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# Impact of single reagent extraction using $NH_4OAc$-EDTA on the solid phase distribution of metals in a contaminated dredged sediment

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## ABSTRACT

The solid phase distribution of metals in a contaminated dredged sediment as affected by a single reagent extraction (0.5 mol/L $NH_4OAc$ + 0.02 mol/L EDTA) was studied. A sediment was dried and portions were heated at 250°C and 450°C. From each treatment, a portion was extracted with $NH_4OAc$-EDTA. Both the extracted and the unextracted portions were then subjected to a sequential fractionation.

$NH_4OAc$-EDTA extraction decreased both the acid extractable and the reducible fractions. The oxidizable and residual fractions were not significantly affected. Larger portions of the acid extractable and reducible fractions were extracted with $NH_4OAc$-EDTA when the sediment was previously heated at 250°C. After heating the sediment at 450°C the $NH_4OAc$-EDTA-extractable portions decreased.

Fractionation procedures can provide reliable information on the chemical associations of pollutants in sediments. To estimate short and medium term metal availability, single reagent leaching tests appear more appropriate.

## INTRODUCTION

Two approaches can be discerned to characterize the pollution status of soils and sediments (Cottenie and Verloo, 1984; Lake et al., 1984; Calvet et al., 1990). The first concerns single reagent extractions to assess mobile and bioavailable fractions of metals. The second approach involves the use of sequential fractionation techniques to distinguish between different physico-chemical associations of metals (Tessier et al., 1979; Emmerich et al., 1982; Förstner, 1984).

Single reagent extraction with 0.5 mol/L ammonium acetate, containing 0.02 mol/L EDTA at pH 4.65 is used for the determination of trace elements in soils (Cottenie et al., 1979; Cottenie and Verloo, 1984) and correlates well with plant concentrations (Kiekens et al., 1984). It could also be useful to identify mobile pollutant pools in sediments (Tack and Verloo, 1991).

The application of fractionation is still subjected to much controversy. Nonselectivity of the reagents and trace element redistributions among phases during fractionation are the main problems reported (Rendell and Batley, 1980; Tipping et al., 1985; Belzile et al., 1989; Bermond and Sommer, 1989; Calvet et al., 1990; Shannon and White, 1991; Bermond, 1992; Bermond and Eustache, 1993; Förstner, 1993; Xiao-Quan and Bin, 1993). Despite all the restrictions, sequential fractionation procedures have proved to be useful in the field of environmental analytical chemistry (Tessier and Campbell, 1991).

In previous experiments, Tack and Verloo (1993) showed that heating a sediment influenced the extractability in $NH_4OAc$-EDTA strongly while effects on the solid phase distribution were minor. In this paper, the impact of this single reagent extraction on the solid phase distribution of metals in a contaminated dredged material was studied. A sediment was dried and portions were heated at 250°C and 450°C. From each treatment, a portion was extracted with $NH_4OAc$-EDTA. Both the extracted and the unextracted portions were then subjected to a sequential fractionation. The $NH_4OAc$-EDTA-extractable amounts of the sequential fractions were measured by the difference in the Tessier fraction contents before and after extraction with the single $NH_4OAc$-EDTA-reagent.

## EXPERIMENTAL

A sediment sample was dried at 120 °C for 24 hours. Separate portions were heated for four hours at 120, 250, and 450 °C, respectively.

Carbonate content was determined by back titration of an excess of 0.5 mol/L HCl added to one gram of the sample with 0.5 mol/L NaOH (Allison and Moodie, 1965). Organic matter was estimated by the Walkley-Black method and converted (1.72 x C) to percent organic matter (Allison, 1965).

For each thermal treatment, two three-gram sub-samples of the sediment were weighed into polyethylene centrifuge tubes. One sub-sample was extracted with 15 ml $NH_4OAc$-EDTA pH 4.65 (38.5 g $NH_4OAc$ + 25 ml of glacial acetic acid + 5.845 g EDTA in 1 L) for 30 minutes under continuous agitation at room temperature. The second sub-sample was not extracted. All sediment samples were then subjected to the Tessier sequential fractionation procedure (Tessier et al., 1979).

