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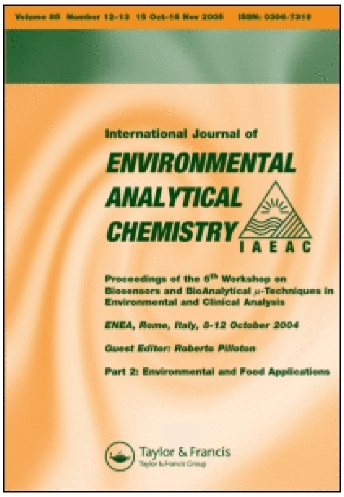

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Leaching Behaviour and Solid Phase Fractionation of Selected Metals as Affected by Thermal Treatment of a Polluted Sediment

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LEACHING BEHAVIOUR AND SOLID PHASE FRACTIONATION OF SELECTED METALS AS AFFECTED BY THERMAL TREATMENT OF A POLLUTED SEDIMENT

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A contaminated dredged sediment was subjected to a thermal treatment at temperatures ranging from 120 to 450°C. The leaching behaviour of selected metals (Cd, Cu, Pb, Zn, Fe, Mn) was studied using NH_4OAc-EDTA extraction. In addition, solid phase fractionation was carried out by means of a sequential extraction procedure.

The NH_4OAc-EDTA extraction showed a sharp increase in metal leachability from sediments treated at intermediate temperatures (120 - 350°C). The metal fractionation of the solid phases at the different temperatures did not reveal relevant shifts except for Cu. The decrease of the oxidizable Cu fraction was highly correlated ($P < 0.001$) with the disappearance of organic matter at higher treatment temperatures. It is suggested that binding energy changes within the fractions rather than shifts between chemical forms account for the observed leaching behaviour.

KEY WORDS: Metal fractionation in sediments, leaching of metals from sediments.

INTRODUCTION

Assessing the environmental quality of sediments based solely on total chemical analysis does not allow a differentiated approach towards a cost effective and environmentally acceptable treatment strategy for contaminated dredged sediments[1-5]. Therefore, during the last decades analytical techniques aimed at assessing metal mobility and bioavailability have been developed and modified. From the analytical point of view, two different approaches can be discerned to characterize the pollution status of soils and sediments[6]. The first concerns single reagent leaching tests, using extractive reagents which are considered to be able to extract bioavailable fractions of metals. The second approach involves the use of sequential extraction techniques to distinguish between different physico-chemical states of metals[6]. This is thought to give detailed information on the origin, mode of occurrence, biological and physicochemical availability, mobilization, and transport of trace metals[7-9].

In this study, chemical changes were induced in a sediment by thermal oxidation at

Table 1 General characteristics of the sample.

Granulometry (%)	0-2 µm	34.5
	2-50 µm	56.9
	> 50µm	8.6
pH-H_2O (1:5)		7.1
Eh (mV vs SHE)		2
Buffering capacity pH = 4.3 (mmoles HCl/kg dry soil)		2357
Organic matter (%)		9.6
$CaCO_3$ (%)		11.2
Total contents (mg/kg dry soil)		
Cd		13.2
Cu		140
Pb		178
Zn		1200
Fe		68399
Mn		997

increasing temperatures. Changes in leaching behaviour were evaluated by NH_4OAc-EDTA extraction, releasing soluble, adsorbed and complexed element forms[10,11,12].

Additionally, a sequential extraction procedure[7] was carried out to assess species distribution in the solid phase as affected by the thermal treatment.

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MATERIALS AND METHODS

The sediment (Table 1) was sampled from an inland river in the Flemish region (Belgium) and was kept flooded to prevent contact with air. pH was measured in a 1/5 soil to water suspension after equilibration for 12 hrs. Redoxpotential was determined by immersion of a platinum electrode and a standard calomel reference electrode in the native sample and waiting for a stable reading. Samples were air-dried and ground to pass a 2 mm sieve. Total metal analysis was done after aqua regia digestion. Organic C was estimated by the Walkley-Black method and converted (1.72 × C) to percent organic matter[13]. Carbonate content was determined by back titrating an excess of HCl 0.5 mol/L added to 1 g of the sample with NaOH 0.5 mol/L[14].

