Fe, Fe is one of the most effective scavengers for trace heavy metals in the northern Adriatic. Ba, Co, Cr, La, Ni, Sc, Ti, Th, V and Zn are also positively correlated with P ($0.43 \leq r \leq 0.70$) and to a lesser degree with Mn ($0.33 \leq r \leq 0.71$). The concentrations of these elements are thus more related to P than to Mn. Pb seems to be associated mostly with Zn ($r = 0.86$). Lack of significant correlation of Hg with any other element suggests no preferred association of this element. It is interesting to note that a positive correlation between organic carbon and trace metal content was found only in the northern Adriatic. This is probably an indication of the often-proposed close association of trace metals and organic matter (DOSSIS & WARREN, 1980; DAVIS, 1984; SIGLEO & MEANS, 1990; COOPER & HARRIS, 1974; SHIMP et al., 1971; HEM, 1972; RUCH et al., 1970). Of the metals studied Zn and Pb showed weak correlation with organic carbon ($r = 0.63$ and 0.60). In the northern Adriatic clay minerals and Fe seem to be the dominant factors in heavy metal bonding, followed by P, Mn and to a lesser extent by the organic matter.

5. CONCLUSIONS

The distribution study of major, minor and trace elements in the surficial part of the sea-bottom sediments from the Adriatic Sea shows that these elements are strongly influenced by the catchment geology, following the structural type of the sediment and the prevalent currents. Their distribution patterns may be further affected by morphological characteristics of the sea bottom, anthropogenic impact and local hydrological and chemical conditions.

The highest trace element concentrations were found in the southern Adriatic and along the Italian coastal areas, with the highest content of clay minerals, while the eastern part of the central and northern Adriatic (Dalmatia and Istria) with the lowest clay mineral contents and the highest carbonate concentrations exhibit lower trace metal levels. The division of the Adriatic into three parts (the southern, central and northern Adriatic) allows demonstration of the differences in geochemical associations of the investigated elements.

In the southern Adriatic, where certain trace element contents reflect the mafic-ultramafic origin, and to a lesser extent the man-made influence, clay minerals and Fe exhibit a dominant role in retention of trace elements, followed by Mg and P. Mn is a possible precipitant only for As and Co, while the fate of organic matter with respect to processes affecting the trace element enrichment is unimportant. If the detrital fraction is considered, it is clear that the trace elements are also incorporated in the heavy mineral fraction.

In the central Adriatic where trace elements are introduced from the southern and northern Adriatic, as well as from the land, the correlation of trace elements with Al, K, Fe and P suggest that they are primarily associated with clay minerals, Fe oxides/hydroxides and sulphides, as well as with ionic species or anionic complexes containing P. Mn seems to play only a limited role in scavenging of Ba, Co, Cr, La, Sc, Ti and Th, while the relatively low association of Mg with trace elements and the negative or lack of correlation between organic carbon and trace elements indicate no affinity of these elements with Mg-bearing compounds and organic matter.

In the northern Adriatic, which is considered to be one of the most polluted parts of the Adriatic Sea due to the anthropogenic activities along the Italian coastal area and in the hinterland, clay minerals and Fe are probably the most important carrier phase for trace elements, followed by P and Mn.

By comparison with published data on heavy metal concentrations from the coastal areas it can be concluded that the trace metal levels in surficial sediments from the offshore direction are generally lower than in the coastal areas. The exceptions are As, Ba, Cu and Zr with the peak anomaly in the central part of the southern Adriatic, and Mn with peak values in the Jabuka Pit (central Adriatic).

6. REFERENCES

ARAKEL, A.V. & HONGJUN, T. (1992): Heavy metal geochemistry and dispersion pattern in coastal sediments, soils and water of Kedron Brook floodplain area, Brisbane, Australia.- Environ.-Geol. Water Sci., 20/3, 219-231.

BELTAGY, A.I., EL-SAYED, M.A.K., EL-SABAROUTY, M. & HALIM, Y. (1983): The distribution of phosphorus, iron and manganese in recent marine sediments off the Nile delta.- Acta Adriatica, 24/1-2, 193-203.

BERNER, R.A. (1973): Phosphate removal from sea water by absorption on volcanogenic ferric oxides.- Earth and Planetary Sci. Letters, 18, 77-86.

BERNER, R.A. (1980): Early diagenesis - A theoretical approach.- Princeton University Press, 241 p.

BRAMBATI, A., BREGANT, D., LENARDON, G. & STOLFA, D. (1973): Transport and sedimentation in the Adriatic Sea.- Publicazioni del Museo Friulano di Storia Naturale, 20, 59 p.

BULJAN, M. & ZORE-ARMANDA, M. (1976): Oceanographic properties of the Adriatic Sea.- Oceanogr. Mar. Biol. Ann. Rev., 14, 11-98.

CELET, P. (1977): The Dinaric and Aegean arcs: The geology of the Adriatic.- In: NAIRN, A.E.M. & KONES, W.H. (eds.): The Ocean basnis and margins., Plenum Press, New York, London, 215-261.

