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# The use of acidimetric titration as a novel approach to study particulate trace metal speciation and mobility: Application to sediments of the Scheldt estuary

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## Abstract

The study of trace metal speciation has benefited from a great deal of interest leading to the development and the diversification of sequential extraction schemes (SES), which triggered the need for harmonization by the standard, measurements and testing programme (SM & T). However, some uncertainties still persist in the application of the harmonized 3-step protocol, because of the difficulty in conceptualizing a technique that can be applied to environmental samples irrespective of their nature. The alternative method proposed in this study is based on the solubility of the sample components progressively dissolved during the course of an acidimetric titration by 1 mol $L^{-1}$ HC1. The major HCl-reactive mineralog-ical components are identified using mass balance calculation of $H^+$ consumed by their dissolution together with the amount of major elements released into solution. The speciation of minor and trace elements is investigated by comparing their titrations to those of the major elements. This approach is much simpler than SES because it uses simple non-selective $H^+$ at room temperature instead of a complex experimental design of so-called specific reagents. The different mineral components of the solid are no longer operationally defined and the problem of selectivity is irrelevant to the titration approach. The method was applied to several sediment samples from the Scheldt estuary and the particulate phase was further examined by Scanning Electron Microprobe and X-ray Diffraction techniques. The nearly complete consumption of $H^+$ in the suspension is balanced by the total dissolution of carbonates and Fe-oxyhydroxides. In contrast to the speciation inferred from the Tessier SES, the acidimetric titration has demonstrated that the carbonate phase does not significantly contain trace metals with the exceptions of 40% of the Mn and 30% of the Co. In contrast, the Fe-oxyhydroxides seem to play a major role and account for 70% of Pb and 20% of Cr, in addition to 60% of P and additional amounts of 20% Co and 40% Mn. 70% of the Cu also occur in the oxyhydroxide phase, more likely coprecipitated with gibbsite. 90% of the Cd and 85% of Zn can be attributed to the Acid Volatile Sulfide (AVS) phase as evidenced from S titration. The acidimetric titration method not only provides information on the speciation of trace metals but also allows the quantification of their reactivity and mobility, if one considers that the titration roughly mimics pH changes that may occur as a result of chemical disequilibrium in the environment. The results demonstrate the potential of the acidimetric titration as an alternative to SES protocols in geo-chemical and environmental regulation studies. This method is applicable to a wide variety of environmental materials with little or minor adjustments.

## 1. Introduction

Scientific works carried out in the past 30 years related to the geochemistry of trace metals in the Scheldt estuary have provided a well constrained framework for the study of speciation. Indeed, over this period, the Scheldt estuary and its tributaries have undergone a significant improvement of their water quality, with the return in the mid-eighties of permanent oxic conditions in the water column of the upper estuary (Zwolsman and van Eck, 1999). In this area, trace metals in sediments are present substantially in reduced chemical forms. Due to the improvement of water quality and thus the return of dissolved $O_2$ in the water column, these mineral species are not long-lived but may potentially become more mobile under oxic conditions (Bouezmarni and Wollast, 2005).

Therefore, speciation of particulate trace metals is of paramount importance for the regulation of pollution levels. Understanding and predicting the fate of trace metals, as well as the hazards due to their toxicity or their assimilation into living organisms depend on the assessment of their chemical/mineralogical forms. In this respect, it is the speciation of trace metals rather than their bulk concentration that controls the extent of their remobilisation arising as a result of chemical disequilibrium between the solid and its surrounding.

Numerous sequential extraction schemes (SESs), based on the principle of selective dissolution, have been developed to assess the speciation of trace metals in the solid phase (Tessier et al., 1979; Salomons and Förstner, 1980; Miller et al., 1983; Hickey and Kitrick 1984; Clevenger, 1990; Dudka and Chlopecka, 1990; Howard and

Shu, 1996; Gee et al., 1997). These protocols assume that a fixed number (depending upon the protocol) of operationally defined phases are readily present in the sample and use specific reagents to perform their dissolution. Since the very first application of the selective extraction procedure to the study of trace metal speciation in soils by Tessier et al. (1979), many modifications of the original protocol have been published. The modified protocols were to be more efficient than the initial scheme with respect to specific type of samples, with changes in the number of reagents, in their chemical form as well as the sequence in which they are used.

