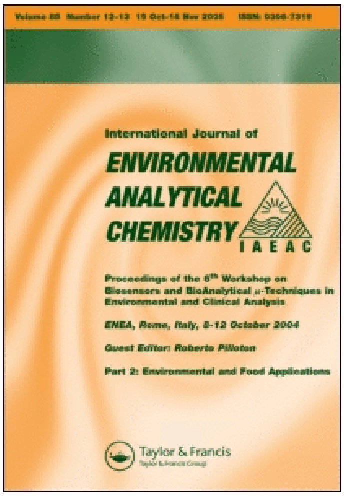

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INFLUENCE OF OXIDATION ON SEQUENTIAL CHEMICAL EXTRACTION OF DREDGED RIVER SLUDGE

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The influence of oxidation on the speciation of transition metal ions in dredged sludge obtained from sequential extraction was investigated. The transition metals cadmium, copper, lead and zinc became more extractable after oxidation. This shift is related with the oxidation of their metal sulfides. Although iron has a similar affinity for sulfides, iron was less extractable from oxidised sediments. The conversion of Fe(II) to Fe(III) and the formation of iron(III)oxide minerals could account for this observation. The results emphasise the need of working under strictly anoxic conditions when studying anaerobic sediments. Three different extraction schemes were compared. Two extraction schemes (Oakley and Wallman) were found to give comparable results. The extraction scheme of Tessier differs largely from the two other methods used. This is probably due to the more severe extraction conditions. The influence of drying of the sediment was also investigated. Drying of sediments does not affect the speciation if the drying process is performed in anoxic conditions. The experiments indicate clearly that all possible precautions to avoid oxidation are prerequisite. Chemical analyses of sludge or sediment can be simplified considerably by anoxically drying the sample prior to analyses in anoxic conditions.

Keywords: sequential extraction; heavy metals; oxidation; dredged material

INTRODUCTION

Chemical speciation as inferred from sequential extraction procedures is based on the selective extraction of one geochemical phase and its associated metals (1,2). In many papers (3–6) criticism is given to these sequential extraction procedures as being non selective and subject to transition metal redistributions during the extraction steps. As a result the methodology is now generally accepted

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to lead only to "operationally defined fractions" which are only poorly correlated with individual geochemical phases. An alternative procedure was proposed by Slavek et al (7) based on a competition with a sequence of ion exchange resins, but this method also leads to operationally defined fractions. Notwithstanding some fundamental drawbacks, sequential extraction techniques have contributed largely to the understanding of transition metal behaviour in soils and sediments, and are still frequently in use.

The redoxpotential of anaerobic sludges is an important factor which influences the metal speciation. In these sludges trace metals are expected to be bound as metal sulphides and are thus very sensitive to changes in redox conditions. Therefore application of sequential extraction to study the speciation in anaerobic sediments without the necessary precautions to avoid oxidation cannot lead to useful information on the behaviour of heavy metals in reducing conditions. Rapin et al (5), Tack et al (6) and Wallman et al (8) already warned for oxygen contamination during sampling, storage and extraction. It is the purpose of this contribution to give experimental evidence for the changes which occur upon oxidation of anaerobic river sludge as inferred from three different extraction procedures.

The influence of oxidation on the speciation will be illustrated :

1. by comparing extraction experiments in air and under anoxic conditions on wet sludge and
2. by studying the influence of drying in air or under anoxic conditions.

MATERIALS AND METHODS

Sludge from the canal Gent-Terneuzen (Belgium) was used in all experiments. Samples were taken with a sludge sampler and transported in fully filled glass containers and brought as soon as possible under anoxic conditions inside a glove box. All further manipulations were made inside the glove box. The upper layer of each container was discarded, because of the risk of oxidation during the transportation to the laboratory. Sludge from different containers were mixed thoroughly to obtain a homogenous mixed sample. All further treatments were done with the same mixed sample. The main composition of this sludge as well as its metal contaminant content and texture are given in Table I.