COOPER, B.S. & HARRIS, R.C. (1974): Heavy metals in organic phases of river and estuarine sediment. - Marine Pollution Bulletin, 5/2, 24-26.

CORREGGIARI, A., GUERZONI, S., LENAZ, R., QURANTOTLO, G. & RAMPAZZO, G. (1994): Dust deposition in the central Mediterranean (Tyrrhenian and Adriatic Seas): Relationships with marine sediments and riverine input.- Terra Nova, 1, 549-558.

DAVIS, J.A. (1984): Complexation of trace metals by adsorbed natural organic matter.- Geochim. Cosmochim. Acta, 48, 679-691.

DE LANGE, G.J., CATALANO, G., KLINKHAMMER, G.P. & LUTHER, G.W. (1990): The interface between oxic seawater and the anoxic Bannoc Brine; its sharpness and the consequences for the redox-related cycling of the Mn and Bo.- Marine Chemistry, 31, 205-217.

DOLENEC, T. & FAGANELI, J. (1996): Some peculiarities of Mn distribution in the Jabuka Pit (central Adriatic).- 7th International Symposium: The Interaction Between Sediments and Water, Baveno, Book of Abstracts, 62.

DONAZZOLO, R., HIEKE MERLIN, O., MENEGAZZO VITTURI, L., ORIO, A.A., PERIN, G. & SEMENZATO, G. (1979): Mercury contamination in sediments of Venice's Gulf: Preliminary results. IVes Journée Etud. Pollutions, CIESM, Antalya, 1978, 245-249.

DONAZZOLO, R., HEIKE MERLIN, O., MENEGAZZO VITTURI, L., ORIO, A.A., PAVONI, B., PERIN, G. & RABITTI, S. (1981): Heavy metal contamination in surface sediments from the Gulf of Venice, Italy.- Mar. Pollut. Bull., 12, 417-425.

DONAZZOLO, R., HEIKE MERLIN, O., MENEGAZZO VITTURI, L., ORIO, A.A., PAVONI, B. & RABITTI, S. (1983): Toxic elements in bottom sediments of the northern Adriatic Sea (the Italian area).- Thalassia Jugoslavica, 19, 111-119.

DONAZZOLO, R., HEIKE MERLIN, O., MENEGAZZO VITTURI, L. & PAVONI, B. (1984): Heavy metal content and lithological properties of recent sediments in the northern Adriatic.- Mar. Pollut. Bull., 15, 93-101.

DOSSIS, P. & WARREN, L.J. (1980): Distribution of heavy metals between the minerals and organic detritus in a contaminated marine sediment. In: BAHER, R.A. (ed.): Contaminants and Sediments, 1. Ann. Arbour, Michigan, 119-139.

DYMOND, J., SUESS, E. & LYLE, M. (1992): Barium in deep-sea sediment; A geochemical proxy for paleoproductivity.- Paleoceanogr., 7, 163-181.

FAGANELI, J., PLANINC, R., PEZDIČ, J., SMODIŠ, B., STEGNAR, P. & OGORELEC, B. (1991): Marine geology of the Gulf of Trieste (northern Adriatic). Geochemical aspects.- Marine Geology, 99, 93-108.

FAGANELI, J., PEZDIČ, J., OGORELEC, B., MIŠIČ, M. & NAJDNEK, M. (1994): The origin of sedimentary organic matter in the Adriatic.- Continental Shelf Research, 14/4, 365-384.

FERRARA, R. & MASSERTI, B.E. (1992): Mercury concentration in the water, particulate matter, plankton and sediment of the Adriatic Sea.- Marine Chemistry, 38, 237-249.

FRASCARI, F., FRIGNANI, M., GUERZONI, S. & RAVAIOLI, M. (1988): Sediments and Pollutions in the Northern Adriatic Sea.- Annls. New York Acad. Sci., 534, 1000-1020.

GIORDANI, P., GUERZONI, S. & ROVATTI, G. (1989): Metali pesanti e nutrienti nei sediments del mare Adriatico.- Boll. Oceannol. Teor. Appl., No. Spec., 167-175.

HATCH, W.R. & OTTO, W.L. (1968): Bestimmung von Quecksilber in wassriger Phase mit Hilfe der flammenlosen Atomabsorption.- Anal. Chem., 40, 2085-2095.

HEM, J.D. (1972): Chemistry and occurrence of cadmium and zinc in surface matter and ground water. - Water Resources Research, 8/3, 661-679.

JANKOVIĆ, S. (1967): Metalogenetske epohe i rudonosna područja Jugoslavije.- Rudarsko-geološki fakultet u Beogradu i Rudarski institut Beograd, 16 p.

JENNE, E.A. (1968): Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. In: BAHER, R.A. (ed.): Trace Inorganics Water. Adv. Chem. Ser., No. 73, 337-387, American Chemical Society.