Part of the sediment was dried at 120°C for 24 hours. Then, separate portions were heated for 4 hours at 120, 150, 205, 250, 300, 350, 405 and 450°C, respectively.

Leaching tests were carried out by shaking 10 g samples for 30 minutes with 50 mL of NH_4OAc 0.5 mol/L + EDTA 0.02 mol/L at pH 4.65. The suspension was filtered on S&S whiteband filterpaper.

For the leaching test on the untreated sample, ascorbic acid (5 g/L) was added to the extractant as an antioxidizing agent[15]. A determination of the dry matter content was carried out to calculate the amount of dry matter used.

Sequential extractions were carried out as described by Tessier et al.[7], except for the residual fraction, where aqua regia digestion was used. All metals were determined by flame atomic absorption (Varian AA-1475) using deuterium background correction. Standards

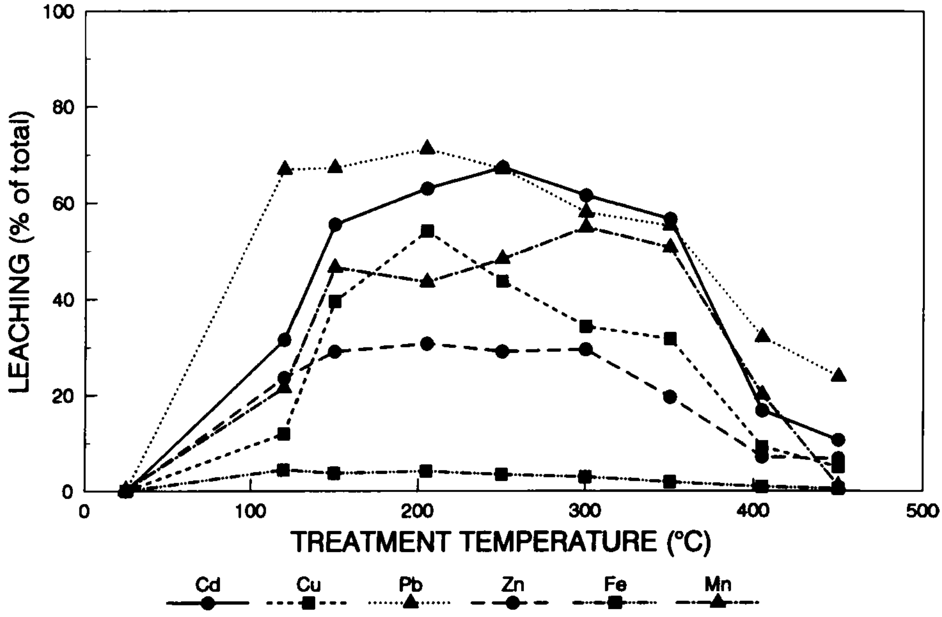

Figure 1 Leaching of Cd, Cu, Pb, Zn, Fe and Mn in NH_4OAc-EDTA 0.5 mol/L + EDTA 0.02 mol/L (1/5 solid/liquid ratio) in function of sample treatment temperature.

were prepared in the corresponding extracting solution. The sum of the metal fractions agreed within 10 % with the total analysis.

RESULTS AND DISCUSSION

Leaching pattern

All metals studied (Cd, Cu, Pb, Zn, Mn and Fe) exhibit a similar leaching behaviour in NH_4OAc-EDTA as a function of treatment temperature (Figure 1). Lowest amounts are leached from the reduced native sediment. A gradual, but steady increase in quantities extracted is observed up to a temperature of about 250 °C. At higher treatment temperatures, the leachability decreases below that of the 120°C dried sample, but remains higher than that of the native sediment. The increased mobility of metals in freshly oxidized sediments has also been observed in field experiments[16,17].

