ASPECTS OF TRACE METAL CONTAMINATION IN THE COASTAL RIVERS OF ISRAEL

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Abstract. Nine trace elements of biological concern: Cr, Co, Cu, Cd, Ni, Pb, Hg, Zn and Ag were investigated in the sediments of the most important coastal steams in Israel. All of these are subjected to some degree of domestic and/or industrial sewage input with the consequent liability of contamination by trace metals. The Ayyalon, Gadura, Qishon and locally the Hadera rivers contain sediments exhibiting severe pollution effects. There is a danger of infiltration through the soils into the ground-waters as well as exposing nearshore fauna to sediments contaminated by possibly toxic trace metals. The other rivers bear smaller levels of trace metals; however, an increase of the Pb and the Zn levels occurs near major highways.

1. Introduction

In Israel there are very shallow rivers that undergo periods of decline and stagnation during the dry summer months, thus increasing the possibility of concentration of precipitated or deposited chemical pollutants. If the input of trace metals is appreciable, local accumulation may occur or the concentration of such materials throughout an entire river may be such as to endanger life forms. This situation may become even more serious when seasonal changes, after first playing a role in the concentration effect, may then assist in the transportation of enriched sediments to areas where they may be introduced into biological food chains, or help to chemically remobilize the elements.

In the coastal plain of Israel the surface sands and the underlying ground-waters are not isolated from each other. Downward infiltration of metals deposited on the surface sediments could conceivably endanger water resources. In addition, the rivers of Israel, though very small, have an important potential as recreation facilities. To utilize to the full this public facility that pollution currently denies us, it is necessary to restore the aquatic biological balances. Reclamation procedures would have to take into consideration the trace metal burden that may have built up in the sediments.

In the present study, we have analyzed trace metals in the sediments of a number of rivers – Co, Cu, Cd, Cr, Ni, Pb, Ag, Hg and Zn – to determine a) whether significant trace metal buildup has occurred; b) which specific metals are the contaminants; c) where pollution has occurred; and d) if ecological hazards are indicated. In addition, the data presented can serve as a baseline against which data obtained on subsequent monitoring can be compared.

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2. Sampling and Analytical Methods

The region investigated comprises the major industrial area of the country which is traversed by five rivers. These are from north to south: the Na'aman river, situated south of the town of Akko and the Qishon river which crosses north of Haifa. Both of which flow into Haifa bay. The Hadera and Alexander rivers near the town of Hadera and the Yarqon river in the Tel-Aviv region.

2.1. Sampling

Samples of sediment were taken from along the banks of the river channels during the summer of 1973. All samples were taken from the top 10 cm layer, using a plastic pipe and scoop, and stored in clean polyethylene jars. In the laboratory, the sediments were air dried, gently disaggregated on an agate mortar, passed through a 0.17 mm nylon sieve and subjected to chemical analysis.

2.2. Analytical methods

From the pollution viewpoint, the total chemical content of the sediments is of less primary importance than that fraction of the metals which resides outside the crystal lattice, or can be easily mobilized. Therefore, a selective chemical attack rather than total chemical decomposition is the analytic procedure which is sought. The procedure of Chester and Hughes (1967), involving leaching with 1 M hydroxylamine-hydrochloride in 25% acetic acid, was used to determine seven of the elements (all except Ag and Hg). This method removes the metal fraction associated with carbonate, some sulphides, soluble salts, ions in exchange positions, and the Fe–Mn oxide phase. The latter is of importance because hydrous Mn and Fe oxides are strong scavenging agents for transition metal ions. That structurally bound cations are little affected by this procedure appears to be corroborated by Presley *et al.* (1972). The Ag analysis involved a concentrated HNO_3 extraction described by Huffman *et al.* (1966). The solutions containing the leached metals were then subjected to spectrophotometric analysis using a Perkin-Elmer Model 303 atomic absorption spectrophotometer. Samples for Hg analysis were prepared according to the method of Polley and Miller (1955), and the subsequent Hg determination followed a procedure reported by Hatch and Ott (1968) using a flameless Perkin-Elmer Mercury Measuring Kit attached to the Model 303 atomic absorption spectrophotometer.