In order to investigate the influence of partial oxidation on the speciation, sequential extractions were made at room temperature in ambient air and under anoxic conditions inside a glove box. The oxygen level in the glove box was continuously monitored. Anoxic conditions were obtained by continuously flushing 95%/5% N_2/H_2- gas over a catalyst inside the glove box. The oxygen concentration as monitored by the trace oxygen analyser (Delta F) was 1000 µg/m^3. The humidity in the glove box was controlled by $CaCl_2$-pellets. Deoxygenated double distilled water was used to prepare all solutions.

TABLE I general characteristics of the sediment from the canal Gent-Terneuzen

WATER CONTENT (%)	55.25 ± 0.04
pH	8.0
Eh (mV)	-314
ORGANIC CARBON (WALKLEY-BLACK) (%)	5.2 %
TOTAL SULFUR (%)	1.3 %
$CaCO_3$ (%)	17.4 ± 0.4
METAL CONTENT (mg/kg dry material)	
CADMIUM	12.9 ± 0.5
COPPER	128 ± 1
LEAD	721 ± 10
ZINC	3200 ± 50
IRON	29000 ± 1000
TEXTURE	
> 50 µm	30 %
50 µ → 20 µm	18 %
20 µ → 2 µm	17%
< 2 µm	36 %

Three series of experiments were made. In the first series wet sludge was used. The influence of oxidation was investigated by applying the sequential extraction procedure of Oakley et al (2) both in ambient air and inside the glove box. The experimental conditions of the Oakley extraction are given in Table II.

In the second series two other extraction procedures (1,8) were examined under anoxic conditions and were compared with the former results from the Oakley procedure.

In the third series the sludge dried in ambient air at 100°C, 70°C and 20°C were compared with sludge dried at 20°C under anoxic conditions in the glove box and with the original undried sludge. In this series the three sequential extraction procedures were compared, and all extractions were made inside the glove box.

The experimental extraction conditions are given in Tables II to IV. Numbered fractions as well as the presumed phases involved in each extraction step are indicated. During each extraction at room temperature, the test tubes were shaken on an end over end shaker. The pH values were measured after each extraction step. Phase separation was effected in all cases by centrifugation of tightly closed centrifuge tubes (10 minutes; 10000 rpm) outside the glove box. The supernatant was removed by pipette in the glove box. Each extraction step was followed by a washing step. It was impossible to heat the samples inside the glove box to high temperatures. Therefore, extraction step three of the Tessier procedure was done in a covered vessel under continuos nitrogen flow outside the glove box. Extraction step four of Tessier et al (1) and Wallman et al (8) and the last step in all procedures were made in ambient air because the extraction media were already highly oxidising.

TABLE II experimental conditions for sequential extraction following Oakley (2)

	Assumed phase involved	*2 g dried sludge or 4 g wet sludge in 250 mL centrifuge vials*
Fraction 1	exchangable	50 mL sea water (20.4 meq $CaCl_2$/L, 107.2 meq $MgCl_2$/L, 10 meq KCl/L and 470 meq NaCl/L)
fraction 2	organic	50 mL 1% NH_3solution
fraction 3	clay	50 mL 1% HNO_3 solution
fraction 4	residual	50 mL HNO_3 solution, heating for 3 hours on sand bath covered with a watch glass

TABLE III experimental conditions for sequential extraction following Tessier (1)

	Assumed phase involved	*1 g dried sludge or 2 g wet sludge in 30 mL centrifuge tubes*
Fraction 1	exchangable	8 mL $Mgcl_2$ 1 M, pH 7, room temperature, during 1 hour
fraction 2	carbonates	8 mL NaOAc 1M, pH 5, room temperature, during 5 hours
fraction 3	iron oxides	20 mL 0.04 M $NH_2OH.HCl$ in 25 % (v/v) HOAc, 96 °C, during 6 hours
fraction 4	organic and sulfides	3 mL HNO_3 0.02 M + 5 mL H_20_230 %, pH 2, 85°C during 2 hours after cooling + 2 mL H_20_2 30 %, pH 2, 85°C during 3 hours after cooling + 5 mL NH_4Ac 3.2 M in HNO_3 20 % (v/v) + 4 mL H_2O, 30 minutes shaking at room temperature
fraction 5	residual	30 mL HNO_3/HCl (1/3) heating for 3 hours on a sand bath covered with a watch glass

