

An index of metal pollution in marine sediments

J. SATSMADJIS, F. VOUTSINO-U-TALIADOURI

Institute of Oceanographic and Fisheries Research, GR-166 04 Hellinikon, Greece.

Received 5/3/84, in revised form 5/3/85, accepted 14/3/85.

ABSTRACT

A method is described for detecting the slightest metal pollution in marine sediments even and assessing its exact degree. It involves a technique leading to a formula that gives the amount of the element in a sediment as a function of the percentage of clay and silt in the latter. Virgin sections of the investigated region or an adjoining unsullied zone afford the data necessary for the establishment of the concentration equations. These permit the calculation of the ratio of the actual content at a particular spot to that estimated from the granulometric determination. This ratio, if it exceeds one, measures the extent of the pollution by the metal in question. The study of three Greek gulfs illustrates the application of the procedure and demonstrates its advantages.

Oceanol. Acta, 1985, 8, 3, 277-284.

RÉSUMÉ

Un indice de pollution des sédiments marins par les métaux.

On décrit une méthode permettant de déceler dans les sédiments marins une pollution même légère par les métaux et d'évaluer son degré exact. Elle utilise une technique qui aboutit à une formule donnant la teneur en un élément d'un sédiment en fonction du pourcentage en argile et en silt de ce dernier. Des parties vierges de la région examinée ou une zone contiguë non souillée fournissent les données nécessaires à l'établissement des équations de concentration. Ces équations servent alors à calculer le rapport entre la teneur vraie à un endroit particulier et celle estimée à partir de la détermination granulométrique. Si ce rapport dépasse 1, il permet de mesurer le degré de pollution par le métal en question. L'étude de trois golfes grecs illustre ce procédé et démontre ses avantages.

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INTRODUCTION

Industrial effluents and domestic wastes frequently contain amounts of heavy metals far in excess of those in natural waters. In consequence, when discharged untreated into the sea, either directly or through a stream, they tend to cause local pollution of the sediments. The usual way for illustrating this kind of impact of man on his environment is to draw isoconcentration curves of each element determined in the investigated area. Heavy contamination results in a steep concentration gradient round the mouth of the river or the sewage outfall. A comparison with distant zones affords an idea of its extent, but not with absolute figures.

To avoid this basic deficiency, Papakostides *et al.* (1975), as well as Grimanis *et al.* (1977) had recourse to a "micropollutant index". The major defect of this index is that it increases with the number of the figures involved, is a collective one and depends on the election

of the spot considered clean. In addition, any change in oligoelement composition of a sediment does not always come from human activity. Natural metal sources do exist and cause local enrichment. Major constituents, through sheer bulk, have some effect. Thus, on the one hand, Voutsinou-Taliadouri and Satsmadjis (1982 *b*) observed percentages of carbonates as high as 77 in the Aegean Sea, while on the other hand, Turkian and Wedepohl (1961) found deep-sea average levels of many elements much lower in carbonates than in clay. Because of that, Chester and Aston (1976) and Shearme *et al.* (1983) quoted all metal concentrations on a carbonate free basis; Trefry and Presley (1976) noticed that the leachable iron content and the percentage of clay in sediments from San Antonio Bay (Gulf of Mexico) had a higher correlation coefficient when the former was calculated on a carbonate free basis. But the cardinal factor influencing the microconstituent composition is the texture of the sediment. Hallbach *et al.* (1979) established that, in a manganese nodule field,

the percentage of silicate increased with the grain size, thereby affecting the concentration of metals. Usually, the finer the particles, the greater the content. In consequence, for making comparisons or assessing the degree of pollution, some workers advocated examining part only of the sample. Copeland (1972) and Thornton *et al.* (1975) chose the fraction passing through a 200 μm nylon sieve, while Cameron (1974) and Chester and Stoner (1975) preferred that finer than 63 or 61 μm . Banat *et al.* (1972 a; b; c), Gadow and Schäfer (1973) and Helmke *et al.* (1975), going a step further, recommended considering only the clay or *pelitic* (2 μm) portion. Obviously, such practices carry a risk, which grows with the percentage of material discarded, especially when the separation process involves dispersion and standing in a large volume of water. De Groot (1964) assumed a linear relationship between the concentration of metal and the percentage of the fraction < 16 μm and extrapolated for 100%. Salomons and De Groot (1977) and Salomons and Mook (1977) elected to refer to a proportion of grains finer than 16 μm of 50% only. Renzoni *et al.* (1973) estimated the level of the constituent, at each site as a function of the logarithm of the inverse of the average diameter of the particles. However, their samples comprised mostly coarse sand, an unfrequent occurrence. Satsmadjis (1982), studying the effect of the texture of the sediment on macrozoobenthos, conceived an index of coarseness, or sand equivalent, s' , based on the percentage of sand, s , and that of silt, t , (4–62 μm), such as:

$$s' = s + t/(0.2s + 5) \quad (1)$$

Voutsinou-Taliadouri and Satsmadjis (1982 a) established the following relationship between the concentration c , and the above index in a homogeneous and nearly unsullied gulf:

$$c = c_1 \cdot k \cdot s'^d, \quad (2)$$

where c_1 , k and d are constants. The sand equivalent ideally suits benthic work, owing to the large particles favouring life on the sea floor and mud checking it (Bogdanos, Satsmadjis, 1983). But its use in the case of metals has the disadvantage of making d negative in equation (2).

