

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

Ronald J. GIBBS* and Michael ANGELIDIS**

 *Center for Colloidal Science, College of Marine Studies, University of Delaware, Newark, DE 19716 (U.S.A.)
 **Environmental Studies, Papadiamantopoulou 2, 115 28 Athens (Greece)

The dumping of sludge from wastewater treatment plants, into the sea, is used 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 (currents, 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 velocities fractions (Gibbs 1986). The chemical characterisation 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	475.4	12.3	165.6
Dissolved (mg/l)	0.058	0.165	0.123	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 89.2% 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	39.8	47.7	94.3	53.1	61.9	46.6
> 6.0 cm/min	59.1	81.7	97.8	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
> 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.

REFERENCES

- ANGELIDIS M. and GIBBS R.J. 1989. Chemistry of metals in anaerobically treated sludges. *Water Research* 23 (1) 29-33.
- ANGELIDIS M. and GIBBS R.J. 1990. The segregation of metals during the ocean dumping of sludge. *The Science of Total Environment* (in press).
- GIBBS, R.J. 1973. Mechanisms of trace metal transport in rivers. *Science* 156: 1734-1737.
- GIBBS, R.J. 1986. Segregation of metals by coagulation in estuaries. *Marine Chemistry* 18: 149-159.
- FORSTNER U. AND WITTMANN G.T.W. 1979. *Metal Pollution in the Aquatic Environment*. Springer-Verlag, Berlin-Heidelberg, 486p
- PEARSON, T.C. 1985. Disposal of sewage in dispersive and non-dispersive areas: contrasting case histories in British coastal waters. *NATO ASI Series*: 577-595.