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Concentrations and Distributions of Some Major and Minor Elements in the Sediments of the River Göksu and Taşucu Delta, Turkey

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The River Göksu is a major freshwater source to the Taşucu delta in the North Eastern Mediterranean basin and as such, may significantly contribute to the transfer of contaminants across this land–sea boundary. The river catchment is predominantly agricultural although it includes some small centres of population. The concentrations and distributions of elements in the sediments along the bottom of the river were studied in order to indicate contamination of the adjacent Mediterranean Sea. Concentrations of the same major and minor elements were also determined in sediment samples collected from the North Eastern part of the Mediterranean basin, adjacent to the River Göksu, in an attempt to investigate the influence of the river on the trace metal concentrations observed in these marine sediments.

Twenty-six surface sediment samples were collected from seven sampling points thought to be representative of the river body and its Mediterranean delta. The freshwater sites were situated up to 100 km from the mouth of the river. Marine sediment samples were collected with a Van Veen-type grab sampler from five different sampling points from three different depths (10 m, 20 m, 50 m). Sampling stations are given in Fig. 1.

Samples were taken from the same embankment throughout the river by coring (15 m depth), using precleaned PVC corers. Immediately after collection the samples were transferred to the laboratory and stored at −20°C in the dark. The samples were oven dried at 70°C (for 24 h) homogenized twice and then digested using hydrofluoric and perchloric acid following the method of Thompson & Walsh (1987).

Digested sediment samples were analysed usings an ARL 3410 Inductively Coupled Plasma (ICP). Precautions were taken at all stages to prevent random or systematic contamination.

Results are given in Table 1. Pearson correlation matrices are displayed in Tables 2 and 3. Table 4 provides enrichment factors and Table 5 compares concentrations of Zn, Cd, and Pb with those reported for other rivers.

Trace metal distributions along the Göksu River and its delta show that there is an increase in Na, K, Co, and Ni concentrations seaward. In contrast, Ca, Sr, and Cr

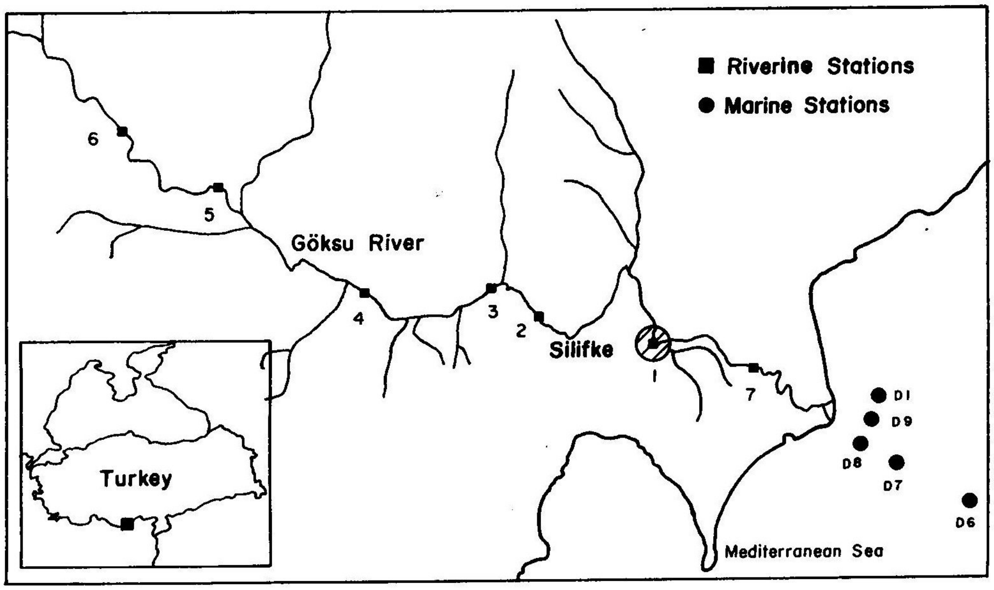

Fig. 1 Riverine and marine sampling stations.

TABLE 1

Concentrations of major and minor elements in sediment samples of the river Göksu and the adjacent Mediterranean Sea (μg g^{-1}).