METHODS

The sediment samples are collected with a grab of the van Veen type and stored in deep freeze. The granulometric composition is estimated according to a procedure adapted and modified from Buchanan's (1971). The wet sample, weighing from 5 to 50 g, is stirred for fifteen minutes with 60 ml of 10% w.w. hydrogen peroxide, left overnight at room temperature and heated at 50–60°C in a water bath for a period of two or three hours. The dispersion is further improved by the addition of 10 ml of 5 g/l sodium hexametaphosphate and ten minute mechanical agitation. Wet sieving

isolates sand (weight g). The remainder is transferred into a glass stoppered 1 litre measuring cylinder, its volume brought to the mark and its temperature adjusted to 20°C. Immediately upon violent shaking, 20 ml are pipetted from a depth of 20 cm and evaporated to dryness (weight h = silt + clay + soluble matter). Two hours and 3 minutes later, 20 ml are withdrawn at a 10 cm depth and their solid content determined (weight i = clay + soluble matter). After a least one day, a volume of 20 ml of clear liquid is taken out from just below the surface and its soluble matter, j , measured. Weight of sample: $g + 50 (h - j)$; % sand (> 62 μm) = $100 g/[g + 50 (h - j)]$; % silt ($\leq 62 \mu\text{m}$, > 4 μm) = $100.50 (h - i)/[g + 50 (h - j)]$; % clay ($\leq 4 \mu\text{m}$) = $100.50 (i - j)/[g + 50 (h - j)]$.

For the estimation of the metal concentrations, the sediment is ground in an agathe mortar to pass a 0.45-mm nylon sieve, in order to reduce the influence of its coarseness on the extent of the analytes recovery. About 5 g of the dry powder, weighed in a 100-ml plastic bottle, are shaken for 16 hours at room temperature with 75 ml of 2 N hydrochloric acid. The 2N strength achieves much the same degree of extraction as the digestion of 1 g of the material in 50 ml of concentrated nitric acid for 1 hour at 130°C (Voutsinou-Taliadouri, Satsmadjis, 1982 b). The method is not novel. Agemian and Chau (1976) agitated overnight at room temperature 5 g of sediment in 100 ml of hydrochloric acid. Chester and Voutsinou (1981) stirred 5 g of sample in 75 ml of cold hydrochloric acid for 16 hours. However, both groups of workers selected an acid concentration of only 0.5 N, which can fully decompose only respectively 50 and 37.5% of calcium carbonate in the 5 g of treated sample. The determination of the metal content of the leachates is performed on an atomic absorption spectrophotometer provided with a deuterium lamp background corrector. In the case of very low levels, the graphite is used, instead of the flame. The procedure followed is that of Satsmadjis and Voutsinou-Taliadouri (1981).

The proportion of organic carbon, often related to pollution, is estimated after Gaudette *et al.* (1974).

PROPOSED INDEX

The assessment of the degree of pollution of a sediment by a certain element requires at first the relation of its content, c , to the granulometric composition of the substratum in clean sections of the investigated region. The authors' well tried equation (2) becomes even more accurate when substituting for the "sand equivalent", s' , an index of fineness, or "clay equivalent", f , such as

$$f = g + t/(0.2 g + 5), \quad (3)$$

where g and t indicate the percentages of respectively clay and silt.

This formula resulted from the analysis of a large number of data, concerning Greek gulfs, which revealed that, in general, g has the greatest effect upon c , while

t plays a usually minor part, which gains import as g diminishes. After replacing in (2) c_1 with E , d with d' and s' with f , the concentration function becomes:

$$c = E \cdot k \cdot f^{d'} \quad (4)$$

Making $d' = \log d / \log (f_1/f_2)$ produces a variant. Thus:

$$\log c = \log (E \cdot k) + d' \log f$$

$$= \log (E \cdot k) + [\log d / \log (f_1/f_2)] \cdot \log f$$

$$\log c = \log (E \cdot k) + \log d [\log f / \log (f_1/f_2)],$$

$$c = E \cdot k \cdot d^{\log f / \log (f_1/f_2)} \quad (5)$$

The advantage of the transformation lies in the "enrichment constant" d expressing the magnitude of the influence of the grain size on the concentration of the metal in a readily intelligible way. For it is equal to the ratio of the concentrations c_1 and c_2 , corresponding to f_1 and f_2 , which may represent two widely different in texture types of sediment, the former muddy, the latter sandy. By adopting once for all values of 65 for f_1 and 13 for f_2 , giving a f_1 to f_2 ratio of 5, equation (5) becomes:

$$c = E \cdot k \cdot d^{(\log f / \log 5)} \quad (5a)$$

The enrichment induced by fine particles is very slight for $d < 1.2$, moderate for $1.2 \leq d < 1.4$, substantial for $1.4 \leq d < 2$, great for $2 \leq d < 4$ and huge for $d \geq 4$. E is arbitrary. It may represent the level corresponding to the average index of fineness of all the samples, or to such an average weighted on the basis of the area ascribable to each station, or to any f reference figure, like 50, more or less indicative of the expanses of sea studied. In the last instance, E and d suffice wholly to characterize the distribution of the constituent in the homogeneous region and permit reliable comparisons of various parts of the world. Equation (5a) leads to

$$\log c = \log (E \cdot k) + (\log f / \log 5) \cdot \log d,$$

$$\log c = \log (E \cdot k) + (\log d / \log 5) \cdot \log f,$$

which, through linear regression analysis, provides the coefficients $\log (E \cdot k)$ and $(\log d / \log 5)$, thereby $(E \cdot k)$ and d , hence also E and k . The percentage ratio q , of the true concentration of the metal, c' to that, c , calculated from equation (5a) on the basis of the grain size composition of the sediment measures its "pollution ratio".