The results produced are strongly dependent on the operational conditions and consequently they cannot be readily compared due to the lack of uniformity of these different schemes. More recently, the community bureau of reference (BCR, now Standards, measurements and testing programme, SM & T) launched a programme to harmonise the procedure for trace metal extraction in soils and sediments and to produce certified reference materials (CRMs) (Ure et al., 1993; Quevauviller et al., 1998). The standardized sequential extraction consists of three steps (Ure et al., 1993). The sample is first treated with acetic acid to extract exchangeable/acid-soluble metals (Step 1). Then the reducible phase is mobilized by hydroxylammonium chloride 0.1 $molL^{-1}$, adjusted to pH 2 with $HNO_3$ (Step 2). Finally, oxidizable fractions are dissolved with repeated aliquots of $H_2O_2$ 8.8$molL^{-1}$, evaporated and redissolved in 1.0$molL^{-1}$ ammonium acetate, adjusted to pH 2 with $HNO_3$ (Step 3).

The BCR protocol contributes to the harmonisation of the SESs and has been extensively applied in European laboratories to soils and sediments. However, some sources of uncertainty still persist in its application (e.g. Sahuquillo et al., 1999; Davidson et al., 2004; van Hullebusch et al., 2005). Selective extraction techniques use, indeed, combinations of reagents that are somewhat complex and responsible for the intricacy of the chemical reactions occurring with the bulk sample. Some chemical drawbacks have been discussed in the literature such as time and temperature dependence and reagent to sample ratio. The most serious problems, however, are related to the non-selectivity of the reagents (e.g. Ma-her, 1984; Martin et al., 1987; Kheboian and Bauer, 1987; Whalley and Grant, 1994; Boughriet et al., 1995) and the redistribution of released metals between the various phases (Kheboian and Bauer, 1987; Belzile and Tessier, 1990; Raksasataya et al., 1996; Gómez-Ariza et al., 1999, 2000; Gismera et al., 2004).

The pH and its changes during the sequential extraction procedure is probably the principal parameter explaining the unresolved problems regarding the application of sequential extraction (Sahuquillo et al., 1999; Bermond et al., 1998). Indeed, most reagents used in the SESs are acidic, but $H^+$ is not selective. The concentration of $H^+$ remaining in solution after reaction with the same given amount of sample will depend on its mineralogical composition, because siliceous materials are less enriched in acid soluble phases than carbonate materials. As the mineralogical composition is variable from one sample to another, it is difficult to design a standardized sequential extraction method appropriate for all types of materials because the amount of a specific reagent must be proportional to the amount of the target phase in the solid, which is not known *a priori.* On one hand, a larger amount of the specific reagent will trigger the extraction of trace metals from other phases and consequently overestimate the specific trace metal content of the target phase (Sahuquillo et al., 1999; Gómez-Ari-za et al., 2000; Mossop and Davidson, 2003). On the other hand, a smaller amount of a specific reagent will not completely extract the target phase and the proportion of the selective trace metals will be consequently underestimated.

This paper proposes an alternative approach for studying trace metal speciation. The principle of the method designed is very different from that of SESs. The method presented is based on the solubility of the different solid phases and relies on stepwise additions of a non-specific reagent (HC1 1 mol $L^{-1}$) as in an acidi-metric titration. The identification of reactive species is quantitatively performed by mass balance calculation of protons consumed by the dissolution reaction and the amount of major/ minor elements (Si, Al, Fe, Ca, Mg, Mn, S) released in solution. The speciation of trace elements (Cd, Pb, Cu, Zn, Cr, Co, P) is determined by comparing their release with those of major/minor elements. Results obtained from this method are compared with those from the classical Tessier SES. In addition to the study of trace element speciation and the determination of mineralogical phases really present, the method should also provide clues for the assessment of the potential availability of trace metals owing to pH changes that may occur in the sedimentary environment.

## 2. Materials and methods

### *2.1. Area of study and sampling*

Surface sediments were sampled with a Van Veen grab in August 1994 in the Scheldt estuary (Fig. 1) at stations Hemiksem, Lin-keroever, Doel, Bath and Terneuzen. Samples were dried overnight at 80 °C on board the R.V. Luctor and were studied for metal speciation by the acidimetric titration method in the laboratory. Only results obtained with the most trace metal rich surface sediment from the Doel station (close to the Dutch-Belgian border) are presented in this study and are compared with the Tessier's SES.

