

This article was downloaded by:

On: 18 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

### Artifacts in the Determination of Trace Metal Binding Forms in Anoxic Sediments by Sequential Extraction

K. Wallmann<sup>a</sup>; M. Kersten<sup>b</sup>; J. Gruber<sup>b</sup>; U. Förstner<sup>b</sup>

<sup>a</sup> University of Bremen, Fachbereich Geowissenschaften, Bremen 33, F. R. G. <sup>b</sup> Dept. of Environmental Science and Engineering, University of Technology Hamburg-Harburg, Hamburg 90, F. R. G.

**To cite this Article** Wallmann, K. , Kersten, M. , Gruber, J. and Förstner, U.(1993) 'Artifacts in the Determination of Trace Metal Binding Forms in Anoxic Sediments by Sequential Extraction', *International Journal of Environmental Analytical Chemistry*, 51: 1, 187 – 200

**To link to this Article:** DOI: 10.1080/03067319308027624

**URL:** <http://dx.doi.org/10.1080/03067319308027624>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# ARTIFACTS IN THE DETERMINATION OF TRACE METAL BINDING FORMS IN ANOXIC SEDIMENTS BY SEQUENTIAL EXTRACTION

K. WALLMANN

*University of Bremen, Fachbereich Geowissenschaften, P.O.Box 330440, D-2800 Bremen 33, F.R.G.*

M. KERSTEN, J. GRUBER and U. FÖRSTNER

*University of Technology Hamburg-Harburg, Dept. of Environmental Science and Engineering, P.O. Box 901052, D-2100 Hamburg 90, F.R.G.*

*(Received in final form, 31 August 1992)*

The binding forms of Co, Cd, Cu, Pb, and Zn in an anoxic, sulfide-bearing sediment were investigated by performing both thermodynamic equilibrium calculations and sequential extractions. Care was taken to maintain oxygen-free conditions during the whole experiment. The calculations suggested that trace metals were bound to sulfidic minerals. Sequential extraction results, however, showed increased importance of exchangeable and reducible fractions in the order  $Cu < Cd < Pb < Zn < Co$ . Thermodynamic equilibrium calculations of the chemical reactions during extraction showed that Cd, Co, Pb, and Zn sulfides are to a significant extent soluble in the acetate-exchangeable (step 1 + 2) and oxalate-reducible (step 3) fractions. Neglecting the dissolution of sulfide minerals would lead to a misinterpretation of the experimental results.

**KEY WORDS:** Sequential extraction, speciation, anoxic sediments, cadmium, cobalt, copper, lead, zinc.

## INTRODUCTION

The approach of solid "speciation" is connected to the complexity of heterogeneous systems, e.g. of soils, sediments and aerosol particles. The term speciation is used here in the meaning of "operational procedures for determining typical metal species in environmental samples"<sup>1</sup>. At present, the only laboratory routine available to determine particulate trace metal speciation is sequential extraction.<sup>2</sup> Incomplete selectivity of the reagents used to attack a given sediment component is most responsible for the operational character of this method. The determination of particulate trace metal binding forms by sequential extraction is demanding, particularly for analysis of anoxic sediments. When sampling, storing and extracting anoxic sediments, oxygen-free conditions have to be maintained.<sup>2,3</sup>

**Table 1** Results of sequential extractions of anoxic sediments from different sources determined by different laboratories, in % of the total non-residual fractions extracted, and total element concentration as sum of the non-residual and residual fractions (in  $\mu\text{g/g}$ ).

Element/ Reference	Step 1 <i>NH<sub>4</sub>OAc</i>	Step 2 <i>NaOAc/ HOAc</i>	Step 3a <i>NH<sub>2</sub>OH• HCl (pH 2)</i>	Step 3b <i>NH<sub>2</sub>OH• HCl/HOAc</i>	Step 4 <i>H<sub>2</sub>O<sub>2</sub>/ NH<sub>4</sub>OAc</i>	Total ( $\mu\text{g/g}$ ) <i>HF/HClO<sub>4</sub>/HNO<sub>3</sub></i>
Cd/ 4	<0.1		10.9		89.1	160
5	<0.1	6.7	22.1		71.2	1.9
6	<0.1	<0.1	<0.1	3.4*	96.6	21
7	2	2		68	28	9
8	3	2.2		83	11.8	1.5
3	0.1	2.7		83.1	14.1	6.0
Cu/ 4	<0.1		<0.1		>99.9	175
5	<0.1	1.0	2.2		96.8	1005
6	<0.1	<0.1	<0.1	0.8*	99.2	1680
7	2.5	3.6		4.7	89.2	133
8	0.7	1.1		5.8	92.4	100
3	<0.1	0.1		0.4	99.5	664
Pb/ 4	0.4		5.8		93.8	125
5	<0.1	1.6	31.7		66.7	286
6	<0.1	<0.1	<0.1	19.8*	80.2	595
7	2.5	6.3		43.1	48.1	210
8	0.8	16.7		73.7	8.8	311
3	<0.1	6.3		67.3	26.4	101
Zn/ 4	0.3		38.6		61.1	2447
5	0.1	14.2	34.5		51.2	591
6	<0.1	2.4	5.9	38.7*	53.0	2275
7	2.6	14.3		72.7	10.4	760
8	0.7	44.9		45.1	9.3	443
3	<0.1	9.1		74.3	16.6	1067

\*other than specified extractant:  $\text{NH}_4\text{Ox}/\text{HOx}$  (pH 3)

The useable information is consequently restricted to relatively few publications. To our knowledge, there are at least six published studies of anoxic sediments using the Tessier extraction procedure which meet the necessary precautions.<sup>3-8</sup> The result of this review is listed in Table 1. In cases where the database has been presented graphically, it has been extended by contacting authors and obtaining their raw data. The results of the more or less polluted sediments were then recalculated to give the non-residual fractionation only for ease of comparison.

Although the anoxic samples came from quite different environments (Canadian lakes<sup>3</sup>; Lake Macquarie, Australia<sup>4</sup>; and harbours of Los Angeles<sup>5</sup>, Hamburg<sup>6</sup>, Rotterdam<sup>7</sup>, and Barcelona<sup>8</sup>), their results show a striking agreement. It is surprising that the sulfide (i.e.  $\text{H}_2\text{O}_2/\text{NH}_4$ -acetate extractable in step 4) fractions were smaller than what is to be expected for anoxic sediments. Moreover, the yield of this fraction seems to be related to the strength of the reducing agent used in the preceding step 3 (3a < 3b; Table 1) to extract the oxides. Recent work on model anoxic sediments with Zn-doped FeS (mackinawite) has confirmed accordingly that a significant portion of Zn was extracted already in step 2 and 3 and that strong odour indicated the generation of hydrogen sulfide.<sup>9</sup> The solvent in step 3 of the Tessier procedure, 25% acetic acid, apparently solubilized much of the mackinawite. As the

major acid-volatile sulfide (AVS) component, FeS is fairly soluble in acidic media, and the degree to which FeS has crystallized will determine whether this phase is extracted primarily in the oxidizing step 4 or in earlier extraction steps.<sup>3,10</sup> The results and interpretations of Kheboian and Bauer<sup>9</sup> were intensely debated since their paper appeared in 1987, yet the question was not satisfactorily answered to what extent such artificial reactions affect the extraction results.<sup>11-14</sup>

In our validation experiment, we will examine trace metal binding forms in an anoxic sediment suspension. A fine grained, organic rich sediment was incubated under anaerobic conditions until the dissolved sulfide concentration in the suspension reached a steady-state and a significant concentration of acid volatile sulfide had built up in the sediment. Thermodynamic equilibrium calculations were performed, (i) to evaluate the selectivity of the extraction agents and redistribution processes among phases during extraction, and (ii) to evaluate the possibility of concurrent precipitation of sulfide minerals and adsorption of trace metals on hydrous ferric oxides.