However, finding the proper data to set up (5a) presents great difficulty, since not easily discernible factors may boost the level of an element in a seemingly virgin zone. In consequence, the suitability of a sampling location as a reference one for a specified constituent should be demonstrated. To that end, all the figures, except those grossly excessive, are at first taken into account roughly to estimate (5a). Those raising q above a certain level, q_0 , are then omitted before determining (5a) again. On the rare occasions the new formula does not lead to q ratios below q_0 for all (possibly but one or two) the stations from which it was established, a third regression analysis takes place. A value of q_0 of 130 proves satisfactory in most cases. Altering it to, say, 120 or 140, only slightly affects the concentration function.

APPLICATION OF THE PROCEDURE

The above method was tried on three Greek gulfs. Patraikos (Fig. 1), though contaminated round its edge (Varnavas, Ferentinos, 1983), appears clean some distance from the shore. Pagassitikos (Fig. 2), reveals a few anomalies. Thermaikos (Fig. 3) suffers from rather heavy pollution. Tables 1, 2 and 3 list both the levels, c' , of analytes and the calculated "pollution ratios", q , at each station. The c' figures marked by an asterisk were discarded when estimating the coefficients of equation (5a).

Table 4, concerning the Patraikos Gulf, demonstrates the reliability of (5a), with the coefficient of variation of q , v , averaging 14 before any exclusion and 13 after omitting four data out of a total of 189. Following rejection of the outliers, the correlation coefficient (corrected), r , between c' and f of all the analytes (mean 0.77) points to a confidence level far better than 1% (for which $r=0.54$). If the granulometric composition

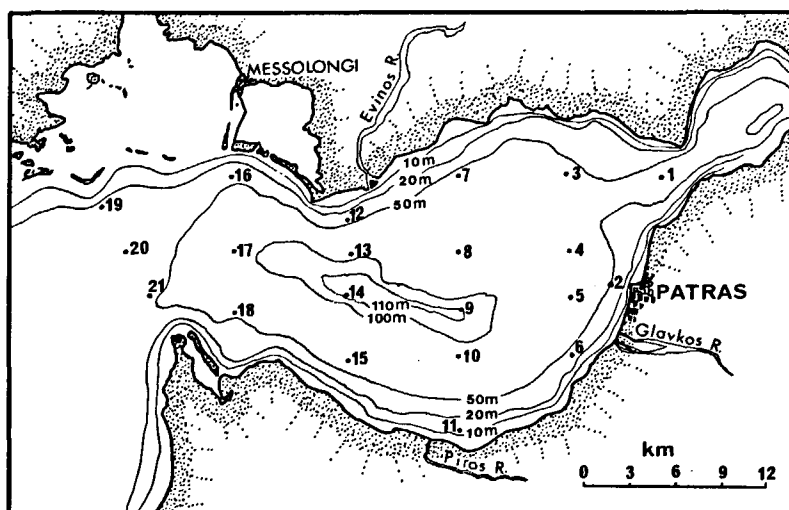


Figure 1
Sampling locations in the Patraikos Gulf.

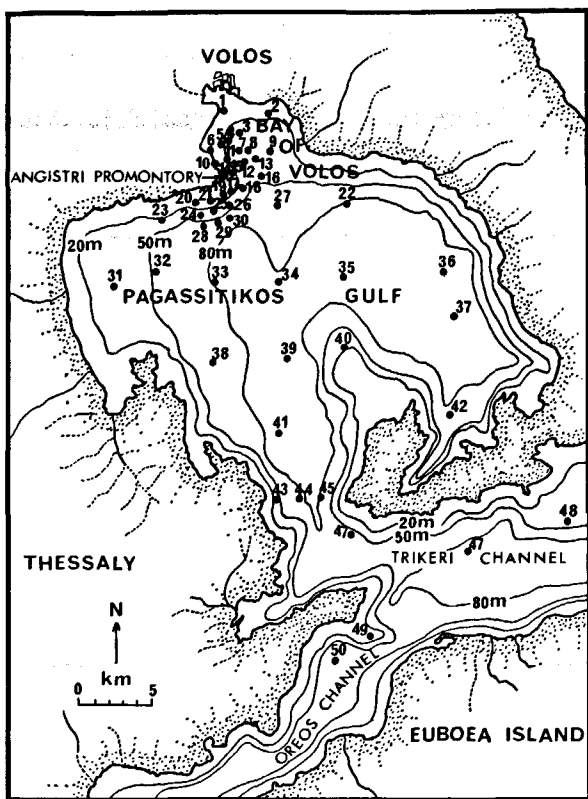


Figure 2
Sampling locations in the Pagassitikos Gulf.