Analyses were carried out in duplicate, or, in some cases in triplicate. Appropriate control analyses were carried out in all cases. The sediment texture was estimated on a surface area basis, determined using the ethylene glycol method of Carter *et al.* (1965). Organic C was determined using a modification of the Allison (1965) procedure, and carbonate, using a pressure-calcimeter method described by Allison and Moodie (1965).

3. Results and Discussion

Analytical data are presented in Table I. Figures 1, 2 and 3 show the location of the

TABLE I

Some physical characteristics and trace metal concentration in the river sediments

Sample number	River	Organic matter %	$CaCO_3$ %	Element concentration in ppm (over dry basis) Cr	Co	Ni	Cu	Zn	Ag	Cd	Hg	Pb
TEL-AVIV-City												
YN 1	Yargon	0.9	7	1	1.1	1	3.3	12	nd[a]	nd	nd	24
YN 2	Yargon	0.8	10	1	1.0	1	3.0	68	nd	nd	nd	48
YN 3	Yargon	1.2	12	2	1.2	1	2.9	57	nd	nd	nd	24
YN 4	Yargon	1.1	6	9	1.0	4	1.6	41	nd	nd	nd	25
YN 5	Yargon	1.4	10	1	0.9	2	3.0	83	nd	nd	nd	20
AY 6	Ayyalon	3.3	7	12	1.9	8	5.6	96	0.1	0.2	nd	23
AY 7	Ayyalon	18.0	6	21	3.9	15	7.0	160	2.1	13.9	nd	42
AY 8	Ayyalon	19.9	6	124	6.0	60	16.0	323	9.1	16.0	nd	65
AY 9	Ayyalon	3.5	8	12	4.0	9	8.1	136	1.0	0.1	nd	34
AY 10	Ayyalon	3.3	8	12	4.8	9	2.3	49	0.1	0.1	nd	12
AY 11	Ayyalon	20.3	4	39	6.1	11	4.0	305	3.6	14.0	nd	226
AY 12	Ayyalon	11.0	6	23	4.2	9	4.1	301	2.8	10.8	nd	166
HADERA REGION												
AX 13	Alexander	3.0	12	11	4.0	7	2.2	48	0.7	nd	0.07	22
AX 14	Alexander	1.9	7	17	3.7	6	3.0	64	0.9	nd	0.07	9
AX 15	Alexander	5.7	11	11	3.6	6	2.1	72	0.9	nd	0.30	7
HE 16	Hadera	12.0	9	17	3.2	9	13.0	176	4.0	nd	1.04	25
HE 17	Hadera	2.1	10	12	3.3	6	3.2	42	0.1	nd	0.46	12
HE 18	Hadera	2.0	10	12	7.1	12	4.0	42	1.0	nd	0.19	5
BAY OF HAIFA												
QN 19	Qishon	9.6	17	6	7.0	18	10.0	180	1.2	1.0	0.13	66
QN 20	Qishon	13.0	25	24	5.2	19	47.8	325	3.9	4.0	nd	72
QN 21	Qishon	6.0	8	17	11.1	18	28.0	125	1.0	traces	nd	12
QN 22	Qishon	4.0	15	7	7.9	15	6.5	92	1.1	traces	nd	16
QN 23	Qishon	3.4	17	8	7.1	16	6.6	126	1.0	traces	nd	30
QN 24	Qishon	6.6	27	20	9.2	13	3.5	51	0.9	traces	nd	15
QN 25	Qishon	9.0	20	56	7.0	12	3.1	125	0.2	traces	nd	11
QN 26	Qishon	2.6	24	3	12.8	11	4.8	20	0.2	traces	nd	9
GD 27	Gadura	12.8	22	220	7.0	23	8.1	898	2.2	64.0	0.28	118
GD 28	Gadura	12.0	21	610	6.9	17	14.0	906	4.0	61.0	0.17	120
GD 29	Gadura	9.6	24	325	6.1	24	5.8	1376	3.0	72.0	0.09	137
GD 30	Gadura	11.4	19	238	8.2	31	42.8	937	3.1	123.0	0.10	205
GD 31	Gadura	14.0	34	313	5.9	22	18.1	1500	3.8	75.0	0.05	162
GD 32	Gadura	10.5	29	350	8.0	20	10.0	938	4.5	41.0	nd	118
GD 33	Gadura	9.7	28	288	7.8	22	9.8	1062	4.8	36.0	nd	93
GD 34	Gadura	10.8	44	237	17.7	18	15.0	405	2.5	20.0	nd	275
GD 35	Gadura	10.5	45	62	10.1	20	31.1	365	4.5	6.8	nd	193
NM 36	Na'aman	2.6	15	12	2.1	5	3.0	14	0.2	nd	0.27	10
NM 37	Na'aman	2.3	18	17	4.8	7	4.7	24	0.1	nd	0.16	16
NM 38	Na'aman	0.8	15	4	2.2	4	2.8	9	0.2	nd	nd	14
NM 39	Na'aman	10.0	21	26	5.0	14	6.0	136	0.2	nd	0.13	10