## EXPERIMENTAL PROCEDURES

### *Sediment sampling and incubation*

Sediment samples were collected from the Elbe estuary in northern Germany. The sampling site was located in an intertidal mud flat near the city of Hamburg which was found to be severely contaminated with trace metals.<sup>15</sup> The fraction <63  $\mu\text{m}$  was separated by wet sieving using a nylon mesh. A wet portion of the fine-grained and organic rich sediment fraction (loss on ignition 22 wt.-%), equivalent to 7.2 g oven dry solids, was transferred to a 400  $\text{cm}^3$  closed filtration cell (Amicon 4002) equipped with a 0.2  $\mu\text{m}$  membrane filter. Artificial estuarine water made of Milli-Q water and pure chemicals (5 mmol/l NaCl, 2 mmol/l  $\text{CaCl}_2$ , 1.5 mmol/l  $\text{Na}_2\text{SO}_4$ , MERCK suprapur® quality) were added to obtain a solid-to-water weight ratio of 1 : 50. The sediment was suspended in the filtration cell by a PTFE-coated hanging stirring bar which was driven by an external magnetic stirrer.

The filtration cell was connected to a water reservoir so that a constant suspension volume was maintained during the experiment. After three days of aerobic pre-incubation the oxygen supply was stopped. The sediment suspension was placed in a glove box flushed with nitrogen gas to exclude penetration of oxygen into the suspension, where it became anoxic due to microbial respiration processes. Filtered water samples were taken from the cell by a magnetic driven PTFE gear pump and continuously analyzed for dissolved oxygen, Fe(II) and total dissolved sulfide using a coupled polarographic system. Concentrations of dissolved trace elements Cd, Co, Cu, Pb, Zn were determined by atomic absorption spectroscopy (AAS). After 28 days, when dissolved sulfide remained constant, subsamples of the sediment suspension were pipetted out for the sequential extraction analysis.

### *Extraction*

Sampled sediment suspensions were partitioned into 5 fractions according to the modified Tessier procedure published by Kersten and Förstner.<sup>6</sup> While the selectivity of this procedure remains in question, it was designed to extract metals that are exchangeable (step 1), specifically adsorbed or bound to carbonates (step 2), bound to Fe/Mn-oxides (step 3), bound to organic matter or sulfides (step 4), or are bound to the mineral matrix ("residual" step 5). Our scheme deviates from the original Tessier procedure in that the reducing solvent of step 3 is less acidic to prevent total solubilization of acid-volatile sulfide components.<sup>3</sup> 50 ml subsamples were taken from the anaerobic suspension in the glove box, transferred into acid-washed polycarbonate centrifuge tubes, and sealed with airtight caps. The centrifuge tubes were then transferred to a centrifuge outside the glove box. The suspensions were centrifuged for 20 min at  $1,800 \times g$  and transferred back to the glove box, where the supernatant was decanted to polyethylene storage bottles containing sufficient hydrochloric acid to lower the  $\text{pH} < 2$ . This procedure was repeated after each of the operational steps listed below:

*Step 1* The sediment was extracted for 2 h at room temperature with ammonium acetate buffer (1 M), adjusted to pH 7.0, at a solid-to-solution ratio of 1:50. The samples were agitated on a horizontal mechanical saker at a rate vigorous enough to prevent settling of the sediment.

*Step 2* The sediment residue from step 1 was extracted for 5 h at room temperature with NaOAc (1 M), adjusted to pH 5.0 with acetic acid, at a solid-to-solution ratio of 1: 50. Agitation method was the same as for step 1.

*Step 3* The residue from step 2 was extracted overnight at room temperature with ammonium oxalate buffer (0.1 M, pH = 3) at a solid-to-solution ratio of 1:50. Agitation method was the same as in the previous steps, but the sample tubes were kept in a dark box to prevent photooxidation artifacts.<sup>16</sup>

*Step 4* The residue from step 3 was digested for 2 h at 85°C in glass beakers on a sand bath with 10 ml of 30%  $\text{H}_2\text{O}_2$ , adjusted with  $\text{HNO}_3$  to pH 2 -3 (MERCK 7210). After 2 h, an additional 10 ml acidified  $\text{H}_2\text{O}_2$  was added, and digestion continued at 85° C till dryness. The samples were occasionally agitated during the entire procedure to prevent foam over. After cooling, the residue was washed by 50 ml of ammonium acetate (1 M) in 6% (v/v)  $\text{HNO}_3$  (pH 2.0) into centrifuge tubes and were shaken overnight at room temperature on a horizontal mechanical shaker.

*Step 5* The residue from step 4 was freeze-dried and subsequently digested in an open teflon beaker with conc.  $\text{HNO}_3$  at 160° C to near dryness. The residual slurry was then diluted to 50 ml by Milli-Q water. Bulk metal concentrations were determined on separate subsamples by the same procedure as for the residual step. Vials with the extracts were stored till analysis in a refrigerator.

### *Analysis*

Water soluble and extracted trace metals were determined directly from the supernatant by Zeeman graphite furnace AAS (Perkin Elmer Model 3030); calibration was performed using matrix-matched standards. The total amounts of metal extracted in steps 1 to 5 agreed within 10 % with the amount released in the bulk acid digestion. Detection limits ranged from 0.1 nmol/l to 20 nmol/l depending on the dissolved metal. For the determination of acid volatile sulfide concentrations, hydrogen sulfide was released by adding 15 ml of HCl (10 M) to 50 ml of the suspension in an oxygen-free nitrogen gas train. Hydrogen sulfide was trapped in a sulfide antioxidant buffer (ORION-SA0B). The total sulfide concentration was high enough to use the conventional silver/silver-sulfide solid-state electrode.<sup>17</sup>

Total sulfide in the suspension filtrates, as well as the dissolved oxygen, Mn(II), and Fe(II) concentrations, were determined by differential pulse polarography on a static mercury drop electrode (DPP/SMDE). This was done in the glove box and immediately after sampling. A Metrohm polarographic system (VA 646 and VA 675) was used for the voltammetric measurements. A more detailed description of the experimental setup and the analytical methods was given by Wallmann.<sup>18</sup>

### *Thermodynamic equilibrium modelling*

The class B metal ions  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and the transition metal ions  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  considered in this paper form stable sulfide minerals.<sup>19,20</sup> They can precipitate in anoxic sediments, where dissolved sulfide is formed due to microbial sulfate reduction. On the other hand, adsorption on iron sulfides, particulate organic substances, manganese and ferric (hydr)oxides, carbonates and clay minerals may as well contribute to the binding of trace metals in those sediments.<sup>21</sup> Thermodynamic equilibrium calculations are often employed to investigate the solubility and binding forms of trace metals in sulfide-bearing natural environments.<sup>20,22,23</sup> In these calculations aquo-ion concentrations are assumed to be controlled by the solubilities of pure solid metal sulfides. Complexes with reduced sulfur compounds and other inorganic ligands are considered to be dominant dissolved species.<sup>24</sup> Adsorption on solid surfaces and complexation of aquo-ions by organic ligands and colloids in the pore water are usually neglected because of lack of thermodynamic data for natural sediment-water systems. Calculated total concentrations are compared with the ones in the pore water and the simplifying assumptions are regarded as valid if predicted and measured concentrations agree within one order of magnitude. The pure sulfide minerals are then believed to control the solubility of the corresponding trace metals. Nevertheless it is possible that large fractions of trace metals are bound in other solid forms, as indicated in Table 1.