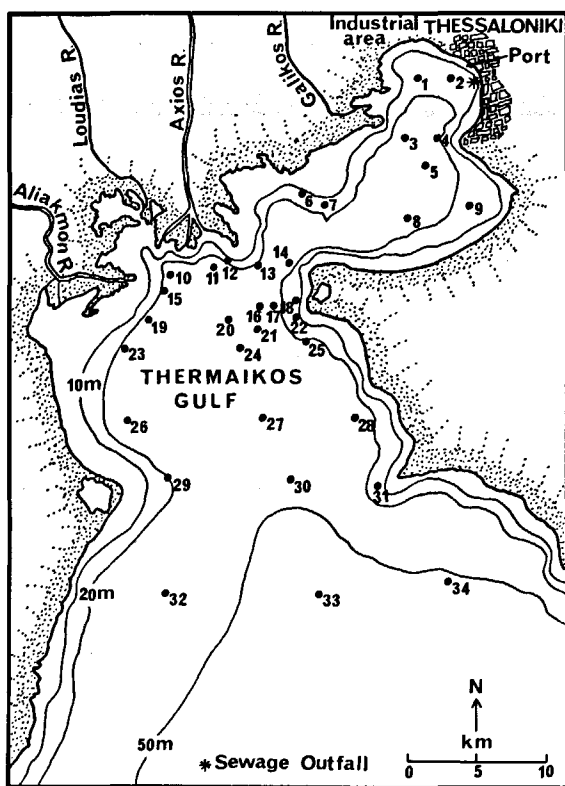


Figure 3
Sampling locations in the Thermaikos Gulf.

of the samples were ignored, comparisons with stations 1, 18 and 16, (see Tab. 1) would suggest pollution elsewhere. The Pagassitikos Gulf, as shown in Table 5, differs somewhat from the Patraikos Gulf. Its rejected concentration figures amount to 15% of the total, instead of barely 2%. Over half of them relate to samples taken in the Bay of Volos, or near the Angistri Promontory. As a rule, they prove some human interference there. On the contrary, the remainder suggests only

natural anomalies. After the removal of abnormal data, *c'* and *f* have a mean *r* exceptionally great, 0.78, with respect to the 42° of freedom. This coefficient reflects a low *v* (mean 16) and a rather high *d* (mean 2.5). When not allowing for the texture of the sediment, the *c'* values give a picture of the state of pollution in the region exactly the converse of the true one. Table 6 indicates that the Thermaikos Gulf, surprisingly enough, has only 25% of its concentration figures

Table 1
Concentration, *c'*, of metals (in mg.kg⁻¹) or of organic carbon (in percent.) and "pollution ratio", *q*, in the Patraikos Gulf.

Stat.	Ind. fin	Org. carb.		Iron		Manganese		Zinc		Copper		Lead		Chromium		Nickel		Cobalt	
		<i>f</i>	<i>c'</i>	<i>q</i>	<i>c'</i>	<i>q</i>	<i>c'</i>	<i>q</i>	<i>c'</i>	<i>q</i>	<i>c'</i>	<i>q</i>	<i>c'</i>	<i>q</i>	<i>c'</i>	<i>q</i>	<i>c'</i>	<i>q</i>	
1	31.2	0.43	95	22000	105	750	111	54	109	27	126	14	122	79	109	94	120	16	116
2	55.2	0.78	120	29000	102	1500	118	74	102	40	116	19	122	107	106	113	103	21	109
3	57.6	0.53	79	30000	103	1320	99	83	112	37	103	18	113	113	110	120	106	22	111
4	64.4	0.78	109	30000	97	1780	118	80	100	39	99	18	106	111	101	124	103	22	104
5	62.1	0.65	93	30000	99	2160	150	80	102	42	110	20	121	115	107	124	105	22	106
6	58.7	0.69	102	31000	106	1200	88	79	105	38	105	16	99	109	104	116	101	21	105
7	67.0	0.77	104	32000	102	1160	74	81	99	42	103	16	93	115	102	128	103	21	97
8	58.7	0.61	90	32000	109	2140	158	88	117	42	116	18	112	113	108	127	111	23	115
9	76.3	0.75	94	31000	92	2610	144	84	94	43	95	18	97	116	96	126	94	23	98
10	64.2	0.66	92	32000	104	1610	107	83	104	43	110	17	101	119	108	132	109	23	109
11	66.6	0.82	112	30000	96	800	51	74	91	34	84	14	81	102	91	108	88	19	88
12	45.1	0.70	122	27000	106	1030	102	64	101	34	116	10	72	94	105	98	100	17	99
13	54.2	0.72	112	27000	96	1680	135	62	87	34	100	14	91	95	95	106	97	18	94
14	66.7	0.76	103	30000	96	2210	141	80	98	39	96	16	93	100	89	118	96	21	97
15	67.6	0.73	98	30000	95	1390	88	78	94	34	83	18	104	99	87	116	93	18	83
16	39.1	0.48	92	28000	118	830	96	62	108	31	120	11	85	94	114	100	111	17	108
17	52.2	0.56	89	30000	109	2180	183	78	112	38	115	17	113	107	110	116	109	20	107
18	35.2	0.87	178	16000	71	800	104	43	80	16	67	12	98	55	71	60	71	11	74
19	42.7	0.61	110	26000	105	770	81	57	93	23	82	11	81	87	100	92	97	16	96
20	42.9	0.48	86	28000	113	980	102	72	118	30	107	16	118	100	115	106	112	18	108
21	44.6	0.63	111	22000	87	890	89	53	84	21	73	14	101	75	84	80	82	15	88

Table 2
Concentration, c' , of metals (in mg.kg^{-1}) or of organic carbon (in percent.) and "pollution ratio", q , in the Pagassitikos Gulf.