In previous experiments, the 'exchangeable' fraction was found to be low compared to the total contents and to the $NH_4OAc$-EDTA extracted amounts (Tack and Verloo, 1993) and was therefore omitted here. The acid extractable, reducible, and oxidizable fractions were estimated as prescribed by Tessier. The residual amounts were determined by the aqua regia method (Ure, 1990).

After each fractionation step, the suspension was centrifuged (3000 g for 20 minutes) and the supernatant liquid withdrawn with a syringe. The solid phase was rinsed with 8 mL of deionized water. The rinse water was separated from the solids in a similar way and discarded.

Concentrations in the supernatants were determined by flame atomic absorption (Varian AA-1475) with external standards, prepared in the corresponding extracting solution. The extract volume was determined by weighing the centrifuge tube just before sampling the liquid phase and accounting for weight losses of the solid material during the subsequent extractions.

The experiment was duplicated.

## RESULTS AND DISCUSSION

The sequential fractionation of the sediment, before and after extraction with $NH_4OAc$-EDTA, is presented in Table 1. In principle $NH_4OAc$-EDTA could extract metals from any solid fraction. The Tessier fractions and the $NH_4OAc$-EDTA-extractable portions for Cd, Co, Cu, Ni, Pb, and Zn are illustrated in Figs 1 to 3. The $NH_4OAc$-EDTA-extractable portions of the Tessier fractions were estimated as the difference between the determinations before and after $NH_4OAc$-EDTA-extraction. Only significant differences were plotted. When the difference was not significant, the $NH_4OAc$-EDTA-extractable portion was estimated to be zero.

In the dried sediment, Cd and Zn were mainly present in the acid extractable and reducible fractions. Cu was found mainly in the oxidizable fraction while Ni, Co, and Pb were almost equally partitioned over all Tessier fractions. The residual fraction increased when the sediment was treated at higher temperature while all other fractions generally decreased. For Cd and Zn, however, the acid extractable fraction was highest for the 250°C heated sediment.

The acid extractable and reducible fractions were significantly affected by extraction with $NH_4OAc$-EDTA. The portions released were considerably higher for the sediment heated at 250°C, and mostly insignificant for the 450°C treated sediment.

### *Acid extractable fraction*

Conceptually, the acid extractable step is believed to release the heavy metals associated with carbonates (Tessier et al., 1979; Lake et al., 1984; Brümmer, 1986). The carbonate content was about 16% (Table 2), corresponding with 64 000 mg Ca/kg dry sediment. The Ca-amounts extracted (Table 1) suggest that the carbonates were only partially dissolved, the remaining being released in the reducible fraction. The experimental conditions of this step therefore are not suited for estimating carbonate bound metals in sediments with a high carbonate content.

A small amount of Fe, compared to the amount released in the reducible fraction, was extracted in the acid extractable step (Table 1). This indicates that iron oxyhydroxides were not significantly affected during this step of the sequential fractionation. Iron released by $NH_4OAc$-EDTA however was much higher, suggesting that part of the iron oxyhydroxides and associated metals were also released. For some metals (Co, Cu, Pb) the total amount dissolved in $NH_4OAc$-EDTA thus exceeded the amount in the acid extractable fraction.

The acid extractable fraction of most metals was significantly affected by heating the sediment at 250°C and 450°C. The acid extractable Ca, however, remained constant, suggesting that the solubilization of carbonates was unaffected (Table 1). The metals involved presumably were rather sorbed on solid phases than included in carbonates: at the intermediate temperature, the decrease of organic matter may effect a more efficient desorption of metals. For the 450°C heated sediment, metals may be strongly retained in crystalline iron oxides. The $NH_4OAc$-EDTA-extractable portion of the acid extractable fraction followed the same trend (Figs 1 to 3).