The adsorption of trace element ions onto amorphous ferric hydroxides was considered because a relevant amount of Fe and other trace metals has been found in step 3. This is a common feature of sequential extraction studies of anoxic sediments (Table 1). Adsorption was calculated using the "Stanford Generalized Model of Adsorption" as implemented in the MINEQL code.<sup>26</sup> In this model, adsorbing ions form complexes with surface sites. The centers of the ions are located either in an inner or an outer "compact" layer, depending on the ionic radii. The widths of the layers (represented as the layers' electrostatic capacities

which are inversely proportional to the widths) are adjustable parameters. Dzombak & Morel<sup>27</sup> remodeled adsorption of 12 metal cations and 10 inorganic anions on hydrous ferric oxides assuming two site types differing in their affinities to ions in solution. The width of the inner and outer compact layers are assumed to be zero, i.e. all adsorbed species are supposed to be located on the surface, regardless of their radii. An electrostatic potential develops at the surface due to the adsorbed ions. It is assumed to be the same for both site types, justified perhaps by the long range of the Coulomb force. Large capacities of inner and outer compact layers in MINEQL were chosen so that the width of these layers were negligible and the parameters given for the model of Dzombak & Morel<sup>27</sup> could be used in the calculations. In the rather odd units that MINEQL uses for capacities, their numerical values were  $1.1 \cdot 10^4$  and  $2 \cdot 10^6$ , respectively.

Surface area was assumed to be  $600 \text{ m}^2$  per gram of hydrous ferric oxides and a site density of 0.2 mole and  $5 \cdot 10^{-3}$  mole per mole of Fe for weak and strong affinity sites was used, respectively.<sup>27</sup> The content of am. ferric hydroxides in the anaerobic sediment suspension was estimated from the amount of iron extracted in step 3 of the sequential extraction procedure assuming that all ferrous iron minerals (mackinawite, siderite and vivianite) had been extracted in the preceding steps of the sequential extraction procedure.<sup>18</sup> The oxalate buffer used in this step dissolves (hydr)oxide phases and possibly partly magnetite and organic iron complexes.<sup>28</sup> The concentration of the total particulate ferric iron in the sediment suspension was calculated from extraction data as  $4.76 \cdot 10^{-3} \text{ mol/l}$ .

Equilibrium concentrations of dissolved trace elements in the sediment suspensions during incubation and the various extraction steps were calculated using the computer program MINEQL.<sup>25</sup> Complexation of trace elements by chloride-, hydroxide-, acetate- (step 1 and 2), oxalate- (step 3), carbonate-ions, reduced sulfur compounds, and formation of pure solid metal sulfide solids were considered. The table in the appendix lists the chemical reactions considered. MINEQL corrects for ionic strength effects by using the Davies equation with the parameters  $A = 0.509$  and  $b = 0.3$ .

## RESULTS AND DISCUSSION

### *Modelling of the sediment incubation*

Table 2 gives the input data used in the equilibrium calculations, i.e., the chemical composition of the investigated sediment suspension system. The results of the MINEQL calculations are listed in Tables 3 and 4. Adsorbed Ca and  $\text{PO}_4^{3-}$  ions determine the properties of the ferric oxide surface. The surface sites with strong affinities are almost entirely filled with Ca ions. Little less than one half of the low affinity sites are filled with phosphate ions and another one third with protons. Because of the competition of  $\text{Ca}^{2+}$ ,  $\text{PO}_4^{3-}$  and  $\text{H}^+$  ions with the trace metals and because of the poor solubility of the sulfides, the adsorbed concentrations of the trace metals are orders of magnitude smaller than the experimentally determined particulate metal concentrations (Table 3). No significant portions of these metals are to be expected in step 3 of the extraction procedure if our choice of the solid

**Table 2** Total soluble concentrations, adsorption site densities  $\equiv\text{Fe}^{\text{w}}$  and  $\equiv\text{Fe}^{\text{s}}$ , and pH-value used in trace metal speciation calculations for the anoxic sediment incubation and the extraction steps 1–3.

Component, site	in incubation	Concentrations (mol/l)		
		step 1	step 2	step 3
Ca	$2.0 \cdot 10^{-3}$	-	-	-
Na	$8.0 \cdot 10^{-3}$	0	1	0
Cl	$9.0 \cdot 10^{-3}$	0	0	0
SO <sub>4</sub>	$1.5 \cdot 10^{-3}$	0	0	0
NH <sub>4</sub> <sup>+</sup>	-	1	0	0.1
Ac <sup>-</sup>	-	1	1	0
Ox <sup>-</sup>	-	0	0	0.1
$\Sigma\text{H}_2\text{S}$	$6.0 \cdot 10^{-7}$	$10^{-5.1}$	$10^{-2.9}$	$10^{-3.8}$
$\Sigma\text{CO}_2$	$3.0 \cdot 10^{-4}$	-	-	-
$\Sigma\text{PO}_4$	$9.0 \cdot 10^{-5}$	-	-	-
$\equiv\text{Fe}^{\text{w}}$	$9.5 \cdot 10^{-4}$	-	-	-
$\equiv\text{Fe}^{\text{s}}$	$2.4 \cdot 10^{-5}$	-	-	-
pH	7.6	7.0	5.0	3.0

sulfide phases is reasonable and if step 3 dissolves only the ferric oxides.

Table 4 compares calculated and measured trace metal concentrations in the sediment suspension. The corresponding values are similar for Zn and Co, which is a basic requirement for our hypothesis that the chosen sulfide solids control the dissolved concentrations of both these trace metals. The equilibrium concentration of dissolved Cd was calculated with two separate combinations of sulfide and bisulfide complexes.<sup>29,30</sup> Unfortunately the real speciation of Cd in sulfide-bearing solutions is not known.<sup>29</sup> Table 4 shows, in fact, that the two calculated values deviate by about two orders of magnitude either above or below the measured concentration. The calculations indicate an oversaturation for both dissolved Pb and Cu with respect to their sulfide minerals. It is possible that Cu and Pb were bound to dissolved organic ligands or colloids which could not be considered in the calculations.

**Table 3** Adsorption of trace metal ions on hydrous ferric oxides.  $C^{\text{eq}}_{\text{Ads}}$  (in mol/l) is the calculated maximum concentration bound onto the hydrous ferric oxides of the sediment. For comparison,  $C^{\text{x}}_{\text{s}}$  (in mol/l) gives the experimentally determined particulate trace metal concentration.