Stat.	Ind. fin f	Org. carb.		Iron		Manganese		Zinc		Copper		Lead		Chromium		Nickel		Cobalt	
		c'	q	c'	q	c'	q	c'	q	c'	q	c'	q	c'	q	c'	q	c'	q
1	21.2	1.49	336	33 000	125	600	105	121	172	45	202	29	105	96	117	96	88	24	105
2	19.5	0.72	173	30 000	118	490	90	111	166	23	109	28	102	85	108	132	130	26	118
3	22.6	0.85	183	35 000	129	600	101	391	536	32	138	30	108	88	103	109	95	26	111
4	19.3	0.79	191	26 000	103	520	97	65	98	27	128	27	99	70	90	121	120	24	109
5	18.0	0.62	158	21 000	85	360	70	60	94	19	94	28	103	51	68	86	90	22	102
6	21.0	0.48	109	18 000	69	340	60	53	76	117	528	25	91	46	56	135	125	29	128
7	14.7	0.40	118	33 000	146	570	126	96	170	22	124	28	105	71	106	81	99	24	120
8	22.4	0.47	102	39 000	145	660	112	90	124	25	108	30	108	85	100	148	130	29	125
9	17.5	0.50	130	33 000	136	650	128	155	247	30	152	33	121	129	175	101	108	22	103
10	24.8	0.56	113	19 500	69	430	68	65	84	23	94	31	111	62	69	116	94	19	79
11	19.4	0.69	166	34 000	134	480	89	77	115	19	90	27	99	72	92	128	126	25	113
12	16.1	0.70	193	32 000	136	560	117	77	129	22	117	30	111	89	126	88	100	22	107
13	15.7	0.61	172	23 000	99	660	140	59	100	19	103	26	97	85	122	83	97	20	98
14	29.6	0.75	132	33 000	109	500	71	103	120	28	102	27	95	70	71	145	102	26	101
15	25.3	0.55	109	36 000	127	750	117	77	99	28	112	29	104	86	95	154	123	28	115
16	13.5	1.80	565	53 000	242	1 660	390	99	184	38	226	28	105	130	203	76	100	18	93
17	18.5	0.62	155	30 000	120	610	116	66	102	22	107	29	106	79	104	82	84	19	88
18	26.3	0.63	121	28 000	97	620	95	93	116	25	98	30	107	91	98	143	111	26	106
19	33.6	0.78	125	40 000	126	740	97	116	126	37	124	29	101	129	122	158	101	26	97
20	41.0	0.82	114	39 000	113	830	96	152	146	37	110	28	96	135	114	162	89	25	86
21	43.2	0.80	107	33 000	93	810	90	126	118	39	112	30	103	151	124	213	112	29	98
22	47.8	0.77	96	43 000	117	2 220	233	131	115	46	124	20	68	173	134	213	103	35	115
23	33.5	0.68	110	32 500	102	660	87	126	137	24	81	27	94	91	86	129	83	23	86
24	47.3	0.84	105	39 000	106	1 000	106	107	95	40	109	29	98	142	111	220	107	30	99
25	43.0	0.82	110	39 000	111	950	106	105	98	39	112	29	99	143	118	216	114	29	99
26	36.5	0.90	136	38 000	115	830	103	127	131	38	121	27	94	151	136	188	113	28	101
27	15.4	0.46	131	23 000	100	600	129	234	402	14	77	27	100	74	108	66	78	19	94
28	44.4	0.78	102	40 000	112	760	83	173	159	40	113	30	102	144	117	213	109	29	97
29	44.0	0.78	103	38 000	107	940	104	119	110	35	99	29	99	105	85	211	109	28	94
30	47.6	0.85	106	40 500	110	920	97	119	105	40	108	27	92	134	104	185	90	27	88
31	20.1	0.38	89	21 000	81	700	127	38	56	18	83	28	102	72	90	81	78	17	76
32	17.7	0.31	80	34 000	139	850	167	106	168	21	105	26	96	90	121	102	108	20	94
33	52.2	0.79	92	39 000	102	1 700	169	147	123	33	84	31	104	173	128	228	103	30	95
34	63.7	0.90	91	39 000	94	1 920	168	212	157	40	90	32	106	140	93	203	78	29	86
35	65.7	0.71	70	41 000	98	2 500	214	193	140	44	97	32	106	177	115	207	78	34	99
36	46.6	0.98	124	44 000	121	2 090	226	151	135	48	132	30	102	194	153	237	117	38	126
37	47.8	1.10	137	44 000	119	2 820	296	101	89	47	127	33	112	171	133	245	119	35	115
38	47.7	0.77	96	40 000	109	1 110	116	112	99	35	95	27	92	124	96	179	87	28	92
39	60.5	0.85	89	35 000	86	2 520	228	323	247	40	93	34	113	126	86	242	97	32	96
40	59.8	0.87	92	42 000	104	1 940	177	154	118	41	96	35	117	151	104	231	94	33	100
41	60.1	0.65	68	32 000	79	920	83	99	76	30	70	32	106	112	77	222	90	30	90
42	53.7	0.98	112	38 000	98	2 080	203	112	92	45	113	30	101	122	89	213	94	42	132
43	52.7	0.76	88	37 000	97	1 560	154	103	85	37	94	31	104	105	77	219	98	29	92
44	27.4	0.67	125	30 000	102	1 100	164	153	187	20	76	28	99	90	95	164	123	25	100
45	13.2	0.13	42	24 000	111	880	208	46	87	12	72	23	87	79	125	63	84	17	88
46	16.0	0.24	67	22 000	94	830	174	65	109	11	59	23	85	68	97	80	92	16	78
47	49.7	0.71	86	38 000	102	1 200	123	105	90	35	92	29	98	119	91	360	169	32	103
48	46.1	0.68	87	39 000	107	1 060	114	132	118	38	105	28	95	125	99	367	183	34	113
49	31.2	0.77	131	26 000	84	670	92	156	176	19	67	22	77	99	97	184	125	23	88
50	51.9	1.04	122	37 000	97	1 000	99	77	64	28	72	29	98	114	85	327	108	33	105

deemed too high. Thus, iron, cobalt and also, except for a single value, chromium have statistically normal levels everywhere. The industrial area, the port and the main sewage outfall of the city of Thessaloniki enrich the sea bottom in organic carbon, zinc, copper, lead and cadmium at the sites 1 and 2, as well as, further south, at some of the locations 3, 4, 5, 6, 8 and 9. The Axios River spreads the same elements to the south east of its delta, while the Aliakmon River seems responsible for the boosted amounts of nickel at stations 10, 15, 19, 23, 26, 29, 27 and 30. As in the other gulfs, the contents of the analytes and the index of fineness, on the data retained by the method, exhibit a very high mean correlation coefficient (0.81), owing to v being low (15) and d substantial (2.2).