	Mediterranean sea stations					River Göksu stations						
	Station D1	Station D6	Station D7	Station D8	Station D9	Station 1	Station 2	Station 3	Station 4	Station 5	Station 6	Station 7
Na	11 830±65	12 700±55	12 300±45	11 700±100	11 100±90	4260±320	3950±160	3830±85	3980±180	4120±15	4800±100	4000±120
K	10 900±275	14 310±50	13 750±60	10 400±25	11 000±35	8600±900	7440±100	6900±300	6900±140	8750±250	8700±970	7310±30
Mg	20 200±50	20 100±10	20 590±30	19 960±130	21 250±185	21 600±60	19 680±600	19 900±380	19 700±300	21 000±155	21 900±1250	19 920±570
Ca	178 700±600	160 600±400	162 150±450	188 600±1550	175 700±1600	177 400±1500	195 700±6900	197 800±7000	203 500±6900	181 200±4800	177 800±±4800	193 900±5900
Sr	660±2	580±1	596±1	820±6	560±4	700±40	860±90	920±40	900±80	670±70	650±50	825±40
Ba	300±4	140±1	190±2	400±0.9	195±7	315±115	316±70	190±30	130±2	140±7	170±25	480±95
Al	32 500±80	42 875±5	40 695±5	30 150±165	32 710±180	26 800±2600	22 715±170	20 700±750	20 800±250	26 600±460	24 700±840	22 480±70
Cr	100±1	90±2	97±1	100±2	120±2	230±40	180±35	275±145	300±30	360±50	550±80	270±45
Fe	22 450±60	27 200±5	25 740±60	21 100±200	22 360±170	19 850±830	17 250±165	16 370±32.4	16 500±30	19 700±290	19 300±590	17 320±115
Co	15.5±0.5	17.8±0.3	17.0±0.3	5.0±0.3	15.8±0.25	15.0±0.35	13.0±0.24	12.1±0.11	12.25±0.10	14.63±0.38	14.5±0.50	13.20±0.30
Ni	120±1	130±1	116±0.25	120±2	117±1.5	124±1	107±3	109±6.72	106±2	120±3	120±7	110±3
Cu	23±1	26±1	25±1	22±1	22±0.12	20±2	17.92±0.31	16.54±0.64	15.94±0.68	18.88±1.25	17.67±0.40	16.83±0.25
Ag	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
Zn	38±1	47±1	45±0.5	36±0.25	38±1	35±5	28±1	26±1	26±1	33±1.25	31±0.40	27.42±0.51
Cd	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Pb	6.25±1.25	—	8.75±1.25	6.25±1.25	7.5±0.25	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0

concentrations were higher in the delta than in the marine sediments.

The two major cations, Na and K, in sea water were present in the highest concentrations (>50 μmol kg^{-1}) in the sediments. The increase of these elements in the marine sediments is due to sorption from sea water onto particulate matter.

Concentrations of Ca, Sr, and Cr were of the order of 100 000, 1000, and 100 μg g^{-1} (Table 1) respectively. Concentrations of these elements were lower in the marine sediments than in the river sediments. The riverine sediments originated from calcium rich minerals (carbonates). The decrease of Cr concentrations is probably the result of the effects of discharges from manganese mines on upstream riverine sediments.

Concentrations of Fe, Cr, Ni, and Co were of the order of 10 000, 1000, 100, and 10 μg g^{-1} respectively (Table 1). The increase in salinity with its concomitant increase in the concentrations of the major sea water cations (Na, K, Ca, Sr) and therefore in ionic strength, can lead flocculation and sedimentation of elements such as Ag and Fe (Bruland, 1983) and this must be at least part of the explanation for the increase in concentrations of Fe and other trace elements in Mediterranean Sea sediments.

Concentrations of Ag, Cd, and Pb were generally lower than the detection limit of the ICP analysis (1, 0.5, 5 μg g^{-1} respectively). Thus, the values for Pb are lower than those reported by Whitehead *et al.* (1988) for sediments in the Northern Mediterranean rivers (River Var and River Roya) and by Huynh-Ngoc *et al.* (1987, 1988) for carbonate-rich sediments from the River Rhine. In the absence of any source of lead in these rivers (e.g. lead rich source rocks), it seems clear that the higher values reported by Whitehead *et al.* (1988) and by Huynh-Hgoc *et al.* (1987, 1988) were due to anthropogenic inputs not present in the River Göksu.

In the River Göksu sediments Zn is observed but not Cd. In contrast Whitehead *et al.* (1988) noted the absence of Zn but not Cd in the rivers Var, Roya, and Rhone. Normally Zn and Cd are absent or present together due to geochemical similarity.

Correlation analysis (Jaquet *et al.* 1988) applied to the composition on the River Göksu sediments reveals Al, Fe, and K as components of the carrier substance. Kersten and Klatt (1988) observed the bulk of heavy metals such as Fe to occur in the clay and oxide components of sediments, silicate, and carbonate fractions being practically devoid of such metals. One therefore expects the major component of the carrier substance to be clay minerals known to occur in Göksu Valley.