Adsorbed metal	$C^{\text{eq}}_{\text{Ads}}$	$C^{\text{x}}_{\text{s}}$
Co	$10^{-6.8}$	$10^{-5.2}$
Zn	$10^{-10.4}$	$10^{-3.2}$
Cu	$10^{-17.0}$	$10^{-4.1}$
Cd	$10^{-13.6}$	$10^{-5.7}$
Pb	$10^{-9.1}$	$10^{-4.6}$



**Table 4** Calculated and experimentally determined trace metal concentrations  $C^{cd}_{Diss}$  and  $C^x_{Diss}$  (in mol/l), respectively, dissolved in the suspension system at a pH = 7.6. Column 4 lists the dominant reactions by a reaction number denoted in the appendix.

<i>Element</i>	<i>Dominant sulfide mineral</i>	<i>Dominant solution species</i>	<i>Relevant reactions</i>	$C^{eq}_{Diss}$	$C^x_{Diss}$
Co	$\beta$ -CoS	$Co^{2+}$	Co-5	$10^{-8.3}$	$10^{-8.2}$
Zn	ZnS	ZnS (aq.)	Zn-6, Zn-7	$10^{-5.9}$	$10^{-5.9}$
Cu	CuS (am.)	$Cu(S_5)S^{2-}$	Cu-7, Cu-8, H-5	$10^{-8.7}$	$10^{-7.1}$
Cd	CdS	CdS (aq.)	Cd-7, Cd-8	$10^{-6.85}$	$10^{-9.3}$
Cd	CdS	$Cd(HS)(S)^-$	Cd-6, Cd-8, Cd-7 ignored	$10^{-10.7}$	$10^{-9.3}$
Pb	PbS (galena)	$PbCO_3$ (aq.)	Pb-5, Pb-6, H-9	$10^{-13.2}$	$10^{-8.4}$

The overall agreement between calculated and measured concentrations is thus weak as usual with anoxic sediment pore water studies.<sup>2</sup>

### *Results of the sequential extractions*

The results of the sequential extraction procedure are listed in Table 5. The equilibrium calculations discussed above indicate that e.g. Zn and Co are bound to their sulfide phases, ZnS and  $\beta$ -CoS, in the extracted sediment. It is usually assumed that the trace element sulfides are extracted in the fourth step ("oxidizable fraction") of the sequential extraction procedure.<sup>2</sup> However, large amounts of both these trace metals already dissolved in the preceding steps 1-3 of the sequential extraction procedure. The weight-percentages of trace elements extracted in these steps increase in the following order: Cu (<0.1 %) < Cd (8.5%) < Pb (17.5%) < Co (62.4%) < Zn (68.5%). The results of the sequential extraction results are comparable to those listed in Table 1, however, they are not validated by the equilibrium calculation results of the sediment chemistry.

### *Modelling of the extraction procedure*

Equilibrium calculations with MINEQL were carried out for the extractants to examine

**Table 5** Results of sequential extraction of the sediment suspension from the Elbe estuary (in % of total extracted metal).

<i>Element</i>	<i>Step 1</i>	<i>Step 2</i>	<i>Step 3</i>	<i>Step 4</i>	<i>Step 5</i>
Fe	8.4	30.2	26.8	3.6	31.0
Co	8.2	23.2	31.0	15.0	22.6
Zn	0.2	13.0	55.3	24.8	6.9
Cu	<0.1	<0.1	<0.1	73.1	26.9
Cd	2.4	<0.1	5.6	86.7	5.1
Pb	<0.1	3.3	14.2	65.3	17.1

chemical reactions that may affect the sequential extraction results. The acetate buffers used for extraction of fractions 1 and 2, as well as the oxalate buffer used in the third step, may have an impact on the sulfide equilibrium because stable acetate and oxalate complexes form. They were considered in the calculations.

Dissolved sulfide concentration in the acetate and oxalate buffers was estimated as follows: The concentration of total extractable iron was 41.2 mg Fe per g dry sediment and the acid volatile sulfide (AVS)-concentration was 2.3 mg S per g dry sediment. Therefore at most 10 wt.-% of the iron in the anoxic sediment was supposed to be bound as amorphous FeS. Furthermore thermodynamic equilibrium calculations and Mössbauer spectra indicated that significant amounts of ferrous iron carbonates and phosphates formed during the anaerobic incubation.<sup>18</sup> These iron phases dissolved in the first two steps of the sequential extraction and thus increased the ferrous iron concentrations in excess of sulfide in the solid phase and in the extraction solutions.<sup>18</sup> In that case, the total dissolved sulfide concentration  $[\Sigma\text{H}_2\text{S}]$  is controlled by the solubility of FeS (am.) and the dissolved ferrous iron concentration  $C_{\text{Fe}}$ . Dissolved sulfide concentrations in the acetate buffers used in step 1 and 2 were calculated from the following equation:

$$[\Sigma\text{H}_2\text{S}] = \frac{K'_{\text{sp}} a_{\text{H}^+} (1 + K'_{\text{H}_2\text{S}} a_{\text{H}^+})}{C_{\text{Fe}}} (1 + K'_{\text{FeAc}} [\text{Ac}^-])$$

where  $K'_{\text{sp}}$  is the solubility product of FeS (am.; reaction Fe-2 in the appendix),  $K'_{\text{H}_2\text{S}}$  the acid association constant of hydrogen sulfide (reaction H-3),  $K'_{\text{FeAc}}$  the stability constant of the  $\text{FeAc}^+$ -complex (reaction Fe-1),  $a_{\text{H}^+}$  the proton activity, and  $[\text{Ac}^-]$  the acetate concentration. The acetate buffers used for the extraction of fractions 1 and 2 had a high ionic strength ( $I = 1 \text{ M}$ ). Thus stability constants valid for  $I = 1 \text{ M}$  were used for the determination of the equilibrium concentrations in these media. They are listed in the appendix. For those reactions where no stability constants for  $I = 1 \text{ M}$  were available the ionic strength effects were considered by using the Davies equation.  $[\Sigma\text{H}_2\text{S}]$ -values of 7.6  $\mu\text{mol}$  and 7.7  $\text{mmol/l}$  were calculated from this equation for steps 1 and 2, respectively. However, the value for step 2 was higher than the concentration of AVS in the extraction solution (1.4  $\text{mmol/l}$  at a solid-to-solution ratio of 1 : 50). It could be supposed, therefore, that FeS (am.) was completely dissolved in the second step. The sulfide concentration in step 2 was thus assumed to be controlled by the FeS (am.)-content of the sediment (Table 2).

The Zn-content in the third step exceeded the amount of other sulfide forming trace elements by at least one order of magnitude (excluding Fe, which is no longer bound by sulfide phases at that step as discussed above). The calculations suggest that the remaining portion of ZnS completely dissolved in the third step (cf. Table 6). The total dissolved sulfide concentration was then assumed to be equal to the concentration of Zn measured in the oxalate buffer (0.15  $\text{mmol/l}$ ) assuming that Zn was mobilized only from ZnS and not from oxide phases.

The results of equilibrium calculations listed in Table 6 suggest also a complete dissolution of  $\beta$ -CoS. Only am. CuS, which is the least soluble of the considered sulfide minerals, was not dissolved in the three steps preceding step 4 originally designed as the only one to extract metal sulfide minerals. The weight-percentages of the other trace metal sulfides solubilized in steps 1 - 3 increase in the following order: Cd (4.2 - 29.3 %)  $\leq$  Pb (12.6%)  $<$  Co (100%) = Zn (100%).