Solid phase fractionation

The distribution of the metals over the different fractions is shown in Figures 2 to 7 and reveals clear differences between the elements. Copper (Figure 2) is mainly associated with

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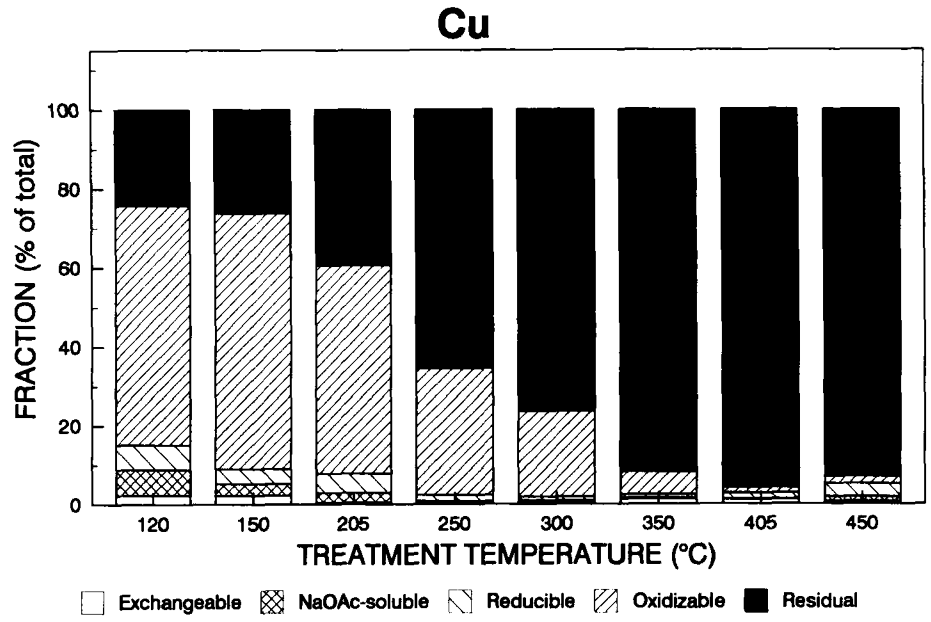

Figure 2 Chemical fractionation of Cu for different sediment treatment temperatures.

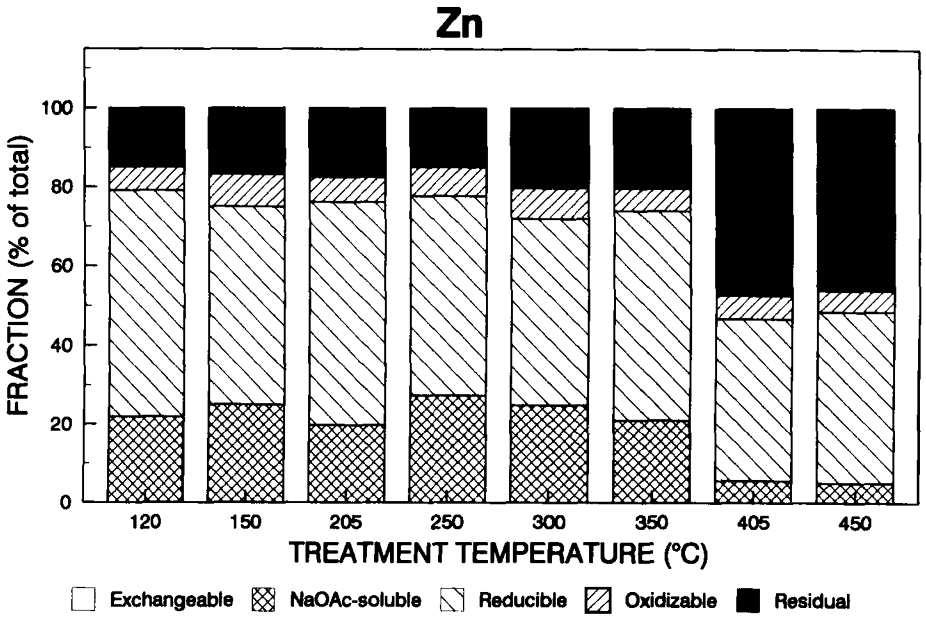

Figure 3 Chemical fractionation of Zn for different sediment treatment temperatures.