## *Reducible fraction*

Metals in the reducible step are associated with manganese oxides and amorphous iron oxyhydroxides (Tessier et al., 1979; Lake et al., 1984). Because of the high carbonate content and the insufficient solubilization of carbonates in the previous step, a considerable portion of the reducible fraction was originating from carbonate-associated metals.

A considerable amount of Fe is released with $NH_4OAc$-EDTA, suggesting that part of the iron oxyhydroxides and associated metals were solubilized. Specific adsorption of metals on iron oxyhydroxides can take place within the surface layer or inside the oxide (Jenne, 1968; Benjamin and Leckie, 1981; Brümmer, 1986), but mainly occurs in the surface areas (Benjamin and Leckie, 1981; Bleam and McBride, 1985; McBride, 1989). The data support this statement: the ratio between the $NH_4OAc$-EDTA-extractable portion of the reducible fraction and the total reducible fraction is higher for metals other than Fe.

The decrease of the reducible fractions, observed for the sediment heated at 250°C and 450°C, resulted from the conversion of amorphous iron hydroxides to more crystalline forms (Jenne, 1968). These are not extracted by acidified $NH_2OH$ (Chao, 1972; Shuman, 1982; Chao and Liyi Zhou, 1983). Associated metals were released in the residual fraction.

## *Oxidizable fraction*

Metals in the oxidizable fraction are mainly associated with organic matter and with sulfides (Tessier et al., 1979; Kim and Fergison, 1991). The oxidizable fraction of Cu in particular, and of Co, Ni, and Ca to a lesser extent, decreased with higher treatment temperature, clearly showing they were associated with organic matter: during the heating process, organic matter is destroyed while sulfides are protected from further oxidation by an oxide coating that develops.

The oxidizable fraction was not significantly affected by $NH_4OAc$-EDTA-extraction (Table 1).

## *Residual fraction*

The residual fraction increased after thermal treatment. This increase is mostly explained by the dehydratation and conversion of iron oxyhydroxides to more crystalline forms, not soluble in acidified $NH_2OH$ (Chao, 1972; Shuman, 1982; Chao and Liyi Zhou, 1983; Tipping et al., 1985; Shannon and White, 1991). For Cu, it is observed that the large organic pool was mainly shifted into the residual fraction. Only a small amount was transferred to the reducible fraction. It thus appeared that, during heating, metals released from the organic matter were scavenged by iron oxyhydroxides and immobilized.

## SUMMARY AND CONCLUSIONS

$NH_4OAc$-EDTA-extractable metals increased when a sediment was previously heated at 250°C, and were lowest after heating at 450°C. The solid phase distribution was also influenced. The residual fraction increased while the reducible and oxidizable fractions decreased. With the $NH_4OAc$-EDTA-extraction, metals from both the acid extractable and the reducible fractions were removed. The fact that the portions of the sequential fractions extracted by the $NH_4OAc$-EDTA reagent changed with the treatment temperature showed that the metal species extracted at each Tessier stage were not the same for all temperature treatments. This means that the sequential extraction reagents do not uniquely define the metal species extracted. These differences in the $NH_4OAc$-EDTA extractability of the Tessier phases certainly reflect changes in metal mobility. As the $NH_4OAc$-EDTA extractable contents of whole soils have been shown to correlate with plant metal contents (Cottenie and Verloo, 1984; Kiekens et al., 1984), they may also be related to availability to aquatic biota.

Sequential fractionation procedures may provide useful indications on the chemical associations of pollutants in sediments. Metals in a same chemical association may however exhibit a different short and medium term mobility. Sequential fractionations therefore are less suited for estimating metal mobility and bioavailability. Appropriate single reagent leaching tests, mobilizing the metals in defined conditions, are probably more appropriate. Moreover, they often are less elaborate and therefore more reproducible and easier to standardize than sequential fractionations.