**Table 6** Solubility of trace metal sulfide minerals in step 1–3 of the sequential extraction procedure. Calculated and experimentally determined soluble concentrations  $C^{\text{eq}}_{\text{Diss}}$  and  $C^{\text{x}}_{\text{Diss}}$  (in mol/l) are listed in column 6 and 7, respectively. Column 5 lists the considered reactions by a reaction number denoted in the appendix.

Element	Step	Dominant sulfide mineral	Dominant solution species	Reactions	$C^{\text{eq}}_{\text{Diss}}$	$C^{\text{x}}_{\text{Diss}}$
Co	1	$\beta$ -CoS	CoAc <sub>2</sub>	Co-1, Co-2, Co-5	$10^{-6.9}$	$10^{-6.4}$
	2		CoAc <sub>2</sub>	Co-1, Co-2, Co-5	$10^{-5.4}$	$10^{-5.9}$
	3		Co <sup>2+</sup>	Co-3, Co-4, Co-5	$10^{-1.8^*}$	$10^{-6.2}$
Zn	1	ZnS	ZnS (aq.)	Zn-1-3, Zn-6, Zn-7	$10^{-5.9}$	$10^{-5.8}$
	2		ZnS (aq.)	Zn-1-3, Zn-6, Zn-7	$10^{-5.9}$	$10^{-4.5}$
	3		ZnOx <sub>2</sub>	Zn-4, Zn-5, Zn-8	$10^{-2.6^*}$	$10^{-3.8}$
Cu	1	CuS (am.)	Cu(S <sub>5</sub> )S <sup>2-</sup>	Cu-7, Cu-8, H-5	$10^{-7.3}$	(< $10^{-7.1}$ )**
	2		Cu(S <sub>5</sub> )S <sup>2-</sup>	Cu-7, Cu-8, H-5	$10^{-8.6}$	(< $10^{-7.1}$ )**
	3		CuOx <sub>2</sub>	Cu-5, Cu-6, Cu-8	$10^{-8.2}$	(< $10^{-7.1}$ )**
Cd	1	CdS	CdS (aq.)	Cd-7, Cd-9	$10^{-6.9}$	$10^{-7.3}$
	1		Cd(HS)(S) <sup>-</sup>	Cd-6, Cd-9	$10^{-9.7}$	$10^{-7.3}$
	2		CdS (aq.)	Cd-7, Cd-9	$10^{-6.6}$	(< $10^{-8.3}$ )**
	2		Cd(HS)(S) <sup>-</sup>	Cd-1-4, Cd-6, Cd-9	$10^{-8.7}$	(< $10^{-8.3}$ )**
	3		CdOx	Cd-5, Cd-7, Cd-10	$10^{-6.5}$	$10^{-7.0}$
	3		CdOx	Cd-5, Cd-6, Cd-10	$10^{-6.8}$	$10^{-7.0}$
Pb	1	PbS (galena)	PbAc <sub>2</sub>	Pb-1, Pb-2, Pb-6	$10^{-10.5}$	(< $10^{-8.3}$ )**
	2		PbAc <sub>2</sub>	Pb-1, Pb-2, Pb-6	$10^{-9.2}$	$10^{-6.1}$
	3		PbOx	Pb-3, Pb-4, Pb-6	$10^{-5.2}$	$10^{-5.4}$

\*: Calculated soluble concentration is higher than total concentration associated with the solid phase of the sediment. The sulfide mineral is thus assumed to be completely dissolved.

\*\* : Detection limits were  $10^{-7.1}$  mol/l for Cu,  $10^{-8.3}$  mol/l for Cd and Pb.

The overall good agreement between calculated solubility of trace metal sulfides and the respective concentrations in the various sequential extraction steps is striking and suggests that the extractability of all considered trace metals is controlled by the sulfide minerals listed in Table 6. Oxalate complexes of well known stoichiometry and stability are the dominant dissolved trace metal species in step 3 of the extraction procedure. Ill-defined Cd-sulfide and bisulfide complexes and natural organic ligands or colloids, which probably influence the CuS, CdS and PbS solubility in the anoxic suspension, are of minor importance in the step 3 solution because of the formation of stable Cu-, Cd- and Pb-oxalate complexes. Both experimental results and equilibrium calculations show that the trace metal sulfide minerals are not all together extracted in the same step of the sequential extraction procedure but in all fraction to an amount depending on their solubility. The attendant generation of dissolved sulfide anions, especially due to the solubilization of FeS (am.) and ZnS, might thus precipitate trace metals originally bound in non-sulfidic sedimentary phases as sulfide minerals during the extraction. This process rather than an insufficient reactivity of the reducing reagent is the probable explanation for the observation that Pb and Cu were removed later than expected in the experiment of Kheboian and Bauer<sup>9</sup>. The similarity in the trace metal extraction results of anoxic (sulfidic) sediments from different environments as indicated in Table 1 is also probably caused by these artificial dissolution/precipitation equilibrium reactions. When using the same (Tessier's) procedure, the proportions of trace metals extracted in the step 1-3 are determined only by the sulfide equilibrium adjusting during each step and the pollution degree of the anoxic sediments: the higher the particulate

metal concentrations, the more proportions are transferred down the extraction sequence as sulfide precipitates in spite of the increasing acid-induced sulfide dissolution.

## CONCLUSIONS

Sulfide minerals are important binding forms of the considered trace metals in the sulfide-bearing sediment suspension. However, it has been verified with equilibrium modelling, that these sulfide minerals have more or less increased solubilities in all the reagents of the most commonly used sequential extraction procedures. Such procedures, therefore, do not give any direct information on trace metal partitioning in anoxic sediments owing to elemental redistribution by dissolution/precipitation reactions. In anoxic systems, however, this redistribution process is not controlled by competitive adsorption, even in the presence of reactive ferric hydroxides or organic matter. In fact, it has been shown by this and other studies that postextraction readsorption in sediments may not significantly bias the results obtained by the (modified) Tessier procedure for both anoxic and oxic sediments or soils.<sup>44,45</sup>

The results of sequential extractions for anoxic sediment are biased in a way, however, which still may pass a lot of information about trace metal geochemistry. They are at least consistent with an interpretation of the results based on equilibrium speciation calculations. We suggest therefore that sequential extractions should be regarded as a procedure in which the natural sediment is transferred in a well defined artificial environment and induced shifts in reaction equilibria are registered. In future work on sequential extractions not only trace metals but also major compounds as sulfide and calcium which influence dissolution/precipitation and adsorption/desorption equilibria should be measured in the extraction solutions. The extraction time should be long enough to reach equilibrium and agents with strong metal binding capacity should be used to minimize the influence of unknown natural ligands and colloids on speciation of dissolved metals. In this way, sequential extractions can be used as effective conformational tools to reduce the complexity of the natural system and to gain a more complete understanding of trace metal speciation and mobility in sediments. By this way a misleading interpretation of sequential extraction data owing to a purely operational definition of extraction fractions is avoided.

## Acknowledgement

We are grateful to A. Tessier, H. Kerdijk and P. del Castilho for their helpful comments on drafts of this paper.

## References

1. M. Bernhard, F. E. Brinckman and K. J. Irgolic, in: *The Importance of Chemical Speciation in Environmental Processes* (M. Bernhard, F. E. Brinckman and P. S. Sadler, eds. Springer-Verlag, Berlin, 1986) pp. 7–
2. M. Kersten and U. Förstner, in: *Trace Element Speciation: Analytical Methods and Problems* (G. E. Batley, ed. CRC-Press, Boca Raton, 1989) pp. 245–317.
3. F. Rapin, A. Tessier, P. G. C. Campbell and R. Carignan, *Environ. Sci. Technol.* **20**, 836–840 (1986).