JURAČIĆ, M. & PRAVDIĆ, V. (1983): Geochemical and Physico-Chemical Studies on Sediments of the Rijeka Bay. Properties of Sediments as Depositories of Polutants.- Thalassia Jugoslavica, 17, 339-349.

MAJORI, L., NEDOCLAN, G., MODONUTTI, G.B. & DARIS, F. (1979): Level of metal pollutants in sediments and biota of the Gulf of Trieste: a long

term survey.- IVes Journées Etud. pollutions CIESM, Antalya, 1978, 237-243.

MANHEIN, F.T. (1965): Manganese-iron accumulation in the shallow marine environment.- Woods Hole Coll. Rep. Cont., 1637, 217-276.

MEISCHNER, D. & RUMOHR, J. (1974): A light-weight, high-momentum gravity corer for subaqueous sediments.- Senckenbergiana Marit., 6, 105-117.

PANDARINATH, K. & NARAYANA, A.C. (1992): Clay minerals and trace metal association in the Gangolli estuarine sediments, west coast of India.- Estuarine, Coastal and Shelf Science, 35, 363-370.

PAUL, J. & MEISCHNER, D. (1976): Heavy metal analyses from sediments of the Adriatic Sea.- Senckenbergiana Marit., 8, 91-102.

PIGORINI, B. (1967): Aspetti sedimentologici del mare Adriatico.- Memorie della Societa Italiana di Scienze Naturali, Museo Civico di Storia Naturale Milano, 16, 131-199.

PIGORINI, B. (1968): Sources and dispersion of recent sediments of the Adriatic Sea.- Marine Geology, 6, 187-229.

PROHIĆ, E. & JURAČIĆ, M. (1989): Heavy metals in sediments. Problems concerning determination of the anthropogenic influence. Study in the Krka River estuary, eastern Adriatic coast, Yugoslavia.- Environmental Geology and Water Sciences, 13, 145-151.

RUCH, R.R., KENEDY, E.J. & SHIMP, N.E. (1970): Distribution of arsenic in unconsolidated sediments from southern Lake Michigan.- Illinois Geol. Survey Environmental Geology Note, 37, 16 p.

SADIQ, M. (1990): Arsenic chemistry in marine environments: a comparison between theoretical and field observations.- Marine Chemistry, 31, 285-297.

SHIMP, N.F., SCHLEICHER, J.A., RUCH, R.R., HECK, D.B. & LELAND, H.V. (1971): Trace element and organic carbon accumulation in the most recent sediments of southern Lake Michigan.- Illinois Geol. Survey Environmental Geology Note, 41, 25 p.

SIGLEO, A.C. & MEANS, J.C. (1990): Organic and inorganic components in estuarine colloids: Implication of sorption and transport of pollutants.- Reviews of Environmental Contamination and Toxicology, 112, 123-147.

SONDI, I., JURAČIĆ, M., PROHIĆ, E. & PRAVDIĆ, V. (1994): Particulates and the environmental capacity for trace metals. A small river as model for a land-sea transfer system: the Raša River estuary.- Science of the Total Environment, 155, 173-185.

STEFANINI, S. (1971): Distribuzione del Li, Na, K, Sr, Cr, Mn, Fe, Ni, Cu, Zn e Pb nei sediments superficiali dell Adriatico settentgrionale tra Venezia e Trieste.- Mem. Mus. Trident. Sci, Nat., 18, 177-209.

STEGNAR, P., VUKADIN, J., SMODIŠ, B., VAKSELJ, A. & PROSENC, A. (1981): Elements in sediments and organisms from Kaštela Bay.- Ves Journée Etud. Pollutions, CIESM, Cagliari, 1980, 595-600.

TAYLOR, R.M., MCKENZIE, R.M., FORDHAM, A.W. & GILLMAN, G.P. (1983): Oxide minerals in soils: an Australian viewpoint.- Division of Soils, CSIRO, CSIRO - Melbourne/Academic Press - London), 309-334.

VDOVIĆ, N., BIŠĆAN, J. & JURAČIĆ, M. (1991): Relationship between specific surface area and some chemical and physical properties of particulates. Study in the northern Adriatic.- Marine Chemistry, 36, 317-328.

VDOVIĆ, N. & JURAČIĆ, M. (1993): Sedimentologic and geochemical characteristics of the northern and central Adriatic sediments.- Geologia Croatica, 46, 157-163.

VUKADIN J., STEGNAR, P. & SMODIŠ, B. (1982): Fate and distribution of toxic heavy metals in sediments and organisms of the Kaštela Bay.- Acta Adriatica, 23, 307-312.

WALDICHUK, M. (1985): Biological availability of metals to marine organisms.- Mar. Pollut. Bull., 16, 7-11.

WEDEPOHL, K. H. (1978): Handbook of Geochemistry. Vol. 2/3.- Springer-Verlag, Berlin - Heidelberg - New York.

ZVONARIĆ, T. & STEGNAR, P. (1987): Total mercury, cadmium, copper, zinc and arsenic contents in surface sediments from the coastal region of the central Adriatic.- Acta Adriatica, 1-2, 65-71.

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