TABLE IV experimental conditions for sequential extraction following Wallman (8)

	Assumed phase involved	*0.5 g dried sludge or 1 g wet sludge in 30 mL centrifuge tubes*
Fraction 1	exchangable	25 mL NH_40Ac 1 M, pH 7, room temperature, during 2 hours
fraction 2	carbonates	25 mL NaOAc 1M, pH 5, room temperature, during 5 hours
fraction 3	iron and aluminium oxides	25 mL ammonium oxalate (0.1 M, pH 3), overnight
fraction 4	organic and sulfides	10 mL H_20_2 30 %, adjusted to pH 2 with HNO_3, 85°C during 2 hours after cooling + 2 mL H_20_2 30 %, pH 2, 85°C until dryness after cooling + 50 mL NH_4Ac 1 M in HNO_3 6 % (v/v), room temperature, overnight
fraction 5	residual	30 mL HNO_3/HCl (1/3) heating for 3 hours on a sand bath covered with a watch glass

The cadmium, copper, lead, zinc and iron concentrations were measured in all extracts by flame atomic absorption spectroscopy (AAS) on a Varian AA-20. The standard solutions were prepared in the appropriate extraction solution. The total amount was determined by AAS after micro wave (milestoneMLS-1200 MEGA) destruction in presence of 3 mL HNO_3, 1 mL HCl and 1 mL $HClO_4$.

RESULTS AND DISCUSSION

The sum of the metals in the extracts was made and found to be the same within a range of 10% in all three sequential extraction methods and agreed with the total amount of contaminants. All results of metal extracts will be expressed as percentage of the total amount.

Influence of oxidation on extraction from the Oakley method

Figures 1 and 2 show that the metal speciation following Oakley et al. (2) obtained in absence of oxygen (glove box) largely differs from extractions made in ambient air. For these extractions wet sludge was used. Concerning the extractions performed in the glove box (Figure 1), the largest part of the metals, except iron, occur in fraction 4. This fraction is attributed to the presence of metal sulphides. Speciation calculations indeed show that at the pH and Eh of the sediment and in presence of an excess of FeS all transition metal ions should be present in the sulfide form. The observation that a larger part of zinc and iron is found in fraction 3 can be explained by the larger solubility of their sulphides. None of the metals except a very small amount of copper, were measured in the first two fractions which respectively correspond to the easily exchangeable metals and the metals complexed with organic matter.

The results for the same extraction procedure but performed in ambient air are shown in Figure 2. A colour change from black to brown was noticed. This change is due to the quick oxidation of the black iron sulphides. The strong influence of oxidation on the metal speciation is obvious by comparing Figure 1 and 2. Upon oxidation an important part of the metals initially present in fraction 4 is found in fraction 3 for Cu and Pb and also in fraction 2 and 3 for the case of Cd and Cu. Thus oxidation increases the availability of heavy metals in agreement with literature (9).

The behaviour of iron differs from that of the other transition metals. Iron was extracted more easily (fraction 3) in anoxic circumstances compared to oxidising conditions. This result can be ascribed to oxidation of Fe^{2+} to Fe^{3+}. Indeed in the