4. G. E. Batley, *Aust. J. Mar. Freshw. Res.* **38**, 591–606 (1987).
5. S. K. Gupta and K. Y. Chen, *Environ. Letts.* **10**, 129–158 (1975).
6. M. Kersten and U. Förstner, *Mar. Chem.* **22**, 299–312 (1987).
7. R. C. H. Steneker, H. A. van der Sloot and H. A. Das, *Sci. Total Environ.* **68**, 11–23 (1988).
8. G. Rauret, R. Rubio, J. F. López-Sánchez and C. Samitier, in: *International Conference on Heavy Metals in the Environment*, Vol. 1 (J.-P. Vernet, ed. CEP-Consultants, Edinburgh, 1989) pp. 590–593.
9. C. Kheboian and Ch. F. Bauer, *Anal. Chem.* **59**, 1417–1423 (1987).
10. R. D. Shannon and J. R. White, *Biogeochem.* **14**, 193–208 (1991).
11. A. Tessier and P. G. C. Campbell, *Anal. Chem.* **60**, 1475–1476 (1988).
12. C. F. Bauer and C. Kheboian, *Anal. Chem.* **60**, 1477 (1988).
13. P. Nirel and F. M. M. Morel, *Water Res.* **25**, 1055–1056 (1990).
14. A. Tessier and P. G. C. Campbell, *Water Res.* **25**, 115–117 (1991).
15. U. Schwertmann, Z. Pflanzenernähr. Düng. Bodenkd. **84**, 194–202 (1959).
16. M. Kerner, H. Kausch and M. Kersten, *Arch. Hydrobiol. Suppl.* **75**, 118–131 (1986).
17. Orion Research Inc., *Application Bulletin 12* (Cambridge, 1969) 10 pp.
18. K. Wallmann, *Die Frühdiagenese und ihr Einfluß auf die Mobilität der Spurenelemente As, Cd, Co, Cu, Ni, Pb und Zn in Sediment- und Schwebstoffsuspensionen* (Ph. D. Thesis, University of Technology Hamburg-Harburg, 1990), 195 pp.
19. W. Stumm and J. J. Morgan, *Aquatic Chemistry* (Wiley Interscience, New York, 1981), 2nd ed., 583 pp.
20. S. Emerson, L. Jacobs and B. Tebo, in: *Trace Metals in Sea Water* (C. S. Wong, E. Boyle, K. W. Bruland, J. D. Burton and E. D. Goldberg, eds. Plenum Press, New York, 1983) pp. 579–608.
21. W. Salomons and U. Förstner, *Metals in the Hydrocycle* (Springer Verlag, Berlin, 1984) 349 pp.
22. K. Kremling, *Mar. Chem.* **13**, 87–103 (1983).
23. J. Boulegue, C. J. Lord III. and T. M. Church, *Geochim. Cosmochim. Acta* **46**, 453–464 (1982).
24. L. R. Gardner, *Geochim. Cosmochim. Acta* **38**, 1297–1302 (1974).
25. J. C. Westall, J. L. Zachary and F. M. M. Morel, *MINEQL, a computer program for calculation of chemical equilibrium composition of aqueous systems* (Tech. Note no. 18, Water Quality Lab. Dept. of Civil Eng., M.I.T., 1976) 76 pp.
26. J. A. Davis, R. O. James and J. O. Leckie, *J. Colloid Interface Sci.* **67**, 90–107 (1978).
27. D. A. Dzombak and F. M. M. Morel, *Surface complexation modeling: hydrous ferric oxides* (Wiley-Interscience, New York, 1990) 379 pp.
28. T. T. Chao and L. Zhou, *Soil Sci. Soc. Am. J.* **47**, 225–232 (1983).
29. L. Jacobs and S. Emerson, *Earth Planet. Sci. Lett.* **60**, 237–252 (1982).
30. D. Dyrssen, *Mar. Chem.* **24**, 143–153 (1988).
31. A. D. Uhler and G. R. Helz, *J. Cryst. Growth* **66**, 401–411 (1984).
32. A. E. Martell and R. M. Smith, *Critical Stability Constants* (Plenum Press, New York, 1976) Vol. 3, 495 pp.
33. W. Davison, *Geochim. Cosmochim. Acta* **44**, 803–808 (1980).
34. R. M. Smith and A. E. Martell, *Critical Stability Constants* (Plenum Press, New York, 1989) Vol. 6, 643 pp.
35. R. M. Smith and A. E. Martell, *Critical Stability Constants* (Plenum Press, New York, 1982) Vol. 5, 604 pp.
36. G. B. Naumov, B. N. Ryzenko and I. L. Khodakovskiy, *Handbook of thermodynamic data* (National Technical Information System, U.S. Department of Commerce, 1974) 328 pp.
37. R. M. Smith and A. E. Martell, *Critical Stability Constants* (Plenum Press, New York, 1976) Vol. 4, 257 pp.
38. A. D. Uhler and G. R. Helz, *Geochim. Cosmochim. Acta* **48**, 1155–1160 (1984).
39. D. Shea and G. R. Helz, *Geochim. Cosmochim. Acta* **53**, 229–236 (1989).
40. D. Shea and G. R. Helz, *Geochim. Cosmochim. Acta* **52**, 1815–1825 (1988).
41. W. F. Giggenbach, *Inorg. Chem.* **13**, 1724–1730 (1974).
42. J. D. Hem, *Geochim. Cosmochim. Acta* **40**, 599–609 (1976).
43. L. N. Plummer, B. F. Jones and A. H. Truesdell, WATEQF - A Firtran IV version of WATEQ. U.S. Geological Survey Water-Resources Investigation 76–13 (1976).
44. N. Belzile, P. Lecomte and A. Tessier, *Environ. Sci. Technol.* **23**, 1015–1020 (1989).
45. N. D. Kim and J. E. Ferguson, *Sci. Total Environ.* **105**, 191–209 (1991).

**Appendix:** Reaction equilibria considered in the calculations of Table 3, 4 and 6. I is the ionic strength at which equilibrium constant K has been determined and for which it is valid. Reactions with number (0) have little or no influence on partitioning of trace metals and surface sites.