***Fig. 1.*** *Map of the Scheldt estuary where the sampling locations are indicated. The sample presented in this study was collected at Doel.*

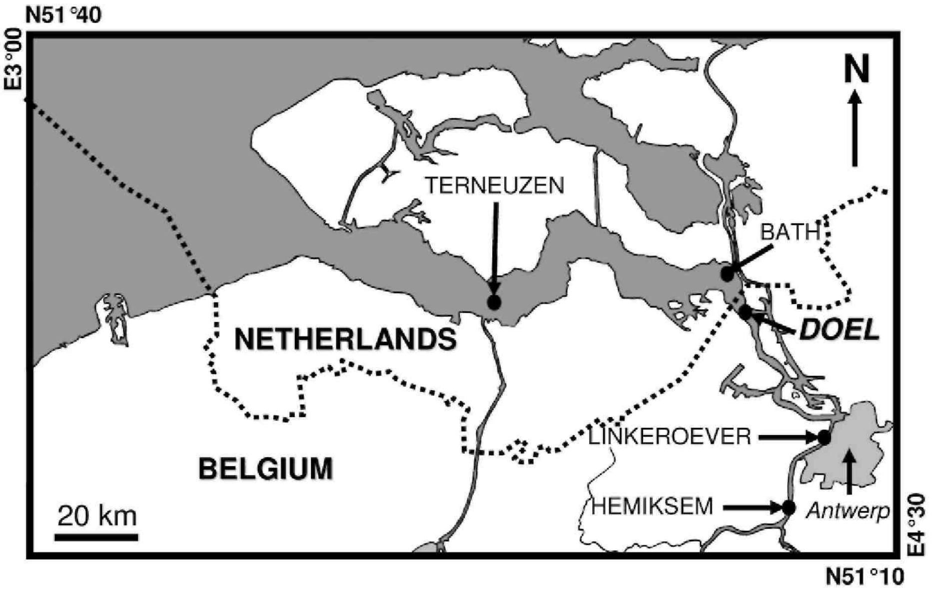
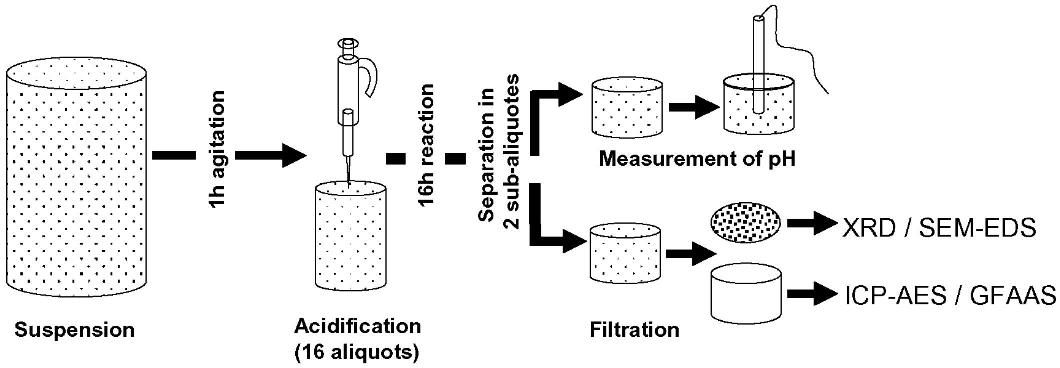


***Fig. 2.*** *Scheme of the acidimetric titration method.*



*2.2. Titration procedures*

The preparation of the sample intended for the study of trace metal speciation by the acidimetric titration is summarized in Fig. 2. A known amount of solid, about 4 g, was suspended in 500 mL of MQ water in a 1 L acid-cleaned polyethylene bottle and agitated for an hour on an "Edmund Bulher Swip" shaking table. The density of the suspension was determined by measuring precisely 10 times the cumulated weight of repeated additions of 1 mL of the suspension. Fifteen aliquots of about 20 mL of the suspension were transferred in acid-cleaned Falcon tubes and weighed in order to precisely calculate their volume. Before each withdrawal of a sub-sample from the initial suspension, the bottle was thoroughly shaken for homogeneity. 13 aliquots out of 15 were then acidified with increasing volumes of 1 mol $L^{-1}$ HCl (25, 50, 100, 150, 200, 250, 300, 400, 500, 600, 700, 1000 and 1500 µL) and agitated together with two unacidified aliquots for 16 h on a shaking table. This duration was experimentally determined by a kinetic study in order to ensure that chemical equilibrium was reached in the suspension. Sub-samples of 10 mL from each aliquot were further filtered with acid-cleaned 0.2 µm Sartorius cellulose nitrate filter of 25 mm diameter by means of an acid-cleaned syringe and a Millipore "Swinnex" filter holder. The filtered solution was acidified to pH 1 with 1 mol $L^{-1}$ HC1 prior to chemical analyses, whereas the filter itself was kept for mineralogical analysis. The final pH of the aliquot was measured in the supernatant of the remaining 10 mL of suspension. The entire titration experiment was performed at room temperature.