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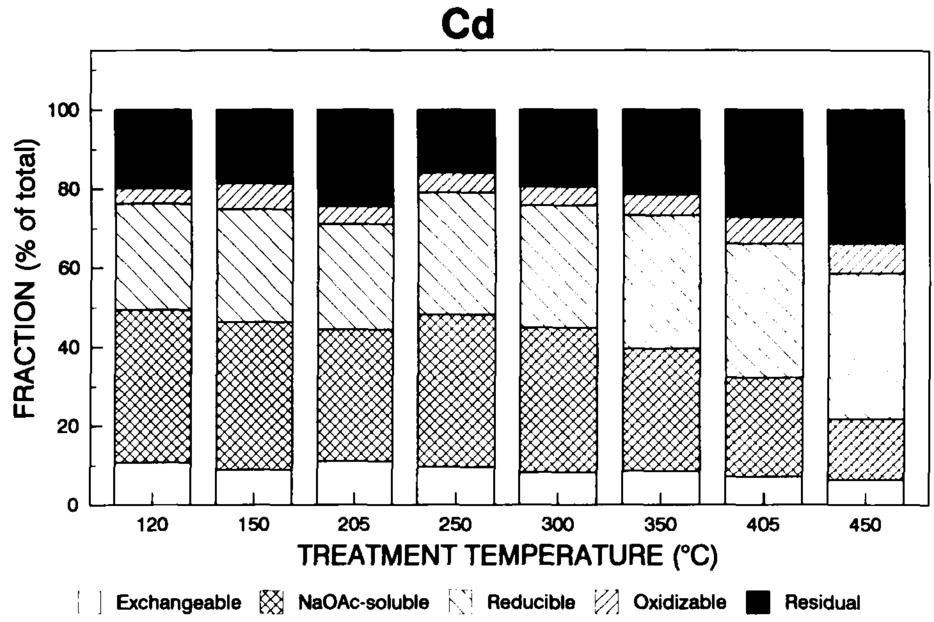

Figure 4 Chemical fractionation of Cd for different sediment treatment temperatures.

the oxidizable fraction at the lowest temperature treatments. The strong association of Cu with the oxidizable phase has been frequently reported[18-21]. For the higher temperature treatments, where the organic matter gradually is destroyed, the residual fraction becomes the most important. Zinc and Cd (Figure 3 and 4), which have a comparable environmental behaviour[22], are both distributed mainly in the NaOAc-soluble and in the reducible fraction. Lead (Figure 5) is mainly extracted in the residual fraction, while, in contrast with findings of others[20,21], relatively low amounts are found in the NaOAc-soluble or reducible fractions. This would suggest that, despite of the relative high total content (Table 1), Pb originates from natural rather than from anthropogenic sources[8,23]. Iron (Figure 6) also is predominantly associated with the residual form, while Mn (Figure 7) is present in the NaOAc-soluble and in the reducible fraction to an equal extent.

Although shifts in the fraction distribution for the different treatment temperatures can be observed, it is difficult to distinguish a general pattern for all elements. The residual fraction becomes more important while the NaOAc-soluble is retreating at higher treatment temperatures. As during ashing organic matter is oxidized, a gradual disappearance of the oxidizable fraction is expected. This appears very clearly for Cu and Pb but not for Cd and Zn. The correlation between the remaining organic matter and the oxidizable fraction was indeed significant for Cu ($r = 0.964$, $P < 0.001$) and Pb ($r = 0.748$, $P < 0.01$) but not significant for Zn ($r = 0.632$ ns) and Cd ($r = -0.521$ ns). This illustrates the decreasing affinity for organic matter in the order Cu > Pb > Zn > Cd, a sequence that also has been reported by others[24-26].

For Pb, Zn and Cd a significant oxidizable fraction persists even when organic matter content has fallen to zero after ashing at 450°C. This remaining fraction might be sulfide bound.