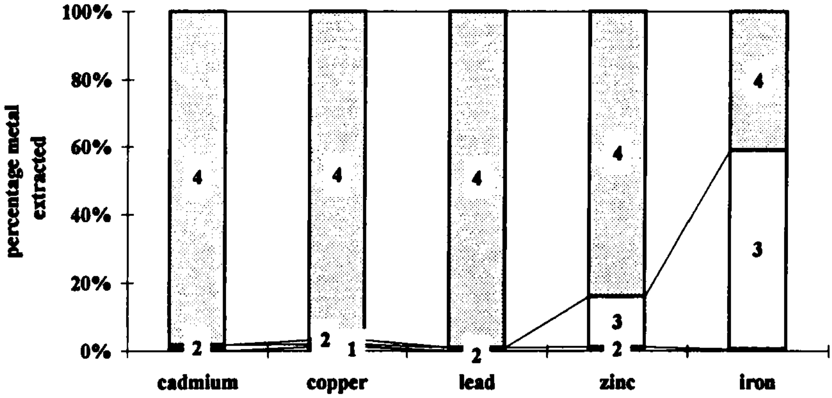

FIGURE 1 Metal distribution over the different extraction steps of a sequential extraction (Oakley et al, 2). The extractions are done inside a glove box (nitrogen). Native undried sludge was used. The numbers correspond to the fractions obtaind from the extraction steps as indicated in Table II

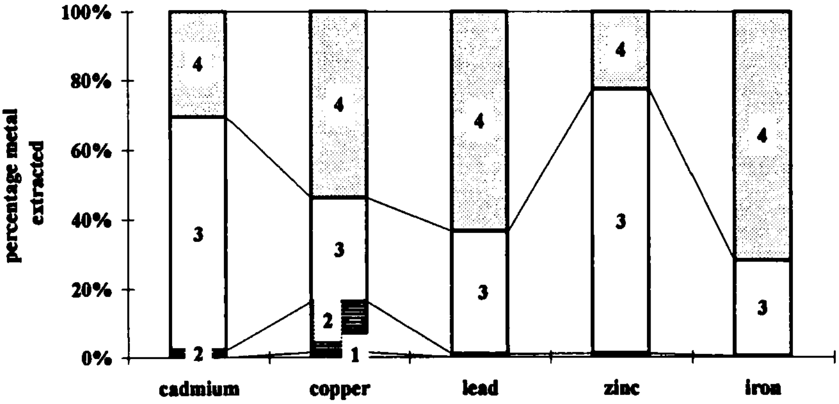

FIGURE 2 Metal distribution over the different extraction steps of a sequential extraction (Oakley et al, 2). The extractions are done in air. Native undried sludge was used. The numbers correspond to the fractions obtained from the extraction steps as indicated in Table II

case of iron also the redox equilibrium interferes as is well known at the redox front in sediments (10) unlike the situation for bivalent transition metals copper, cadmium, lead and zinc. Kostka et al (11) demonstrated that iron oxide minerals, like goethite and hematite are not extrac Table with hydroxylamine, oxalate or HCl 0.5 M. Under anoxic conditions the high iron content in fraction 3 is due to the dissolution of iron sulfide as proven by Oakley et al (2) with synthetic sediment systems. Iron in fraction 4 is then mainly ascribed to its presence in clay minerals (2) or as pyrite. Extractions made in ambient air result in Fe^{2+} oxidation to Fe^{3+}. Consequently the FeS content in fraction 3 decreases (see Figures 1 and 2). The speciation of Fe^{3+} found in fraction 4 (Figure 2) remains however unclear. Since the final pH in step 3 was about 2, different scenarios remain possible. Crystalline iron oxides may be formed which are insoluble at this pH. Also Fe^{3+} may be ion exchanged into clay minerals.

It is concluded that sequential extractions of reducing sediment samples should be measured under anoxic conditions (e.g. in the glove box) in order to avoid a shift towards more oxidised forms upon extractions in ambient air. It is also concluded that the speciation procedure as proposed by Oakley et al (2), agrees with the thermodynamically expected sulfide form of the transition metal ions cadmium, copper, lead and zinc, but only if the extractions are made under anoxic conditions as for example in a glove box.