Reaction	Reaction number	I in mol/l	log K	Ref.
$\text{Fe}^{2+} + \text{Ac}^- \rightleftharpoons \text{FeAc}^+$	Fe-1	1.0	+0.70	32*
$\text{Fe}^{2+} + \text{HS}^- \rightleftharpoons \text{FeS(am.)} + \text{H}^+$	Fe-2	0.0	+2.97	33
$\text{Fe}^{2+} + \text{HS}^- \rightleftharpoons \text{FeS(am.)} + \text{H}^+$	Fe-3	>0.4	+2.00	33
$\text{H}^+ + \equiv\text{Fe}^{\text{S}}\text{O}^- \rightleftharpoons \text{Fe}^{\text{S}}\text{OH}$	(0)	0.0	+8.93	27
$\text{H}^+ + \equiv\text{Fe}^{\text{S}}\text{OH} \rightleftharpoons \text{Fe}^{\text{S}}\text{OH}_2^+$	(0)	0.0	+7.29	27
$\text{H}^+ + \equiv\text{Fe}^{\text{W}}\text{O}^- \rightleftharpoons \text{Fe}^{\text{W}}\text{OH}$	(0)	0.0	+8.93	27
$\text{H}^+ + \equiv\text{Fe}^{\text{W}}\text{OH} \rightleftharpoons \text{Fe}^{\text{W}}\text{OH}_2^+$	Fe-4	0.0	+7.29	27
$\text{Ca}^{2+} + \equiv\text{Fe}^{\text{S}}\text{OH} \rightleftharpoons \equiv\text{Fe}^{\text{S}}\text{OHCa}^{2+}$	(0)	0.0	+4.97	27
$\text{Ca}^{2+} + \equiv\text{Fe}^{\text{W}}\text{OH} \rightleftharpoons \equiv\text{Fe}^{\text{W}}\text{OCa}^{2+} + \text{H}^+$	Fe-5	0.0	-5.85	27
$\text{SO}_4^{2-} + \equiv\text{Fe}^{\text{W}}\text{OH} \rightleftharpoons \equiv\text{Fe}^{\text{W}}\text{OHSO}_4^{2-}$	(0)	0.0	+0.79	27
$\text{SO}_4^{2-} + \text{H}^+ + \equiv\text{Fe}^{\text{W}}\text{OH} \rightleftharpoons \equiv\text{Fe}^{\text{W}}\text{SO}_4^{2-} + \text{H}_2\text{O}$	(0)	0.0	+7.78	27
$\text{PO}_4^{3-} + \text{H}^+ + \equiv\text{Fe}^{\text{W}}\text{OH} \rightleftharpoons \equiv\text{Fe}^{\text{W}}\text{PO}_4^- + \text{H}_2\text{O}$	(0)	0.0	+17.7	27
$\text{PO}_4^{3-} + 2 \text{H}^+ + \equiv\text{Fe}^{\text{W}}\text{OH} \rightleftharpoons \equiv\text{Fe}^{\text{W}}\text{HPO}_4^- + \text{H}_2\text{O}$	Fe-7	0.0	+25.4	27
$\text{PO}_4^{3-} + 3 \text{H}^+ + \equiv\text{Fe}^{\text{W}}\text{OH} \rightleftharpoons \equiv\text{Fe}^{\text{W}}\text{H}_2\text{PO}_4 + \text{H}_2\text{O}$	(0)	0.0	+31.3	27
$\text{H}^+ + \text{S}^{2-} \rightleftharpoons \text{HS}^-$	H-1	0.0	+13.9	35
$\text{H}^+ + \text{S}^{2-} \rightleftharpoons \text{HS}^-$	H-2	1.0	+14.0	35
$\text{H}^+ + \text{HS}^- \rightleftharpoons \text{H}_2\text{S}$	H-3	0.0	+7.02	35
$\text{H}^+ + \text{HS}^- \rightleftharpoons \text{H}_2\text{S}$	H-4	1.0	+6.75	35
$\text{HS}^- + 3/8 \text{S}_8(\text{s}) \rightleftharpoons \text{S}_4^{2-} + \text{H}^+$	(0)	0.0	-9.44	41**
$\text{HS}^- + 1/2 \text{S}_8(\text{s}) \rightleftharpoons \text{S}_5^{2-} + \text{H}^+$	H-5	0.0	-9.56	41**
$\text{H}^+ + \text{Ac}^- \rightleftharpoons \text{HAc}$	H-6	1.0	+4.72	36
$\text{H}^+ + \text{Ox}^{2-} \rightleftharpoons \text{HOx}^-$	H-7	0.0	+4.27	36
$\text{H}^+ + \text{HOx}^- \rightleftharpoons \text{H}_2\text{Ox}$	H-8	0.0	+1.25	36
$\text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^-$	H-9	0.0	+10.3	45
$\text{Co}^{2+} + \text{Ac}^- \rightleftharpoons \text{CoAc}^+$	Co-1	1.0	+0.65	34
$\text{Co}^{2+} + 2 \text{Ac}^- \rightleftharpoons \text{CoAc}_2$	Co-2	2.0	+0.80	34
$\text{Co}^{2+} + \text{Ox}^{2-} \rightleftharpoons \text{CoOx}$	Co-3	0.0	+4.72	35
$\text{Co}^{2+} + 2 \text{Ox}^{2-} \rightleftharpoons \text{CoOx}_2^{2-}$	Co-4	0.0	+6.90	35
$\text{Co}^{2+} + \text{HS}^- \rightleftharpoons \text{Co(HS)}^+$	(0)	0.0	+5.70	36
$\text{Co}^{2+} + 2 \text{HS}^- \rightleftharpoons \text{Co(HS)}_2$	(0)	0.0	+8.80	36
$\text{Co}^{2+} + \text{HS}^- \rightleftharpoons \beta\text{-CoS(s)} + \text{H}^+$	Co-5	0.0	+7.10	36
$\text{Co}^{2+} + \equiv\text{Fe}^{\text{S}}\text{OH} \rightleftharpoons \equiv\text{Fe}^{\text{S}}\text{OCo}^+ + \text{H}^+$	(0)	0.0	-0.46	27
$\text{Co}^{2+} + \equiv\text{Fe}^{\text{W}}\text{OH} \rightleftharpoons \equiv\text{Fe}^{\text{W}}\text{OCo}^+ + \text{H}^+$	Co-6	0.0	-3.01	27
$\text{Zn}^{2+} + \text{Ac}^- \rightleftharpoons \text{ZnAc}^+$	Zn-1	1.0	+0.90	34
$\text{Zn}^{2+} + 2 \text{Ac}^- \rightleftharpoons \text{ZnAc}_2$	Zn-2	1.0	+1.20	34
$\text{Zn}^{2+} + 3 \text{Ac}^- \rightleftharpoons \text{ZnAc}_3^-$	Zn-3	3.0	+1.57	34
$\text{Zn}^{2+} + \text{Ox}^{2-} \rightleftharpoons \text{ZnOx}$	Zn-4	0.0	+4.87	32
$\text{Zn}^{2+} + 2 \text{Ox}^{2-} \rightleftharpoons \text{ZnOx}_2^{2-}$	Zn-5	0.0	+7.65	32
$\text{Zn}^{2+} + \text{S}^{2-} \rightleftharpoons \text{ZnS(aq.)}$	Zn-6	1.0	+18.5	30
$\text{Zn}^{2+} + \text{S}^{2-} \rightleftharpoons \text{ZnS(s)}$	Zn-7	1.0	+24.4	30
$\text{Zn}^{2+} + \text{HS}^- \rightleftharpoons \text{ZnS(s)} + \text{H}^+$	Zn-8	0.0	+10.8	37
$\text{Zn}^{2+} + \equiv\text{Fe}^{\text{S}}\text{OH} \rightleftharpoons \equiv\text{Fe}^{\text{S}}\text{OZn}^+ + \text{H}^+$	(0)	0.0	+0.99	27
$\text{Zn}^{2+} + \equiv\text{Fe}^{\text{W}}\text{OH} \rightleftharpoons \equiv\text{Fe}^{\text{W}}\text{OZn}^+ + \text{H}^+$	Zn-9	0.0	-1.99	27
$\text{Cd}^{2+} + \text{Ac}^- \rightleftharpoons \text{CdAc}^+$	Cd-1	1.0	+1.24	34
$\text{Cd}^{2+} + 2 \text{Ac}^- \rightleftharpoons \text{CdAc}_2$	Cd-2	1.0	+1.86	34
$\text{Cd}^{2+} + 3 \text{Ac}^- \rightleftharpoons \text{CdAc}_3^-$	Cd-3	1.0	+2.04	34
$\text{Cd}^{2+} + 4 \text{Ac}^- \rightleftharpoons \text{CdAc}_4^{2-}$	Cd-4	3.0	+2.00	34
$\text{Cd}^{2+} + \text{Ox}^{2-} \rightleftharpoons \text{CdOx}$	Cd-5	0.0	+3.89	32
$\text{Cd}^{2+} + \text{S}^{2-} + \text{HS}^- \rightleftharpoons \text{Cd(HS)S}^-$	Cd-6	1.0	+20.6	29