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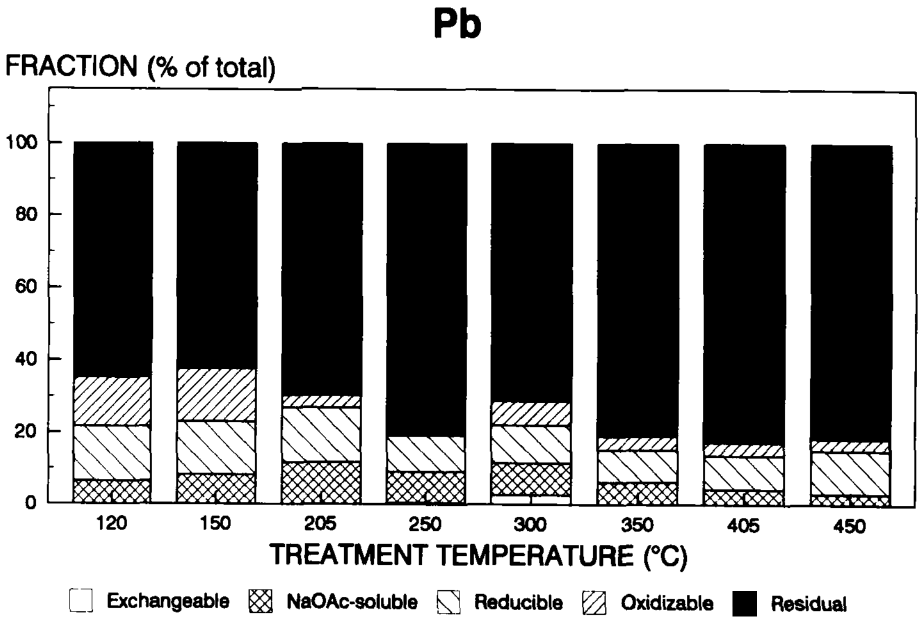

Figure 5 Chemical fractionation of Pb for different sediment treatment temperatures.

Relation between leaching behaviour and fractionation

When comparing results of the single and sequential extraction, it appears that the shift between fractions cannot explain the leaching pattern, observed from the single reagent leaching test. Since thermal treatment did not alter the distribution in the solid phase systematically (except for Cu), the changes in NH_4OAc-EDTA-extracted amounts might be attributed to shifts in the binding energy distributions of the solid fractions as a result of thermal treatment. Unger et al.[27] experimentally investigated a continuous distribution model of metal binding to natural sediments, showing that the average binding energy increases for the subsequent fractions of a fractionation procedure. Overlaps between the binding energy distributions of different dredged material constituents might however exist. Thus, binding sites associated with different constituents can have the same retention energy values. This has been denoted as one of the reasons for the lack of relation between sequential extraction and single reagent leaching tests[6].

Therefore, one must be cautious when interpreting sequential extraction data for assessing short and medium term metal mobility under field conditions. In natural aquatic environments, reactions such as colloidal adhesion, dissolution, adsorption, and surface precipitation can create multicomponent solids with bulk and surface properties different from the original pure solids[28]. Changes occurring in dredged material upon dewatering and consolidation may result in significant modifications in leaching behaviour without influencing the chemical fractionation to an important extent. It thus might be more relevant to assess possible environmental effects using appropriate leaching tests simulating natural field conditions.