[a] = not detected by method used.

sampling position in each river. Since there is no standard reference datum for pollution-free sediment, we cannot discuss 'absolute' pollution quantities, but can compare values either with known soil levels or alternatively the relative abundance of metals among samples from the same river system can be used to gauge the amount of metal input between sites or between rivers. It is readily apparent from Table I that the most polluted stream is the Gadura extension of the Qishon river. The source of the metals is apparently the industrial wastes fed into it by the numerous factories situated along its banks. This tributary is a major cause of the subsequent contamination of the Qishon river which directs the sediments into the Haifa Bay.

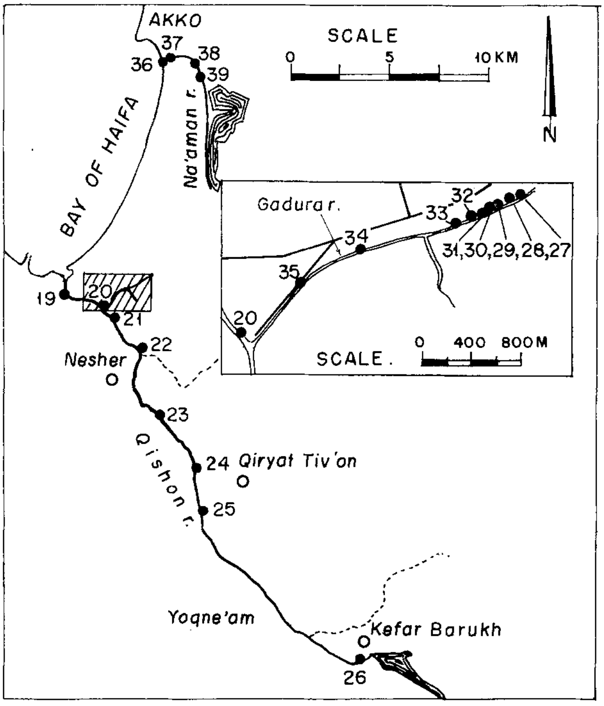

Fig. 1. Location of sampling sites along the Haifa bay rivers.

The Na'aman river, situated south of the city of Akko (Figure 1) is the second river input into Haifa bay. It is markedly less contaminated and the lower reaches can be considered essentially as a recreational area. The main source of contamination here is from sewage, near kibbutz Ein Hamifrats. The metal contamination is localized and of small magnitude (sample No. 39). It would appear that at its present level of contamination, the Na'aman river should be able to cleanse itself naturally of any metal burdens once the sewage is directed elsewhere.

The Qishon river, because of the heavy industrialization in its surrounding area, offers less recreational potential; it would be difficult to conceive that it could be cleaned up without first cleaning or rerouting its Gadura tributary.