## REFERENCES

Allison, L.E., 1965. In: C.A. Black et al. (Eds), Methods of soil analysis. Part 2. Am. Soc. of Agron., Madison, Wisconsin, pp. 1367-1378.

Allison, L.E. and C.D. Moodie, 1965. In: C.A. Black et al. (Eds), Methods of soil analysis. Part 2. Am. Soc. of Agron., Madison, Wisconsin, pp. 1379-1396.

Belzile, N., P. Lecomte and A. Tessier, 1989. Heavy metal extractability in long-term sewage sludge and metal salt-amended soils. Environ. Sci. Technol., 23: 1015-1020.

Benjamin, M.M. and J.O. Leckie, 1981. Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. J. Colloid Interface Sci., 79: 209-221.

Bermond, A.P., 1992. Thermodynamics applied to the study of the limits of sequential extraction procedures used for the speciation of trace elements in sediments and soils. Environ. Technol., 13: 1175-1179.

Bermond, A. and G. Sommer, 1989. Simulation of heavy metal extraction in soil samples compared with experimental results. Environ. Technol. Let. 10: 989-994.

Bermond, A.P. and S. Eustache, 1993. Hydroxylamine extraction of trace-metals in soils; kinetic aspects. Environ. Technol. 14: 359-365.

Bleam, W.F. and M.B. McBride, 1985. Cluster formation versus isolated-site adsorption. A study of Mn(II) and Mg(II) adsorption on Boehmite and Goethite. J. Colloid Interface Sci. 103: 124-131.

Brümmer, G.W., 1986. Heavy metal species, mobility and availability in soils. In: M. Bernhard, F.E. Brinckman and P.J. Sadler (Eds), The importance of chemical "speciation" in environmental processes. Springer-Verlag, Berlin, Heidelberg, pp. 169-192.

Calvet, R., S. Bourgeois and J.J. Msaky, 1990. Some experiments on extraction of heavy metals present in soil. Intern. J. Environ. Anal. Chem., 39: 31-45.

Chao, T.T., 1972. Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. Soil Sci. Soc. Am. Proc., 36: 764-768.

Chao, T.T. and Liyi Zhou, 1983. Extraction techniques for selective dissolution of amorphous iron oxides from soils and sediments. Soil Sci. Soc. Am. J., 47: 225-232.

Cottenie, A., R. Camerlynck, M. Verloo and A. Dhaese, 1979. Fractionation and determination of trace elements in plants, soils and sediments. Pure Appl. Chem., 52: 45-53.

Cottenie, A. and M. Verloo, 1984. Analytical diagnosis of soil pollution with heavy metals. Fresenius Z. Anal. Chem. 317: 389-393.

Emmerich, W.E., L.J. Lund and A.C. Chang, 1982. Solid phase forms of heavy metals in sewage sludge-treated soils. J. Environ. Qual. 11: 78-181.

Förstner, U., 1984. Chemical forms and reactivities of metals in sediments. In: R. Leschber, R.R. Davis and P. L'Hermite (Eds), Chemical methods for assessing bio-available metals in sludges and soils. Elsevier, London, pp. 1-30.

Förstner, U., 1993. Metal speciation - general concepts and applications. Intern. J. Environ. Anal. Chem., 51: 5-23.

Jenne, E.A., 1968. Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: The significant role of hydrous Mn and Fe oxides. Adv. Chem. Ser., 73: 337-387.

Kiekens, L., A. Cottenie and G. Van Landschoot, 1984. Chemical activity and biological effect of sludge-borne heavy metals and inorganic metal salts added to soils. Plant Soil 79: 89-99.

Kim, N.D. and J.E. Fergusson, 1991. Effectiveness of a commonly used sequential extraction technique in determining the speciation of cadmium in soils. Sci. Total Environ. 105: 191-209.

