

## Problem of the selective partitioning of trace metals in various sediment size fractions

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The geochemical cycle of anthropogenic trace metals in the marine environment is determined to a large degree by the interaction of the metals with sediments. One of the parameters affecting trace metal distribution in various sediment fractions is fraction dimension. Therefore, it is recommended that studies related to the anthropogenic heavy metal contamination of sediments be conducted on a particular sediment fraction: either on the sediment fraction less than 0.063 mm, or less than 0.250 mm. The generally accepted opinion is that the smaller the size of the sediment fraction, the larger the amount of trace metals bound to this fraction, and that trace metals are mainly present in the clay/silt fraction consisting of particles with grain size less than 0.063 mm. We studied trace metal distributions in various sediment size fractions for southern Haifa Bay (Israel), and were surprised to observe an anomalous fraction distribution of trace metals and organic matter (Krumgalz, 1989): namely, unusually high enrichment of trace metals and organic matter in the fractions of coarse and medium sand (fractions with particles larger than 0.250 mm). The curves characterizing either trace metals (cadmium, copper, lead, zinc and iron) or total organic matter content distributions on various size sediment fractions have a clearly defined minimum, like a "saddle", for the fine sand fraction of grain size 0.125-0.250 mm. The unusual enrichment of all the studied trace metal and organic matter contents in the coarse and medium sediment fractions (>0.250 mm) was sometimes even more than the enrichment of the same elements in the clay/silt fraction. The explanation of the observed phenomenon was suggested to be the formation of large agglomerates (clusters larger than 0.250 mm) from the smaller particles enriched by contaminants. The formation of such large agglomerates occurs during the generally accepted drying procedures, all of which are carried out without prewashing the studied sediments. During any drying procedures (either freeze-drying or heating), the small sediment particles will be cemented both by dissolved organic matter and by sea salts, present in the marine sediment, to form large agglomerates. Since small sediment particles are enriched by various contaminants, kept on their large specific area by adsorption forces, the total amounts of either trace metals or organic matter retained by each agglomerate particle will be much larger compared to the amounts which could be adsorbed only on the outer surface of such an agglomerate.

The formation of large agglomerates from small particles during the drying procedure will lead to biased distribution curves for such sediments with an increase of the large size sediment fraction at the expense of the smallest sediment fraction. The results obtained demonstrate that the standard mechanical sieving procedure and other sample treatment operations are not vigorous enough to destroy the formed agglomerates. We are sure that such an abnormal fraction distribution can probably be corrected by careful washing of the studied sediments with distilled water before any drying procedure. However, such prewashing may cause another problem: how will the prewashing affect trace metals or organic matter loosely bound on the sediment surface? The agglomerate formation can also lead to incorrect results related to the balance calculations of various contaminants, and will manifest itself when various fractions are used for trace metal studies. Until now, this phenomenon was only observed at a single site, i.e. Haifa Bay. However, we believe that such agglomerate formation is a widespread phenomenon and could be observed at other locations with similar sediment treatment. The possibility of the formation of large agglomerates from small contaminated particles should be seriously considered when developing standard methods related to studies of the anthropogenic metal contamination of sediments.

The widely used "fingerprint" approach to trace the sources of local pollution or of fine sediment fraction movement in particular polluted areas can be used only under certain conditions (Krumgalz, 1988). Among them are the absence of significant trace metal fractionation and sediment fractionation. Therefore this approach cannot be automatically recommended to be applied to any case of sediment pollution studies. This approach can give correct results only for sediment fractions where agglomerate formation does not occur. Another question is, how do trace metal distribution "fingerprints" for an area with only a point pollution source depend on sediment fraction size? In order to answer this question, we studied trace metal distribution in various sediment size fractions in which agglomerate formation was not observed. As a study case, we chose the polluted area in the southern part of Haifa Bay with only one source of contamination (Krumgalz, 1988; Hornung et al., 1989; Krumgalz et al., 1989). Regression analysis of the data obtained in this study demonstrates that the sediment fractions 0.125-0.250 mm and 0.063-0.125 mm have similar trace metal distributions "fingerprints" in most cases. However, the finest fraction (<0.063 mm) possesses "fingerprints" of trace metal distributions which differ from the other fractions, with a few exceptions. It may be concluded, on the basis of selective partitioning of trace metals in various size fractions, that sediments should not be compared only on the basis of chemical composition unless they have similar textural characteristics. In the obtained results, profound selective partitioning of some heavy metals (especially lead) between various grain size sediment fractions was observed. It was found that the lead background increases with a decrease in the fraction size: 15.8±1.8 ppm (fraction 0.125-0.250 mm), 21.3±2.6 ppm (fraction 0.063-0.125 mm), and 38.0±3.0 ppm (fraction <0.063 mm). The background lead content for the sediment fraction <0.250 mm (generally recommended for studies dealing with pollution) is 17.1±1.8 ppm. All these lead background values found for Haifa Bay sediments are in good agreement with those determined by various authors and reviewed by Scoullous (1986).