Southward lies the Hadera river, which passes through Hadera city, and the Alexander river (Figure 2). Both are subjected to sewage inflow, but there is no very large metals accumulation in their sediments. The stream sediment characteristics and metal concentrations are similar in both rivers, with the exception of the lower stretch of the Hadera. Here the metal levels are higher. In this section the water acquires a black color and its characteristic odor can be noted while driving along the Tel-Aviv-Haifa highway. Rotting organic material was observed floating in the water and strewn along the banks; the source of the organic material and/or metals was not traced. It would be of importance to do so, for, apart from the odors and lack of

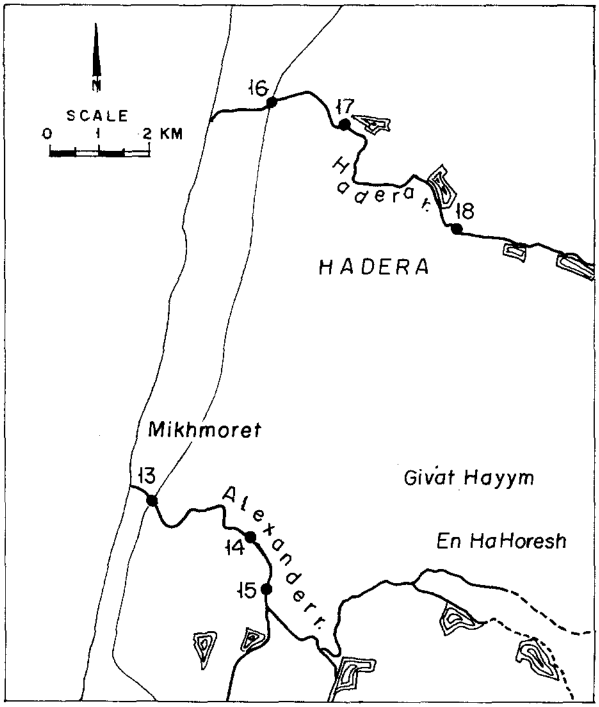

Fig. 2. Location of sampling sites in the vicinity of the city Hadera.

aesthetic appeal, this pollution may pose a health hazard to the settlement situated along the northern bank. Formerly, this settlement directly utilized the river for household purposes. At present, infiltration of Hadera river water into the community well located near the river may be a contributing factor to the poor health that is manifest here. Once sewage inflows are stopped, the health problems may be alleviated and the recreational potential that these rivers offer should be able to be realized.

Further south, at Tel-Aviv, we find the second largest river on the Israeli coast, the Yarqon (Figure 3). The sediments from this river yielded the least amount of leached metals. The Ayyalon tributary suffers an influx of pollutants, which is reflected in its sediments, and, locally, a significant accumulation of certain metals takes place. It is difficult to discuss this body of water in terms of a river like others, because during the summer, parts of the channel dry up and a continuous water connection may exist during the rainy season only. Work is currently in progress to turn this feature into a drainage canal via a pipeline, thereafter it will cease to exist as a river. Therefore, the most serious pollution threat presented by the Ayyalon at the moment is not its own contamination, but that its pollutants continue to be directed toward the Yarqon. Before it was cleaned up, the Yarqon was used for sewage disposal like the other rivers, and was unsuitable for boating or for its banks to be used as picnic grounds. With the cessation of sewage inflow, aquatic balances are being restored and

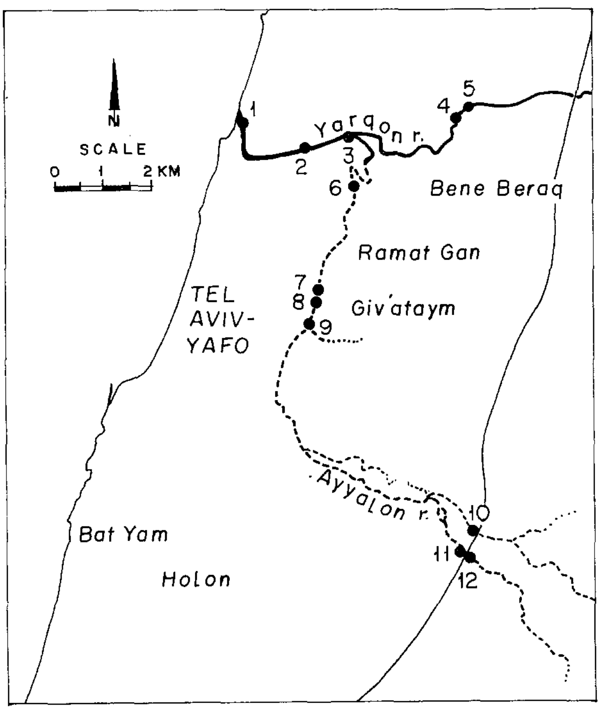

Fig. 3. Location of sampling sites in the vicinity of the city of Tel-Aviv.