Lake, D.L., P.W.W. Kirk and J.N. Lester, 1984. Fractionation, characterisation and speciation of heavy metals in sewage sludge and sludge-amended soils: a review. J. Environ. Qual. 13: 175-183.

McBride, M.B., 1989. Reactions controlling heavy metal solubility in soils. In: R.A. Stewart (Ed), Advances in Soil Science. Volume 10. Springer-Verlag, New York, pp. 1-56.

Rendell, P.S. and G.E. Batley, 1980. Adsorption as a control of metal concentrations in sediment extracts. Environ. Sci. Technol., 23: 314-318.

Shannon, R.D. and J.R. White, 1991. The selectivity of a sequential extraction procedure for the determination of iron oxyhydroxides and iron sulfides in lake sediments. Biogeochemistry, 14: 193-208.

Shuman, L.M., 1982. Separating soil iron- and manganese-oxide fractions for microelement analysis. Soil Sci. Soc. Am. J. 46: 1099-1102.

Tack, F. and M. Verloo, 1991. Estimation and testing of environmental effects of heavy metals in dredged materials. In: Proc. CATS Congress, K.VIV, Antwerpen, pp. 3.55-59.

Tack, F.M.G. and M.G. Verloo, 1993. Leaching behaviour and solid phase fractionation of selected metals as affected by thermal treatment of a polluted sediment. Intern. J. Env. Anal. Chem. 51: 167-175.

Tessier, A., P.G.C. Campbell and M. Bisson, 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem., 51: 844-851.

Tessier, A. and P.G.C. Campbell, 1991. Comment on "Pitfalls of sequential extractions" by P.M.V. Nirel and F.M.M. Morel, Wat. Res. 24, 1055-1056 (1990) Wat. Res., 25: 115-117.

Tipping, E., N.B. Hetherington, J. Hilton, D.W. Thompson, E. Bowles and J. Hamilton-Taylor, 1985. Artifacts in the use of selective chemical extraction to determine distributions of metals between oxides of manganese and iron. Anal. Chem. 57: 1944-1946.

Ure, A.M., 1990. Methods of analysis for heavy metals in soils. In: B.J. Alloway (Ed), Heavy metals in soils. Blackie and Son, Glasgow. pp. 40-73.

Xiao-Quan, S. and C. Bin, 1993. Evaluation of sequential extraction for speciation of trace metals in model soil containing natural minerals and humic acid. Anal. Chem., 65: 802-807.

Table 1. Metal distribution (according to the sequential extraction procedure of Tessier et al. (1979) in sediments, heated at 120°C, 250°C, or 450°C, and not extracted (a) or extracted (b) with NH4OAc-EDTA in mg/kg dry (120°C) sediment.