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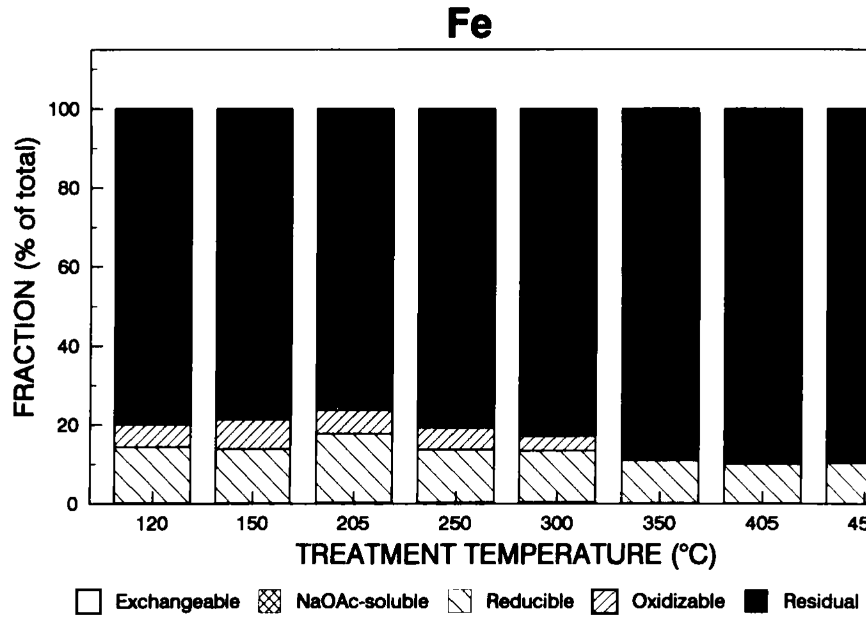

Figure 6 Chemical fractionation of Fe for different sediment treatment temperatures.

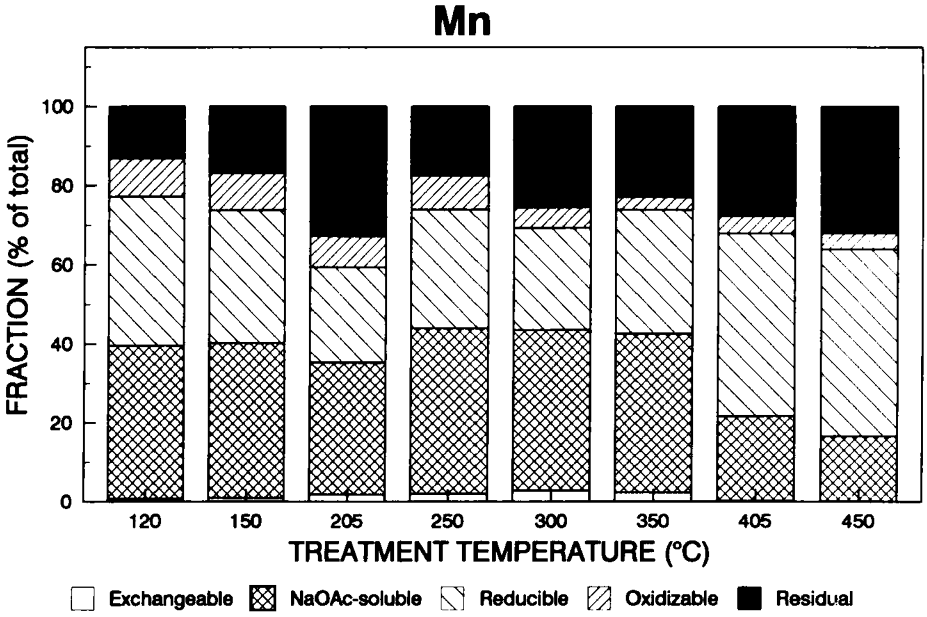

Figure 7 Chemical fractionation of Mn for different sediment treatment temperatures.

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CONCLUSIONS

Dredged material, untreated and thermally treated at increasing temperatures up to 200-250°C showed a significant increase in heavy metal fractions leachable by NH_4OAc-EDTA. At higher temperatures, creating stronger oxidizing conditions, NH_4OAc-EDTA leachable amounts decreased again but remained more important than for the untreated sediment.

The observed leaching pattern of the metals could not be explained by a shift between fractions as determined with the Tessier sequential extraction procedure. It appears that changes of binding strength within the fractions have to be considered.