aquatic life is reappearing. While no data are available as to the metals content in its sediments at that time, logically it may be assumed that trace metal contents were higher, possibly similar to some values measured in the Ayyalon in the present study. If this is so, the present low metal concentration provides an indication that if sewage influx is stopped, self-healing of the river – either as metals are released to the aqueous phase, or as the upper layers of contaminated materials are washed out to sea – can occur within at least a decade. This is important to bear in mind when considering uses for our rivers. It is the authors' contention that the most beneficial use would be as recreational facilities both for the internal population and for tourists.

From the data of Table I, one may conclude that to a lesser or greater degree metals are added to the rivers as a result of man's endeavors. With the exception of the Qishon river which is silty-clay, the sediments are basically sands, or sands and silts. Elements reside in such sediments as precipitants (or as a hydrous Fe or a Mn oxide coating on sand grains) rather than as exchangeable cations which would be adsorbed to clay surfaces. Metals which have low natural background and can therefore be readily detected here as true contaminants are Ag, Cd and perhaps Hg. Although the literature contains much information on pollution, it is difficult to ascertain the limits above which there is serious danger to biological life. It is understood that not only is the total quantity of metals a significant factor, but also their chemical form, since the latter determines their biological availability. The metal concentrations given in Table I are the leachable amounts, and therefore should be more readily biologically available than the total metals content; however, the chemical form of the individual metals which is of importance was not determined.

Several parameters such as organic matter content, carbonates and texture that would give further insight into the chemical behaviour of the metal contaminants were tested. Considering the solubility dependence of the metal, water in contact with the sediment, at these points where the sediment metal content was found to be high (for example: samples 8 and 12) was directly aspirated into an atomic absorption spectrophotometer. No Cr ,Ni, Cd, or Pb could be detected.

Both Ag and Hg showed a tendency to be present in the organic phases; high correlation to sediments with high organic material was obtained with statistical regression coefficient $r_{Ag} = 0.76^*$, and $r_{Hg} = 0.78^*$, while the quantity of these metals is low, their chemical form may make them easily available to organisms thereby enhancing their toxic potential.

Chromium, Co, Cu, Zn, and Pb show a clear trend to the carbonate phase ($r = 0.53^*$; 0.67^*; 0.50^*; 0.53^* and 0.56^*, respectively). It may therefore be considered that its environmental danger potential is minimal at the levels encountered. Two metals, Cd and Pb, both poisons, may be the main concern. The introduction of these two into the Haifa bay via sediment transport may have adverse effects on the bottom fauna. Cadmium in particular, may contribute toward the decline of fishing in the bay, after fish ingestion of organisms that have fed upon Cd-contaminated sediment. Recent studies indicate that Cd, at non-lethal levels, can adversely affect the steroid chemistry of both fish and mammals (Sangalang and O'Halloran, 1972). It should be noted that in dregging to deepen the Gadura channel, which was carried out over the latter part of the year, bluish-hued sediments were piled along the banks. This may relieve metal pressures upon the lower reaches of the Qishon system; yet, subsequent leaching of these metal-enriched sediments, and mobilization through the soil, may offer additional trace metal related problems. Lead contamination may be brought about dually through waste discharged directly into the water as well as by airborne deposition from car exhaust fumes settling into the rivers. Comparison between Pd levels in the sediments and the sample position in proximity to motor traffic indicated that air-

* = significance at the 5% level of probability.

borne Pb can be a significant proportion of the total. The Yarkon river, which is free of most metal additions, is the most intimately geographically related to high car congestion. This is apparent in its Pb content. The same feature is also found in the Alexander (sample 13) and Hadera (sample 16) rivers at the points where a major highway passes over them.

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