## Appendix (continuation)

Reaction	Reaction number	I in mol/l	log K	Ref.
$\text{Cd}^{2+} + 2 \text{S}^{2-} \rightleftharpoons \text{Cd}(\text{S})_2^{-2}$	(0)	1.0	+21.1	29
$\text{Cd}^{2+} + \text{S}^{2-} \rightleftharpoons \text{CdS}(\text{aq.})$	Cd-7	1.0	+18.2	30
$\text{Cd}^{2+} + \text{HS}^- \rightleftharpoons \text{Cd}(\text{HS})^-$	(0)	1.0	+6.40	30
$\text{Cd}^{2+} + 2 \text{HS}^- \rightleftharpoons \text{Cd}(\text{HS})_2$	(0)	1.0	+13.8	30
$\text{Cd}^{2+} + 3 \text{HS}^- \rightleftharpoons \text{Cd}(\text{HS})_3^-$	(0)	1.0	+16.0	30
$\text{Cd}^{2+} + 4 \text{HS}^- \rightleftharpoons \text{Cd}(\text{HS})_4^{-2}$	(0)	1.0	+18.4	30
$\text{Cd}^{2+} + \text{S}^{2-} \rightleftharpoons \text{CdS}(\text{s})$	Cd-8	1.0	+25.1	30
$\text{Cd}^{2+} + \text{HS}^- \rightleftharpoons \text{CdS}(\text{s}) + \text{H}^+$	Cd-9	0.0	+13.1	37
$\text{Cd}^{2+} + \equiv\text{Fe}^{\text{s}}\text{OH} \rightleftharpoons \equiv\text{Fe}^{\text{s}}\text{OCd}^+ + \text{H}^+$	(0)	0.0	+0.47	27
$\text{Cd}^{2+} + \equiv\text{Fe}^{\text{w}}\text{OH} \rightleftharpoons \equiv\text{Fe}^{\text{w}}\text{OCd}^+ + \text{H}^+$	Cd-10	0.0	-2.90	27
$\text{Pb}^{2+} + \text{Ac}^- \rightleftharpoons \text{PbAc}^+$	Pb-1	1.0	+2.10	34
$\text{Pb}^{2+} + 2 \text{Ac}^- \rightleftharpoons \text{PbAc}_2$	Pb-2	1.0	+3.00	34
$\text{Pb}^{2+} + \text{Ox}^{2-} \rightleftharpoons \text{PbOx}$	Pb-3	0.0	+4.91	32
$\text{Pb}^{2+} + 2 \text{Ox}^{2-} \rightleftharpoons \text{PbOx}_2^{-2}$	Pb-4	0.0	+6.76	32
$\text{Pb}^{2+} + \text{Co}_3^{2-} \rightleftharpoons \text{PbCO}_3$	Pb-5	0.0	+7.24	42
$\text{Pb}^{2+} + 2 \text{HS}^- \rightleftharpoons \text{Pb}(\text{HS})_2$	(0)	0.0	+12.2	31
$\text{Pb}^{2+} + 3 \text{HS}^- \rightleftharpoons \text{Pb}(\text{HS})_3^-$	(0)	0.0	+13.8	31
$\text{Pb}^{2+} + \text{HS}^- \rightleftharpoons \text{PbS}(\text{galena}) + \text{H}^+$	Pb-6	0.0	+12.8	39
$\text{Pb}^{2+} + \equiv\text{Fe}^{\text{s}}\text{OH} \rightleftharpoons \equiv\text{Fe}^{\text{s}}\text{OPb}^+ + \text{H}^+$	Pb-7	0.0	+4.65	27
$\text{Cu}^{2+} + \text{Ac}^- \rightleftharpoons \text{CuAc}^+$	Cu-1	1.0	+1.67	34
$\text{Cu}^{2+} + 2 \text{Ac}^- \rightleftharpoons \text{CuAc}_2$	Cu-2	1.0	+2.70	34
$\text{Cu}^{2+} + 3 \text{Ac}^- \rightleftharpoons \text{CuAc}_3^-$	Cu-3	1.0	+3.00	34
$\text{Cu}^{2+} + 4 \text{Ac}^- \rightleftharpoons \text{CuAc}_4^{2-}$	Cu-4	1.0	+2.90	34
$\text{Cu}^{2+} + \text{Ox}^{2-} \rightleftharpoons \text{CuOx}$	Cu-5	0.0	+6.23	34
$\text{Cu}^{2+} + 2 \text{Ox}^{2-} \rightleftharpoons \text{CuOx}_2^{-2}$	Cu-6	0.0	+10.2	34
$\text{Cu}^{2+} + 3 \text{HS}^- \rightleftharpoons \text{CuS}(\text{HS})_2^{-2} + \text{H}^+$	(0)	1.0	+16.0	40
$\text{Cu}^{2+} + 4 \text{HS}^- \rightleftharpoons \text{CuS}(\text{HS})_3^{-3} + \text{H}^+$	(0)	1.0	+16.9	40
$\text{Cu}^{2+} + \text{HS}^- + \text{S}_5^{2-} \rightleftharpoons \text{CuS}(\text{S}_5)^{-2} + \text{H}^+$	Cu-7	1.0	+18.3	40
$\text{Cu}^{2+} + 1/2 \text{HS}^- + 3/2 \text{S}_4^{2-} + 1/2 \text{S}_5^{2-} \rightleftharpoons \text{Cu}(\text{S}_4\text{S}_5)^{-3} + 1/2 \text{H}^+$	(0)	1.0	+24.2	40
$\text{Cu}^{2+} + 1/2 \text{HS}^- + 1/2 \text{S}_4^{2-} + 3/2 \text{S}_5^{2-} \rightleftharpoons \text{Cu}(\text{S}_5)_2^{-3} + 1/2 \text{H}^+$	(0)	1.0	+24.0	40
$\text{Cu}^{2+} + \text{HS}^- \rightleftharpoons \text{CuS}(\text{am.}) + \text{H}^+$	Cu-8	0.0	+18.9	39
$\text{Cu}^{2+} + \equiv\text{Fe}^{\text{s}}\text{OH} \rightleftharpoons \equiv\text{Fe}^{\text{s}}\text{OCu}^+ + \text{H}^+$	Cu-9	0.0	+2.89	27

\*: estimated from corresponding equilibrium constants for Mn, Co and Ni listed in (30)

\*\* : in the equilibrium calculations it is assumed that the activity of elemental sulfur is 1.0