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References

1. R.S. Braman, in: *Analytical aspects of environmental chemistry* (F.S. Natusch and P.K. Hopke, eds. Wiley & Sons, 1983) pp. 1-59.
2. A. Cottenie and M. Verloo. *Fresenius Z. Anal. Chem.*, **317**, 389-339 (1984).
3. J.N. Lester, R.M. Sterritt and P.W.W. Kirk, *Sci. Total Envir.* **30**, 45-83 (1983).
4. V. Spevackova and J. Kucera, *Int. J. Environ. Anal. Chem.* **35**, 241-251 (1989).
5. J. Van Hoof, *Proceedings CATS congress*, (K VIV, Antwerpen, 1991) pp. 4.21-4.27.
6. R. Calvet, S. Bourgeois and J.J. Msaky, *Intern. J. Environ. Anal. Chem.*, **39**, 31-45 (1990).
7. A. Tessier, P.G.C. Campbell and M. Bisson, *Anal. Chem.* **51**, 844-851 (1979).
8. U. Förstner, in: *Chemical methods for assessing bio-available metals in sludges and soils* (R. Leschber, R.D. Davis and P. L'Hermite, eds. Elsevier, London, 1984) pp. 1-30.
9. H.A. Elliott, B.A. Dempsey and P. J. Maille, *J. Environ. Qual.*, **19**, 330-334 (1990).
10. E. Lakanen and R. Ervio, *Acta Agr. Finn.*, **123**, 223-232 (1971).
11. A. Cottenie, M. Verloo, L. Kiekens, G. Velghe and R. Camerlynck, *Chemical analysis of plants and soils* (IWONL, Brussel, 1982) 65pp.
12. L. Kiekens and A. Cottenie, in: *Chemical methods for assessing bio-available metals in sludges and soils* (R. Leschber, R.D. Davis and P. L'Hermite, eds. Elsevier, London, 1984), pp. 32-41.
13. L.E. Allison, in: *Methods of soil analysis. Part 2.* (C.A. Black et al., eds. Am. Soc. of Agron., Madison, Wisconsin, 1965), pp. 1367-1378.
14. L.E. Allison and C.D. Moodie, in: *Methods of soil analysis. Part 2.* (C.A. Black et al., eds. Am. Soc. of Agron., Madison, Wisconsin, 1965), pp. 1379-1396.
15. M. Verloo and A. Cottenie, in: *Mededelingen Fac. Landbouwwetenschappen* (University of Gent, 1985), pp. 47-53.
16. J.G. Skogerboe, C.R. Lee and R.A. Price, *Proceedings 2nd Int. Conf. Environ. Contamination,* (Amsterdam, 1986) pp. 235-237.
17. J.C. Cornwell, *Proceedings Int. Conf. Heavy metals in the Environment,* (New-Orleans, 1987) pp. 1:233-235.
18. W. Salomons and U. Förstner, *Environ. Technol. Letts.*, **1**, 506-517 (1980).
19. A.C. Chang, A.L. Page, J.E. Warneke and E. Grgurevic, *J. Environ. Qual.*, **13**, 33-43 (1984).
20. D. Robbe, D. Demara and P. Six, *Proceedings 2nd Int. Conf. Environ. Contamination,* (Amsterdam, 1986) pp. 221-234.
21. R. Pardo, E. Barrado, L. Perez and M. Vega, *Wat. Res.*, **24**, 373-379 (1990).
22. M. Smies, in: *Trace element speciation in surface waters* (G.G. Leppard, ed. Plenum Press, New York, 1983) pp. 177-191.
23. G. Rauret, R. Rubio, J.F. López-Sánchez and E. Casassas. *Water Res.* **22**, 449-455 (1988).
24. F.J. Stevenson, *Soil Sci. Soc. Am. J.*, **40**, 665-672 (1976).
25. J. Baham, N.B. Ball, and G. Sposito, *J. Environ. Qual.*, **7**, 181-188 (1978).

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26. R.A. Saar and J.H. Weber, *Environ. Sci. Technol.*, **16,** 510-517 (1982).
27. M.T. Unger and H.E. Allen, in: *Heavy metals in the hydrological cycle* (M. Astruc and J.N. Lester, eds. Publications Division, London, 1988) pp. 481-488.
28. P.R. Anderson and M.B. Benjamin, *Environ. Sci. Technol.*, **24,** 1586-1592 (1990).

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