Tables 4, 5 and 6 demonstrate that, as a rule, the exclusion of excessive c' figures only moderately affects the concentration function; hence, the choice of q_0 is

not critical. They also show that, for a specific element, both d and E (the level corresponding to, say, $f=40$, a common sediment fineness) depend on the region. Manganese incurs the most dramatic change of d , and lead that of E . As d rises, it tends to enhance v , since it increases the consequence of the error of the granulometric determination. The available data enable forming an idea of the mistake made in the assessment of the degree of pollution when ignoring the granulometric composition. The highest and the lowest indices of fineness in the region, f_1 and f_0 , allow the calculation of the theoretical maximal and minimal levels, c_1 and c_0 , of a certain element and, hence, of their ratio, $m=c_1/c_0$. Its average of 2.9 in the three gulfs proves the lack of reliability of all metal pollution appraisal techniques that ignore the particle size.

The q figures arrived at with the present method could afford a basis for drawing, by estimation, curves for

Table 3

Concentration, *c*, of metals (in mg.k^{-1}) or of organic carbon (in percent.) and "pollution ratio", *q*, in the Thermaikos Gulf.

Stat.	Ind. fin <i>f</i>	Org. carb.		Iron		Manganese		Zinc		Copper		Lead		Chromium		Nickel		Cobalt		Cadmium	
		<i>c'</i>	<i>q'</i>	<i>c'</i>	<i>q'</i>	<i>c'</i>	<i>q'</i>	<i>c'</i>	<i>q'</i>	<i>c'</i>	<i>q'</i>	<i>c'</i>	<i>q'</i>	<i>c'</i>	<i>q'</i>	<i>c'</i>	<i>q'</i>	<i>c'</i>	<i>q'</i>	<i>c'</i>	<i>q'</i>
1	47.9	1.48	188	41 000	100	750	65	285	238	59	146	246	440	160	93	103	71	22	96	1.0	280
2	52.0	1.57	182	44 000	104	1160	98	198	160	60	141	188	325	150	85	125	85	24	102	0.8	220
3	53.7	1.46	164	41 000	96	1220	102	208	166	48	110	102	174	169	95	105	71	20	84	0.4	109
4	47.0	1.54	200	44 000	107	1240	109	344	289	53	133	74	133	177	104	127	88	24	105	0.4	112
5	43.7	1.38	194	46 000	115	1180	107	138	119	47	123	55	102	174	104	133	93	24	107	0.4	114
6	44.4	1.52	210	44 000	109	1720	155	169	145	45	117	87	161	176	105	139	97	25	111	0.4	114
7	46.7	0.55	72	25 000	61	740	65	84	71	20	50	39	79	140	82	101	70	17	74	0.3	84
8	36.2	0.57	99	44 000	116	1170	114	173	160	46	137	35	70	145	91	114	83	19	89	0.6	178
9	48.4	1.21	152	43 000	104	1190	103	143	119	42	103	49	87	181	105	137	94	24	104	0.9	250
10	45.5	0.76	102	45 000	111	1570	140	245	208	46	118	99	181	165	97	205	143	22	97	0.8	230
11	51.2	0.98	116	44 000	105	1250	106	209	170	54	128	101	176	185	106	150	102	22	94	5.1	1400
12	49.8	1.05	128	41 000	98	1180	101	288	237	52	125	101	178	183	105	137	94	23	99	1.7	470
13	52.7	1.12	128	45 000	106	1390	117	210	169	46	107	83	143	182	103	168	114	24	102	0.7	190
14	47.3	1.03	133	44 000	107	1550	136	166	139	44	110	74	133	177	103	151	105	25	109	0.6	170
15	56.4	0.87	92	44 000	102	1310	107	226	178	50	111	83	138	173	96	304	204	25	104	0.4	110
16	46.6	0.87	114	36 000	88	1550	137	127	107	38	96	66	119	133	78	148	103	24	105	0.4	110
17	45.7	0.85	114	42 000	103	1540	137	281	239	41	105	64	117	163	96	166	116	22	97	0.4	110
18	36.7	1.12	191	34 000	89	1230	119	134	123	41	121	54	108	166	104	147	107	20	94	0.5	150
19	51.1	1.22	144	41 000	98	1270	108	124	101	43	102	63	110	208	119	318	217	26	111	0.4	110
20	43.4	1.02	145	42 000	105	2090	190	162	140	44	116	73	136	195	117	168	118	25	112	0.4	110
21	47.7	0.97	124	35 000	85	1720	150	174	145	41	102	66	118	146	85	174	120	23	100	0.4	110
22	47.1	0.86	111	46 000	112	1570	138	129	108	46	115	72	130	213	125	160	111	25	109	0.4	110
23	64.8	0.78	71	42 000	93	1750	136	131	98	42	85	68	107	205	109	408	266	24	96	0.3	79
24	43.9	0.82	115	45 000	112	1860	168	232	200	42	110	63	117	243	145	183	129	25	111	0.3	86
25	48.3	0.80	101	40 000	97	1160	101	120	100	35	86	70	125	148	86	180	124	22	95	0.3	84
26	47.5	0.88	113	46 000	112	1340	117	112	94	48	119	53	95	207	121	294	203	25	109	0.3	84
27	34.9	0.81	146	43 000	115	1390	138	149	140	39	119	35	72	184	117	194	142	23	109	0.3	90
28	42.6	0.58	84	24 000	60	670	61	112	98	21	56	45	85	71	43	152	107	21	94	0.6	170
29	55.9	0.85	91	45 000	104	1450	119	142	112	40	89	64	107	213	119	229	154	24	100	0.4	110
30	38.5	0.65	105	36 000	93	1100	105	80	72	30	86	63	124	158	98	201	145	21	97	0.3	88
31	5.8	0.78	1030	28 000	128	470	95	64	116	23	226	23	101	103	109	104	107	12	93	0.3	130
32	38.6	0.63	102	41 000	106	1090	104	101	91	32	91	44	86	190	118	187	135	21	97	0.3	88
33	10.6	0.34	230	23 000	88	700	111	115	167	16	106	34	115	117	104	115	105	15	98	0.2	76
34	3.4	0.04	95	16 000	86	400	99	41	90	8	111	18	99	75	92	78	88	12	107	0.2	96