The results obtained in this study show that some methodological recommendations dealing with studies of trace metal contamination of marine sediments should be periodically reconsidered, especially after new observations are obtained, such as those discussed here.

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## Chemical forms of metals in flocs formed during sludge dumping in the sea

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The dumping of sludge from wastewater treatment plants, into the sea as a sewage sludge disposal method in the USA and some European countries.

As the sludge encounters seawater, the particles it contains coagulate to form flocs, which are settling to the bottom with different settling velocities.

The impact that such a disposal method has on the marine environment depends on the quality of the sludge (urban or industrial) and the characteristics of the sea area where the dumping is done (depth, bottom topography, etc) (Pearson 1985). On the other hand, the chemical forms of the metals in the flocs formed after the dumping of the sludge in the sea have a direct influence on their availability for consumption from the marine organisms of the area, and therefore on the potential harm to the marine ecosystem.

In order to study the process, the mixing of the sludge with seawater during the dumping into the sea was simulated in the laboratory using special designed equipment and the flocs formed were separated in four settling velocity fractions (Gibbs 1986). The chemical characterization of the metals in the flocs was performed using a sequential extraction technique (Gibbs 1973, Forstner and Wittmann 1979). The metals analysed were Cd, Cr, Cu, Fe, Pb and Zn (Angelidis and Gibbs 1989, Angelidis and Gibbs 1990).

The characteristics of the sludge used in the experiments are presented in Table 1.

TABLE 1  
Total and dissolved concentration of metals in Bowery Bay Treatment Plant sludge

	Cd	Cr	Cu	Fe	Pb	Zn
Total (mg/l)	0.540	44.37	76.64	475.2	12.3	165.6
Dissolved (mg/l)	0.058	0.165	0.23	2.30	< 0.50	0.369
(percent)	(10.7)	(0.37)	(0.16)	(0.49)		(0.22)

After the coagulation, most of the mass of the sludge (79.1%) formed large flocs with settling velocities > 6.0 cm/min. In these fast settling flocs, the greater part of the metals was present in the oxidizable phase (organic matter and sulfides) [59.1% of Cd, 81.7% of Cr, 97.8% of Cu, 48.9% of Fe, 90.1% of Pb and 66.6% of Zn] (Table 2). The fast settling flocs contained very small quantities of metals (exception Fe) in the reducible phase, which consists mainly of Fe/Mn oxides (Table 3).

The small flocs, with settling velocity < 0.7 cm/min, represented only the 2.6% of the mass of the sludge. The larger part of their metal content was in the reducible phase (67.3% of Cd, 49.6% of Cr, 56.5% of Cu, 59.2% of Fe, 60.4% of Pb and 59.2% of Zn) (Table 3). The oxidizable phase of these flocs contained considerably lower metal concentrations (Table 2).

The adsorbed phase of the metals was negligible in all settling velocity fractions and the residual (detrital) phase didn't show any particular trend in the different settling velocity fractions examined.

TABLE 2  
Relative (%) concentration of oxidizable metals in the different settling velocity fractions (Bowery Bay sludge)

Settling velocity	Cd	Cr	Cu	Fe	Pb	Zn
< 0.7 cm/min	14.9	46.0	37.7	26.5	39.6	7.4
0.7-2.5 cm/min	30.0	41.7	69.2	29.5	39.0	21.5
2.5-6.0 cm/min	35.8	47.7	34.8	48.9	90.1	66.6
> 6.0 cm/min	59.1	81.7	34.8	48.9	90.1	66.6

TABLE 3  
Relative (%) concentration of reducible metals in the different settling velocity fractions (Bowery Bay sludge)

Settling velocity	Cd	Cr	Cu	Fe	Pb	Zn
< 0.7 cm/min	67.3	49.6	56.5	59.2	60.4	89.2
0.7-2.5 cm/min	56.5	56.9	30.6	60.3	61.0	74.8
2.5-6.0 cm/min	59.5	51.1	5.0	36.4	35.8	52.7
> 6.0 cm/min	17.6	15.3	0.7	34.9	6.8	32.0

### CONCLUSIONS

The above results indicate that there is a significant geochemical difference in the chemical forms of metals, between the large and small flocs which are formed after the dumping of the sludge into the sea. The large (and faster settling) flocs, sink to the bottom near the dumping site, forming a floc blanket containing most of the metals in the oxidizable phase (organic matter and sulfides), and therefore, easily available to the marine organisms living in the area.

On the other hand, the smaller microflocs which may be transported to longer distances by the currents, contain most of their metals in the reducible phase (Fe/Mn oxides) and therefore they are not easily available for uptake by the marine organisms.

The above conclusions suggest that the area directly under the sludge dumping site, is not only receiving most of the mass of the sludge dumped, but also the metals contained in this floc blanket are present in a chemical form that can easily be uptaken by the marine organisms in the area.

The smaller flocs, which travel greater distances, don't seem to represent any serious threat to the marine ecosystem, because they don't represent an important mass of the sludge and because their metal content is in a chemical form which is not easily available to the marine organisms.

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