Tables 2 and 3 show the correlation coefficients between the metals comprising the data set for river and sea sediments respectively. It will be observed that Ca was negatively correlated with virtually all the metals present. Calcium being an obvious marker for carbonate minerals, its negative correlation with heavy metals is confirmation of the important role of clay minerals as the carrier substance.

Enrichment factors, shown in Table 4, are in good agreement with Taylor's (1972) crustal abundance

TABLE 2

Significant (0.05) Pearson correlation matrix of major and minor elements measured in sediments taken from the River Göksu.

	K	Mg	Ca	Sr	Ba	Al	Cr	Fe	Co	Ni	Cu
Na	0.737	0.849	—	−0.803	—	—	0.830	—	—	—	0.336
K		0.920	−0.971	−0.983	—	0.958	—	0.989	0.973	0.892	0.841
Mg			0.953	−0.918	—	0.830	—	0.904	0.915	0.939	—
Ca				0.958	—	−0.931	—	−0.967	−0.969	−0.939	−0.833
Sr					—	−0.915	—	−0.965	−0.964	−0.858	−0.749
Ba						—	—	—	—	—	—
Al							—	0.986	0.972	0.900	0.937
Cr								—	—	—	—
Fe									0.991	0.925	0.880
Co										0.942	0.849
Ni											0.814

TABLE 3

Significant (0.05) Pearson correlation matrix of major and minor elements measured in sediments taken from the Taşucu delta.

	K	Mg	Ca	Sr	Ba	Al	Cr	Fe	Co	Ni	Cu	Pb
Na	0.858	—	—	—	—	—	−0.946	—	—	—	0.945	—
K		—	−0.957	—	—	0.988	—	0.992	0.985	—	0.960	—
Mg			—	—	—	—	—	—	—	−0.674	—	—
Ca				—	0.912	−0.967	—	−0.963	−0.967	—	−0.898	—
Sr					0.952	—	—	—	—	—	—	—
Ba						—	—	—	—	—	—	—
Al							—	0.997	0.992	—	0.962	—
Cr								—	—	—	—	—
Fe									0.995	—	0.970	—
Co										—	0.94	—
Ni											—	—
Cu												—

TABLE 4

Enrichment factor derived for sediments from the River Göksu and Mediterranean delta.

Element	D1	D6	D7	D8	D9	7	1	2	3	4	5	6
Na	1.27	1.03	1.05	1.35	1.19	0.62	0.55	0.61	0.65	0.67	0.54	0.68
K	1.32	1.31	1.33	1.36	1.33	1.28	1.27	1.29	1.31	1.31	1.3	1.39
Mg	2.2	1.65	1.79	2.34	2.29	3.13	2.85	3.06	3.39	3.35	2.79	3.12
Ca	10.9	7.43	7.9	12.41	10.65	17.11	13.12	17.09	18.95	19.4	13.53	14.25
Sr	4.48	2.97	3.21	5.95	3.77	8.05	5.77	8.3	9.78	9.52	5.55	5.73
Ba	1.8	0.63	0.9	2.61	1.14	4.15	2.28	2.69	1.81	1.22	1.04	1.31
Al	1	1	1	1	1	1	1	1	1	1	1	1
Cr	2.73	1.78	1.96	2.81	3.08	9.79	7.08	6.55	10.97	12	11.16	18.44
Fe	1.01	0.93	0.92	1.02	1	1.13	1.08	1.11	1.16	1.16	1.09	1.14
Co	1.57	1.36	1.38	1.64	1.59	1.93	1.84	1.84	1.92	1.94	1.81	1.93
Ni	4.04	3.26	3.12	4.39	3.91	5.39	5.09	5.17	5.77	5.62	4.84	5.24
Cu	1.06	0.91	0.91	1.07	0.99	1.12	1.09	1.18	1.2	1.15	1.06	1.07

pattern. The major expectations are Ca (EF ~15), the basin being carbonate rich, and Cr, the EF distribution being that of a contaminant from an upstream point source where manganese is mined. Since the trace metal distributions depended predominantly on the geological structure of the basin rather than on external influences, this data set may be used as a base case against which to compare environmental factors in other rivers.

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TABLE 5

Average trace metal concentrations in sediments reported in the literature (μg g^{-1})

River	Zn	Cu	Cd	Pb	Reference
Göksu	29±3	17±2	<0.5	<5.00	This study
Rhone	68±16	31±13	0.9±0.6	37±9	Huynh-Ngoc *et al.* (1987)
Roya	1.57±0.76	17±11	0.59±0.27	19±17	Whitehead *et al.* (1988)
Var	—	25±11	0.42±0.33	5.6±1.7	Whitehead *et al.* (1988)

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