specified values of it, such as 125, 150, 200, 300, 400 etc. These would have the capital advantage of permitting direct comparisons between elements or regions. However, contour maps in general depend for their preparation on conjectures as to the microconstituent composition of the sediment outside the sampling locations. Data from tight networks of stations demonstrate

that extrapolation, in particular near the shore, incurs such hazard as to call for absolute prohibition. But even interpolation faces excessive risk. For example, in the Thermaikos Gulf, the cadmium contents of 0.8 and 1.7 mg.kg^{-1} at the spots 10 and 12 suggest a 1.4 mg.kg^{-1} value at the spot 11 between them, instead of the real one of 5.1 mg.kg^{-1} , three times as high. Deal-

Table 4

Characteristics of the concentration function of metals in the Patraikos Gulf.

Elements	No. of samples	Corr. coef. <i>c', f</i>	Coef. var. of <i>q</i>	Enrich. const. <i>d</i>	Concentration, <i>c</i> , for index of fineness, <i>f</i> , of						
					10	20	30	40	60	100	
C	corrected	20	0.781	12	2.79	0.21	0.34	0.44	0.53	0.69	0.95
	uncorrected	21	0.542	17	2.00	0.32	0.43	0.51	0.58	0.69	0.86
Fe	corrected	21	0.772	10	2.34	11.5	16.6	20.6	24.0	29.7	38.9
	uncorrected	21	0.772	10	2.34	11.5	16.6	20.6	24.0	29.7	38.9
Mn	corrected	18	0.755	23	5.97	190	411	644	887	1391	2452
	uncorrected	21	0.704	28	6.75	180	409	661	930	1504	2757
Zn	corrected	21	0.839	10	2.89	23	37	48	58	76	107
	uncorrected	21	0.839	10	2.89	23	37	48	58	76	107
Cu	corrected	21	0.768	16	3.81	8	15	21	26	37	57
	uncorrected	21	0.768	16	3.81	8	15	21	26	37	57
Pb	corrected	21	0.660	14	2.37	6	9	11	13	16	21
	uncorrected	21	0.660	14	2.37	6	9	11	13	16	21
Cr	corrected	21	0.764	11	2.54	37	56	71	84	106	142
	uncorrected	21	0.764	11	2.54	37	56	71	84	106	142
Ni	corrected	21	0.777	11	2.61	40	60	77	91	116	157
	uncorrected	21	0.777	11	2.61	40	60	77	91	116	157
Co	corrected	21	0.785	11	2.59	7.0	10.6	13.5	16.0	20.3	27.5
	uncorrected	21	0.785	11	2.59	7.0	10.6	13.5	16.0	20.3	27.5

Table 5
Characteristics of the concentration function of metals in the Pagassitikos Gulf.

Elements		No. of samples	Corr. coef. c', f	Coef. var. of q	Enrich. const. d	Concentration, c , for index of fineness, f , of					
						10	20	30	40	60	100
C	corrected	38	0.830	20	3.26	0.26	0.42	0.57	0.71	0.95	1.38
	uncorrected	50	0.484	46	1.93	0.43	0.57	0.68	0.76	0.90	1.11
Fe	corrected	38	0.813	13	1.94	19	26	30	34	40	50
	uncorrected	50	0.573	21	1.56	24	30	33	36	40	46
Mn	corrected	35	0.801	20	2.76	355	550	711	853	1101	1521
	uncorrected	50	0.675	47	3.19	397	655	877	1079	1445	2088
Zn	corrected	33	0.816	18	2.60	45	68	86	102	130	176
	uncorrected	50	0.462	55	1.98	68	91	108	122	145	180
Cu	corrected	47	0.835	19	2.74	14	22	28	33	43	59
	uncorrected	50	0.595	54	2.22	17	24	30	34	42	54
Pb	corrected	50	0.385	9	1.14	26	27	28	29	30	31
	uncorrected	50	0.385	9	1.14	26	27	28	29	30	31
Cr	corrected	47	0.808	19	2.44	54	79	99	117	146	194
	uncorrected	50	0.724	24	2.21	60	84	103	119	145	187
Ni	corrected	46	0.943	14	3.55	60	104	143	179	247	369
	uncorrected	50	0.913	20	3.69	61	106	148	187	259	393
Co	uncorrected	50	0.814	13	1.79	17	22	26	29	33	40
	uncorrected	50	0.814	13	1.79	17	22	26	29	33	40

Table 6
Characteristics of the concentration function of metals in the Thermaikos Gulf.