### *2.3. Analytical*

The total digestion was performed following Paucot and Wol-last (1997). A sub-sample of a few grams was ground in an agate mortar to <10 µm in order to reduce heterogeneities. Fifty to 100 mg of the sample, previously dried at 110 °C for an hour was dissolved in 4 mL concentrated HF-aqua regia (1:1 volume ratio) prepared from suprapur grade reagents. The dissolution was performed in Teflon bombs, Parr-4781, in a commercial micro-wave oven, Phillips AVM611AT4811, following a thermal regime of 100 W for 3 min and 10 min of cooling; three times at 150W for 3 min and 10 min of cooling and finally 200W for 3 min, followed by an hour long cooling. Hydrofluoric acid was neutralised by adding 0.62 g of boric acid and diluted to 25 mL in a volumetric flask.

Trace elements (Cd, Cu, Pb, Cr, Zn and Co) were measured by Graphite Furnace Atomic Adsorption Spectrometry on a Varian SpectrAA-300. Major/minor elements (Si, Al, Ca, Mg, Fe, Mn) were analysed by Inductively Couped Plasma Atomic Emission Spectroscopy on a Perkin Elmer ICP 6000. Details of the analytical protocol are given in Paucot and Wollast (1997). Mineralogical data were acquired on filters with a Brucker Siemens Microdiffractometer (GADDS) and a Scanning Electron Microprobe (SEM) with imagery by backscattered electron microprobe and chemical analysis by Energy Dispersive X-ray Spectroscopy (EDS).

## 3. Results

The acidimetric titration method, applied to a large set of sample materials (other surface sediments, sediment trap samples, a sediment core from Doel), give results that agree systematically. However, for the purpose of this study, the surface sediment from Doel will be presented solely.

### *3.1. Evolution of pH during the course of the titration*

One could consider the titration of a hypothetical solution such as pure MQ. water in equilibrium with the atmosphere as the initial state of the experimental titration before acid effectively interacts with the suspended solids. The concentration of protons in this solution, as well as pH, can be theoretically calculated for each step of the titration. By comparing the pH values of these "theoretical" conditions with pH values effectively measured in the acidified suspensions after 16 h of contact time (Fig. 3), protons consumed during the course of the titration can be calculated. The figure shows that the acidimetric titration of the sediment is basically identical to the titration of a weak base by a strong acid: it exhibits an abrupt pH drop from ~5.5 to ~3, as well as "buffering" due to the presence of chemical species counter-acting the increase in acidity.

The amount of trace and major elements released into the solution are expressed as a percentage of the bulk composition of the sediment and plotted against the pH of the suspension. These titration curves can be compared for the different metals considered. The % of element leached at the end of the titration, represents the HCl-reactive fraction, or its "reactivity". By contrast, a residual fraction not dissolved by HC1 at pH 1.4 may be (operationally) defined as well. The latter is likely composed of a mineral assemblage rather than one single phase. The pH at which the element starts to be leached from the sample into solution defines its "mobility". One can consider that the acidimetric titration of a sample material mimics the response of that sample to changes in pH that may result from chemical disequilibrium in the surrounding environment. In this respect, the acidimetric titration is a potential proxy to assess the risks due to the release of trace metals owing to changes in pH that are to affect that sample material.

### *3.2. Titration of major (and minor) elements*

Calcium, Mg, Fe, Al and Si are major constituents of environmentally relevant mineral phases for the speciation of trace metals in carbonates, oxyhydroxides, silicates and sulfides. Manganese is not a major element *sensu stricto,* but since it is a minor constituent of former mineral phases, it will be presented together with other major elements. Table 1 summarizes the bulk chemical composition and the HCl-reactive fraction of the sample in terms of major elements. The titration of P and S, acquired separately on the same sample, are integrated in the discussion (Section 4.1.3).

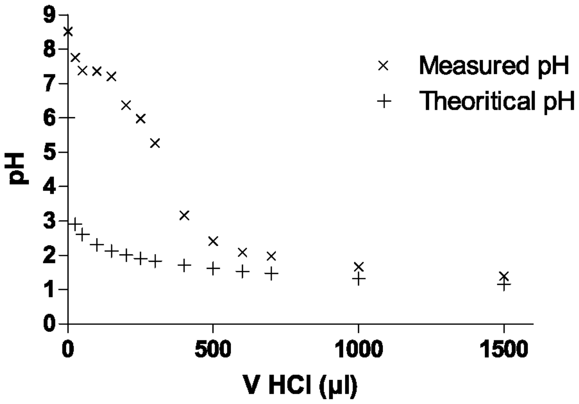
The results of the titrations of Ca, Mg, Mn, Fe, and Al are presented in Fig. 4a-e.