| Metal | Temp (°C) | | $NH_4$OAc-EDTA | Acid extr. | Reducible | Oxidizable | Residual | Sum |
|---|---|---|---|---|---|---|---|---|
| | | | | | (mg/kg DM) | | | |
| Cd | 120 | a) | | 2.7 b | 5.9 d | 0.7 a | 0.5 a | 9.8 |
| | | b) | 2.3 b | 1.1 a | 4.4 c | 0.7 a | 0.6 a | 9.1 |
| | 250 | a) | | 4.0 c | 4.2 bc | 0.7 a | 0.7 a | 9.7 |
| | | b) | 4.7 c | 0.7 a | 2.0 a | 0.5 a | 0.6 a | 8.5 |
| | 450 | a) | | 1.0 a | 3.3 b | 1.7 a | 3.2 b | 9.1 |
| | | b) | 0.9 a | 0.8 a | 3.9 bc | 1.4 a | 2.7 b | 9.8 |
| Co | 120 | a) | | 4.1 c | 6.2 d | 3.3 b | 6.1 a | 19.7 |
| | | b) | 3.8 b | 1.6 a | 4.2 c | 3.3 b | 6.6 a | 19.5 |
| | 250 | a) | | 3.8 c | 6.0 d | 2.5 ab | 8.2 a | 20.5 |
| | | b) | 5.1 c | 1.0 a | 3.3 ab | 2.0 a | 7.3 a | 18.7 |
| | 450 | a) | | 2.6 b | 3.7 bc | 1.3 a | 14.1 b | 21.7 |
| | | b) | 2.0 a | 1.8 ab | 3.0 a | 1.2 a | 13.4 b | 21.5 |
| Cu | 120 | a) | | 1.9 b | 6.6 a | 64.3 b | 20.4 a | 93.2 |
| | | b) | 11.6 ab | 1.1 b | 3.7 a | 48.3 b | 25.4 ab | 90.1 |
| | 250 | a) | | 1.6 b | 3.8 a | 11.0 a | 74.7 c | 91.1 |
| | | b) | 19.2 b | 0.3 a | 2.6 a | 9.5 a | 51.2 bc | 82.8 |
| | 450 | a) | | 2.7 c | 3.7 a | 6.9 a | 78.7 c | 92.0 |
| | | b) | 3.6 a | 2.9 c | 3.7 a | 5.4 a | 76.1 c | 91.8 |
| Ni | 120 | a) | | 6.7 d | 13.4 d | 6.7 b | 16.7 a | 43.5 |
| | | b) | 7.3 b | 2.5 ab | 8.8 b | 7.0 b | 18.4 a | 44.0 |
| | 250 | a) | | 3.8 bc | 11.3 c | 9.1 b | 20.1 a | 44.4 |
| | | b) | 4.8 a | 1.3 a | 8.2 b | 7.5 b | 19.0 a | 40.8 |
| | 450 | a) | | 4.6 c | 6.2 a | 2.7 a | 33.0 b | 46.6 |
| | | b) | 2.8 a | 3.2 abc | 5.6 a | 3.1 a | 36.2 b | 51.0 |
| Pb | 120 | a) | | 24.2 c | 46.1 f | 35.9 a | 31.5 a | 137.7 |
| | | b) | 62.3 b | 5.6 a | 18.7 b | 19.1 a | 25.4 a | 131.2 |
| | 250 | a) | | 16.3 b | 30.5 d | 31.8 a | 57.4 a | 135.9 |
| | | b) | 69.4 b | 3.0 a | 12.0 a | 16.8 a | 37.2 a | 138.4 |
| | 450 | a) | | 6.1 a | 36.3 e | 26.2 a | 71.9 a | 140.4 |
| | | b) | 23.0 a | 6.1 a | 26.7 c | 21.8 a | 65.3 a | 142.8 |
| Zn | 120 | a) | | 142.6 c | 323.8 d | 59.9 a | 47.0 a | 573.2 |
| | | b) | 125.8 a | 55.1 b | 228.9 c | 58.8 a | 57.9 a | 526.5 |
| | 250 | a) | | 180.9 d | 253.9 c | 47.8 a | 89.7 b | 572.3 |
| | | b) | 280.5 b | 26.3 a | 119.3 a | 31.7 a | 78.6 b | 536.3 |
| | 450 | a) | | 26.0 a | 161.2 b | 64.9 a | 294.5 c | 546.6 |
| | | b) | 30.1 a | 20.5 a | 168.5 b | 55.4 a | 280.0 c | 554.4 |

Fractions were compared using a Duncan multiple range test at the 95 % level. Homogeneous groups are denoted with the same letter

Table 1. (cont.)