Sequential extraction procedures under anoxic conditions

The results from three different sequential extraction procedures executed on the original wet sludge under anoxic conditions are shown in Figure 1 (Oakley et al, 2), Figure 3 (Tessier et al, 1) and Figure 4 (Wallman et al, 8). The procedures of Oakley et al (2) and Wallman et al (8) can be considered to lead to similar results. In both procedures a large fraction of the transition metal ions is present in the fourth fraction and is assigned as bound to sulfides as expected on thermodynamic grounds. The Tessier procedure leads to varying percentages of cadmium, copper, lead and zinc present in fraction 3 (iron oxides), 4 (organic matter and sulfides) and 5 (residual). The high recovery of metals in the third fraction of the Tessier procedure is due to the more radical extraction circumstances (low pH and high temperature). Although extraction step 4 and 5 in the Tessier and Wallman procedures are very similar, the results largely differ. The large percentage

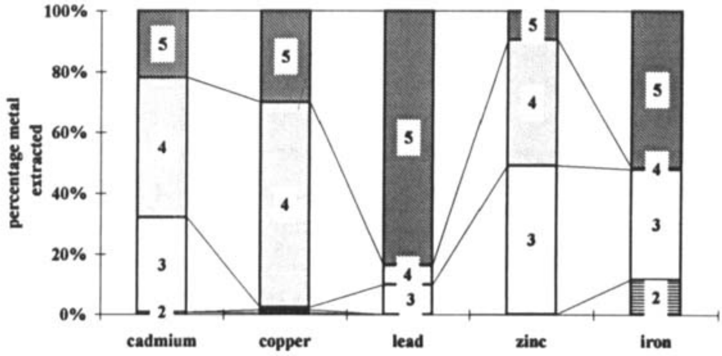

FIGURE 3 Metal distribution over the different extraction steps of a sequential extraction (Tessier et al, 1). The extractions are done inside a glove box (nitrogen). Native undried sludge was used. The numbers correspond to the fractions obtaind from the extraction steps as indicated in Table III

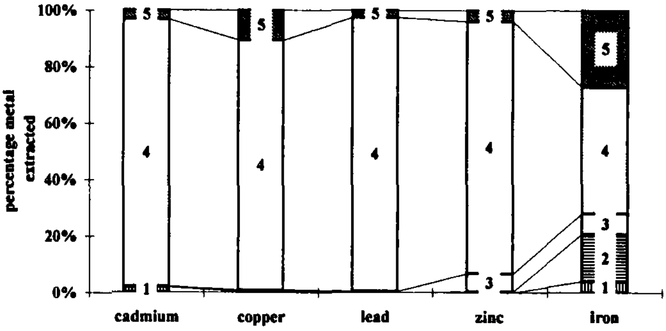

FIGURE 4 Metal distribution over the different extraction steps of a sequential extraction (Wallman et al, 8). The extractions are done inside a glove box (nitrogen). Native undried sludge was used. The numbers correspond to the fractions obtaind from the extraction steps as indicated in Table IV

of cadmium, copper, lead and zinc in the residual fraction 5 of Tessier et al (1) suggests that recristallization into yet undefined structures occurred during step 3 of Tessier. The distribution of iron over the different extraction steps in all three sequential extraction procedures gives no information on the speciation of iron. The solubility of iron sulphide is sufficiently high to dissolve iron sulphide at the pH conditions used to extract iron oxide (step 3 in all three extraction procedures). It is concluded that the Tessier procedure is less reliable to obtain insight in the geochemical phase association of trace metal ions in reduced systems. The Oakley and Wallman procedures are better suited for this purpose.

Influence of drying prior to extraction

In a third series of experiments the impact of oxidation on the speciation is illustrated by comparing extractions on sludges which had been dried both in air and in anoxic conditions in a glove box. Figures 5, 6 and 7 only shows the zinc speciation respectively following the procedure of Oakley et al (2), Tessier et al (I) and Wallman et al (8). In all three speciation procedures, there is a very good similarity between the anoxic extractions made on original wet sludge and on sludge dried under anoxic conditions. All samples that have been in contact with air during the drying stage, differ severely from the samples that were never in contact with air (wet sludge and sludge dried under nitrogen). The temperature of drying is not a critical factor in the speciation : only a slight shift towards higher extractability with increasing drying temperatures is noticed. The shifts in the speciation distribution for cadmium, copper and lead are analogous to the case of zinc, but to a lesser extent. Iron becomes less extractable due to oxidation as discussed earlier. It is concluded that drying under anoxic conditions of river or har-