Elements		No. of samples	Corr. coef. c', f	Coef. var. of q	Enrich. const. d	Concentration, c , for index of fineness, f , of					
						10	20	30	40	60	100
C	corrected	18	0.976	15	5.94	0.14	0.30	0.47	0.64	1.01	1.78
	uncorrected	33	0.879	31	5.55	0.19	0.39	0.60	0.81	1.25	2.16
Fe	corrected	34	0.761	14	1.62	26	32	36	39	44	51
	uncorrected	34	0.761	14	1.62	26	32	36	39	44	51
Mn	corrected	23	0.842	16	1.89	617	811	952	1067	1252	1532
	uncorrected	34	0.754	23	2.06	649	886	1063	1210	1451	1825
Zn	corrected	16	0.879	15	1.80	67	87	101	112	130	157
	uncorrected	30	0.702	28	1.98	78	105	125	141	167	208
Cu	corrected	27	0.883	18	2.86	15	23	30	36	47	65
	uncorrected	34	0.801	22	2.33	19	27	33	39	48	63
Pb	corrected	20	0.869	18	1.98	29	39	46	52	62	76
	uncorrected	32	0.792	25	2.29	29	42	52	60	74	96
Cr	corrected	33	0.679	16	1.57	110	133	149	161	181	209
	uncorrected	34	0.663	17	1.58	110	134	151	163	183	212
Ni	corrected	26	0.589	17	1.35	108	123	133	140	151	166
	uncorrected	30	0.538	21	1.40	111	128	139	147	160	178
Co	corrected	34	0.889	8	1.55	15	18	20	22	24	28
	uncorrected	34	0.889	8	1.55	15	18	20	22	24	28
Cd	corrected	23	0.707	15	1.39	0.29	0.30	0.32	0.34	0.37	0.42
	uncorrected	33	0.440	55	1.68	0.28	0.35	0.40	0.44	0.50	0.59

ing with q instead of c' tends to reduce the error. Despite that, the drawing of curves of equal q remains somewhat arbitrary. A way out of this frustrating difficulty consists in dividing the region into a few only carefully delineated zones and calculating the average values of q in them. In the instance of the Pagassitikos Gulf, five sections appear distinct: (A) the Bay of Volos

(station 1-15), (B) the area immediately to the south of it (16-30), (C) the western (31-34, 38, 39, 41) and (D) eastern (35 - 37, 40, 42) halves of the central part of the gulf and (E) the straits (43 - 50). This data grouping (see Tab. 7) helps elicit shades of pattern otherwise undiscernible. The Bay of Volos, exposed to industrial and port activities, as well as domestic waste,

Table 7
Grouped pollution ratios q in the Pagassitikos Gulf.

Zone	Stations	C	Fe	Mn	Zn	Cu	Pb	Cr	Ni	Co	Mean (*)
A	1-15	159	115	99	155	147	104	100	108	109	125
B	16-30	146	118	129	143	115	98	118	100	96	117
C	31-34, 38, 39, 41	86	99	151	132	89	103	99	92	90	99
D	35-37, 40, 42	107	108	223	115	113	108	119	100	114	110
E	43-50	94	99	141	114	80	93	96	123	96	99
Mean	1-50	118	108	149	132	109	101	106	105	101	110

(*) Manganese excluded.

exhibits some pollution from organic carbon ($q=159$), zinc ($q=155$), copper ($q=147$) and iron ($q=115$). This extends into *B* ($q=146$ for C, 143 for Zn, 115 for Cu and 118 for Fe) and even into *C* in the case of zinc ($q=132$). The eastern side of the gulf discloses a remarkable manganese anomaly ($q=223$), probably caused by a natural source in the vicinity, which spreads into *C* ($q=151$), *E* ($q=141$) and *B* ($q=129$). The same zone looks richer too in other constituents ($q=119$ for Cr, 114 for Co, 113 for Cu, 108 for Fe, 107 for C). The channels present enhanced nickel figures ($q=123$), suggesting the presence of a nearly orebody. When excluding the highly disturbing manganese from the means, these give a clear general picture: moderate pollution around the harbour of Volos ($q=125$), an even slighter one further south ($q=117$) and a perceptible non-anthropogenic enrichment in the eastern half of the gulf ($q=110$).

CONCLUSIONS

In a homogenous and clean marine expanse, an exact relationship exists between the level of dilute hydrochloric acid leachate metals, as well as of organic carbon, and the texture of the sediment expressed as an index of fineness estimated from the percentages of silt and clay. The propounded technique for setting up the equation remains valid even in the instance of a partly contaminated region. The formula needs only reestablishing once or twice after excluding values significantly higher than those computed. The percentage ratio of true to calculated amount indicates the degree of pollution. Contour maps of this ratio, though safer than those displaying concentrations, may still be grossly erroneous. Averaging the data from stations belonging to areas picked after thorough investigation affords a more reliable and sensitive way of detecting and measuring pollution or natural anomalies.

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Acknowledgements

The authors wish to express their gratitude to Basel Marouda-Lambropoulou for drawing the maps.

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