| Metal | Temp | | $NH_4$OAc-EDTA | Acid extr. | Reducible | Oxidizable | Residual | Sum |
|---|---|---|---|---|---|---|---|---|
| | (°C) | | | | (mg/kg DM) | | | |
| Fe | 120 | a) | | 106 ab | 9756 c | 5784 a | 23269 a | 38915 |
| | | b) | 1262 b | 191 c | 8771 bc | 5462 a | 27584 a | 43270 |
| | 250 | a) | | 56 a | 6801 ab | 2585 a | 32857 a | 42299 |
| | | b) | 1126 b | 208 c | 7571 abc | 2285 a | 20505 a | 31695 |
| | 450 | a) | | 68 ab | 5449 a | 2308 a | 38518 a | 46344 |
| | | b) | 347 a | 129 b | 5756 a | 1195 a | 38939 a | 46366 |
| Mn | 120 | a) | | 201 c | 497 c | 88 a | 132 a | 919 |
| | | b) | 168 a | 180 c | 337 b | 87 a | 132 a | 905 |
| | 250 | a) | | 300 d | 338 b | 64 a | 198 a | 900 |
| | | b) | 356 b | 99 b | 223 a | 48 a | 160 a | 886 |
| | 450 | a) | | 45 a | 471 c | 92 a | 328 b | 937 |
| | | b) | 56 a | 47 a | 468 c | 67 a | 301 b | 940 |
| Ca | 120 | a) | | 34889 b | 21959 b | 1339 c | 131 a | 58318 |
| | | b) | 15263 a | 18009 a | 7961 a | 625 ab | 165 a | 42023 |
| | 250 | a) | | 35474 b | 19589 b | 1082 bc | 191 a | 56337 |
| | | b) | 15708 a | 16948 a | 6317 a | 346 a | 131 a | 39449 |
| | 450 | a) | | 37562 b | 16255 b | 473 a | 231 a | 54521 |
| | | b) | 12780 a | 27739 ab | 5072 a | 146 a | 229 a | 45967 |

Fractions were compared using a Duncan multiple range test at the 95 % level. Homogeneous groups are denoted with the same letter

Table 2. $CaCO_3$ and organic matter (OM) content in the sediment heated at different temperatures

| Treatment | $CaCO_3$ (%) | Std |
|---|---|---|
| 120 °C | 16.2% | 0.7% |
| 250 °C | 15.1% | 0.6% |
| 450 °C | 16.1% | 0.8% |

| Treatment | OM (%) | Std |
|---|---|---|
| 120 °C | 2.72% | 0.06% |
| 250 °C | 1.94% | 0.01% |
| 450 °C | 0.09% | 0.05% |

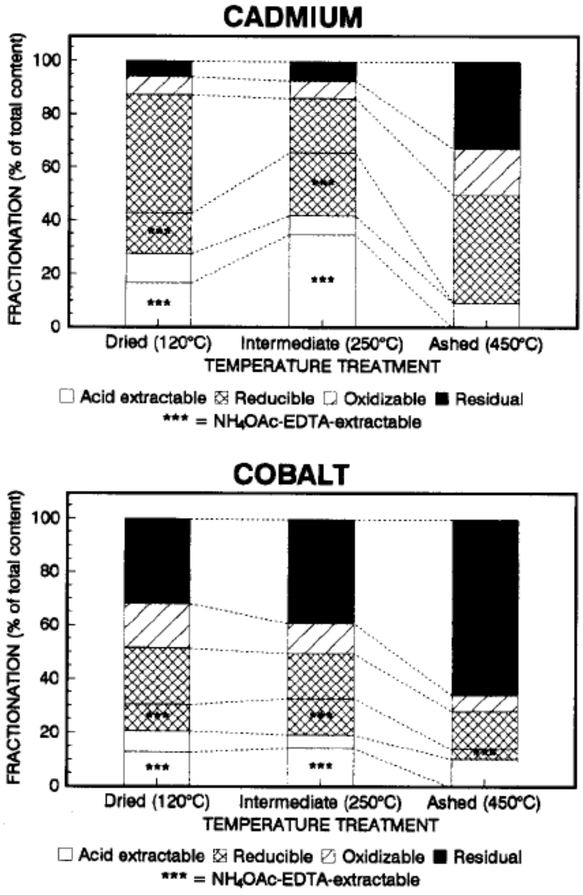

Fig. 1. Sequential extraction (Tessier et al., 1979) of Cd and Co with indication of the portions of the fractions affected by previous extraction with $NH_4OAc$-EDTA