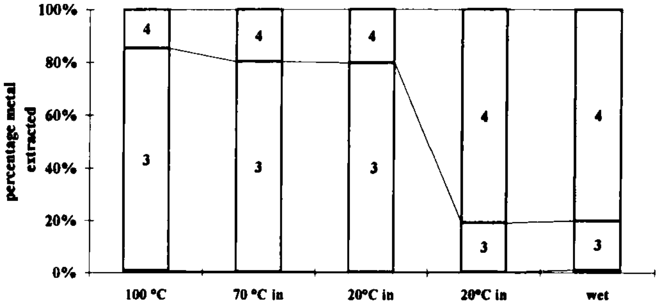

FIGURE 5 Percentage distribution of zinc in the different extracts of the Oakley et al (2) sequential extraction procedure carried out under anoxic conditions inside a glove box. The pretreatment conditions are given in the X axis. Numbers correspond to extraction steps as indicated in Table II

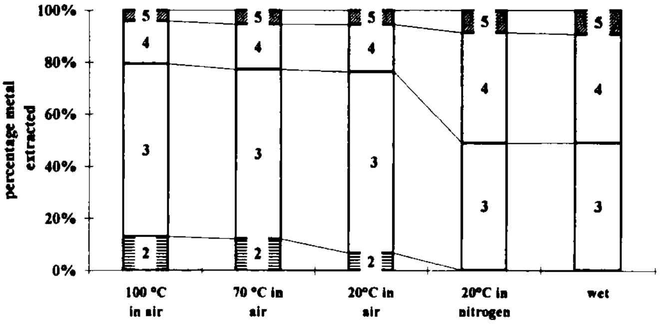

FIGURE 6 Percentage distribution of zinc in the different extracts of the Tessier et al (1) sequential extraction procedure carried out under anoxic conditions inside a glove box. The pretreatment conditions are given in the X axis. Numbers correspond to extraction steps as indicated in Table III

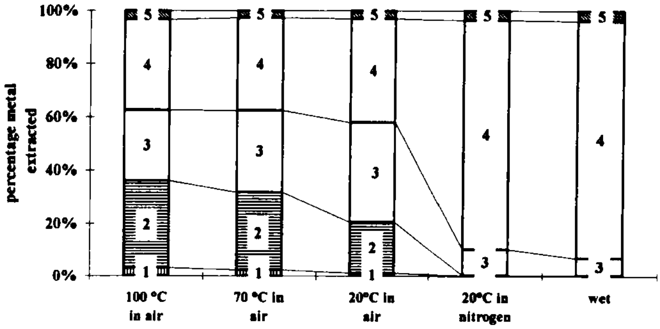

FIGURE 7 Percentage distribution of zinc in the different extracts of the Wallman et al (8) sequential extraction procedure carried out under anoxic conditions inside a glove box. The pretreatment conditions are given in the X axis. Numbers correspond to extraction steps as indicated in Table IV

bour sediments prior to their analysis by sequential extraction techniques leads to identical speciation results as obtained with wet samples under anoxic conditions. Since wet sludge is difficult to handle and to homogenise, drying of the material prior to analysis would simplify the procedure of speciation.

CONCLUSIONS

The difference between transition metal ion speciation as measured from sequential extraction procedures in anoxic atmosphere and in open air can be as large as 70 %. The temperature of drying has only a minor influence, nor does drying itself if performed under anoxic conditions. The main reason for changes in speciation is the contact with air either during drying or during the extraction procedure.

Not all metal sulphides are equally sensitive to oxidation. The speciation of zinc and of iron undergo the greatest change after contact with air. This may indicate that the heavy metals in the anaerobic sludge are not present as a mixed precipitate with the iron sulfide, but as separate sulfide phases. More research is necessary to prove this statement.

Drying under anoxic conditions has no influence on speciation as measured by sequential extraction and is an advised procedure to homogenise sediment samples.

In order to avoid potential speciation changes due to oxidation while investigating soils amended with sludge, even surface soils and subsurface soil samples, in which potential redox conditions in niches may occur, it is advised to use the same procedure as for anaerobic sediment samples.

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