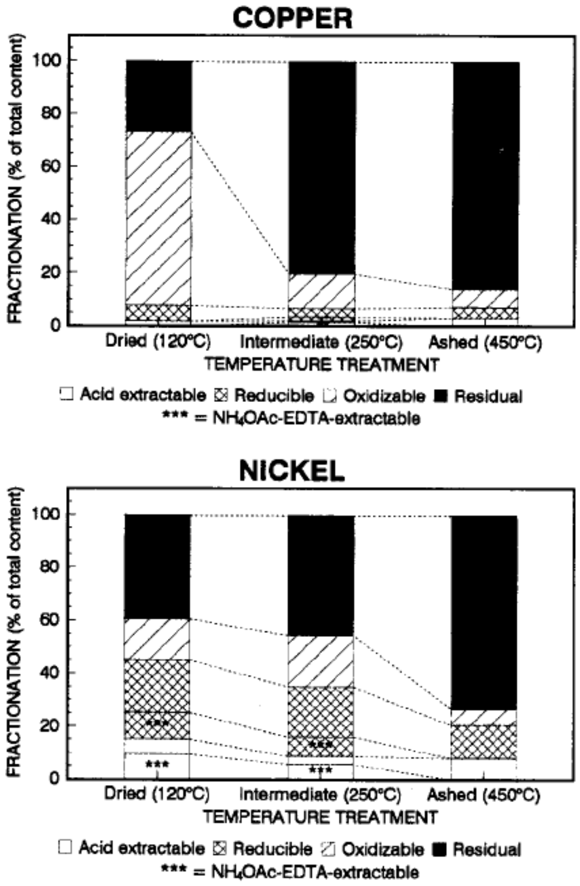

Fig. 2. Sequential extraction (Tessier et al., 1979) of Cu and Ni with indication of the portions of the fractions affected by previous extraction with $NH_4OAc$-EDTA

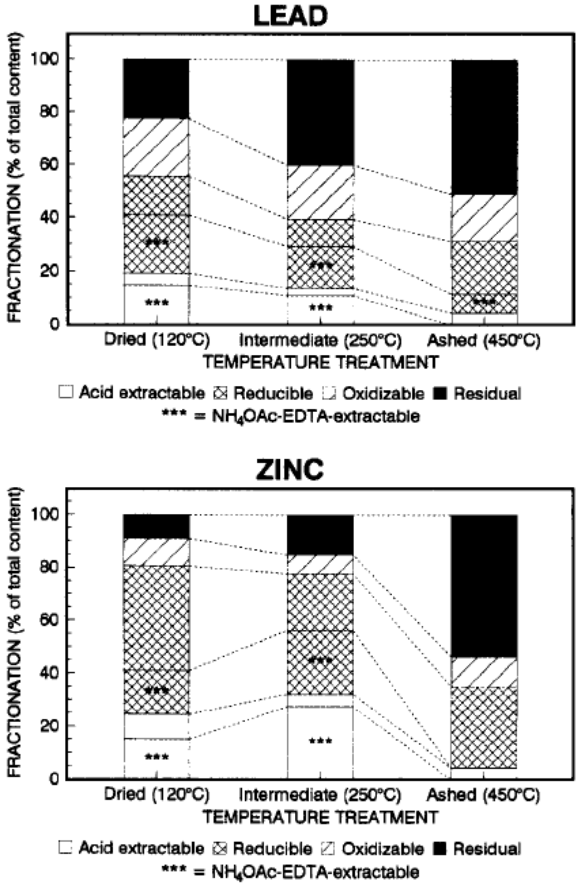

Fig. 3. Sequential extraction (Tessier et al., 1979) of Pb and Zn with indication of the portions of the fractions affected by previous extraction with $NH_4OAc$-EDTA