Calcium, Mg and Mn are very rapidly leached from the solid, starting at pH 7-8. About 80% of Ca is leached from the solid between pH 8 and pH 6, together with ~20% of Mg and ~40% of Mn. It is noticeable that the titration of Mn slows down after pH 6 until pH 3 where it exhibits a secondary inflection point not observed for Ca and Mg. At the end of the titration, ~100% of Ca, ~40% of Mg and ~80% of Mn are dissolved. In contrast, the leaching of Al and Fe starts a lower pH closer to ≈5 and becomes significant from pH 3. The titration of Al is slightly offset toward higher pH compared to Fe. At the end of their titration, ~30% of Fe and less than ~5% of Al are released to solution. The behaviour of Si resembles to that of Fe and Al but only less than 1% of the bulk Si content is leached. For the sake of simplicity, the titration of Si, although systematically investigated, is not presented in Fig. 4.

***Table 1.*** *Bulk concentration and HCl-reactive fraction of major and minor elements. The average analytical uncertainty is about 5% RSD.*

| | Ca | Mg | Fe | Al | Si | Mn | TPP |
|---|---|---|---|---|---|---|---|
| BULK | 4.6% | 0.889% | 4.9% | 4.8% | 25.9% | 860 ppm | 0.38% |
| % HCl-reactive | 99 | 37 | 31 | 4.4 | 0.73 | 80 | 60 |

***Fig. 3.*** *Comparison of the theoretical pH (with no suspension) and the final pH measured (after 16 h of contact time with the suspension) as a function of the volume of HC1 added for the acidimetric titration.*



*3.3. Titration of trace elements*

Table 2 presents the bulk chemical composition of the sample in terms of trace elements and the proportion of the bulk released at each step of the titration. Moreover, Co, Cd, Zn, Cu, Pb and Cr titrations are presented in Fig. 5a-f. This study also provides insights into the P speciation (Section 4.1.2).

Cobalt, Cd and Zn are the first ones to be leached starting at pH 7.5. At pH 6, about ~20% of Co, ~30% of Zn and ~30% of Cd are readily titrated. Cobalt, Cd and Zn titration are rather continuous with respect to pH until pH 2.5. At lower pHs, the amount of Cd released stabilises, Zn continues to be leached at the same rate and Co shows a second abrupt increase. At the end of the titration, ~55% of Co, ~85% to 90% of Zn and ~90% of Cd are leached from the solid. Copper, Pb and Cr are leached at lower pH values and their titration curves exhibit a consistent shape different from the previous group. The leaching of Cu starts between pH 5 and 6, reaches ~20% at pH 3 until ~70% is leached at the end of the titration. Lead titration is offset to lower pH compared to Cu: it starts closer to pH 3, reaches ~20% at pH 2 until ~70% is leached at the end of the titration. Chromium titrations resemble those of Pb, regarding the shape of the titration curve but only ~20% of the bulk Cr content is leached at the end of the titration.

To summarize the behaviour of major and trace elements during the course of the titration, they are classified with respect to their mobility and reactivity, as follows:

Decreasing mobility : Ca = Mg > Mn = Co > Zn = Cd > Cu = Al

> Fe = Pb = Cr > Si.

Decreasing reactivity : Ca > Cd > Zn > Mn > Cu = Pb > Co > Mg

> Fe > Cr > Al > Si.

It is noteworthy that the order of reactivity for major, trace and minor elements in the sediment studied for speciation corresponds roughly to the opposite order of affinity established for simpler, pure or synthetic, mineral surfaces such as Fe oxide (Kinniburgh et al., 1976; Pickering, 1979; Kinniburgh and Jackson, 1981), goe-thite (Forbes et al., 1976; Schmitt and Sticher, 1991), Al oxide (Kinniburgh et al., 1976; Pickering, 1979; Kinniburgh and Jackson, 1981), humic acid (Schnitzer and Khan, 1972; Pickering, 1979; Jackson et al., 1980; Swift and McLaren, 1991) and clay minerals such as montmorillonite, illite and kaolinite (Pickering, 1980).

### *3.4. Source of errors*

Propagated errors related to weight measurements account only for 0.03% RSD, i.e. insignificant compared to a typical average analytical uncertainty of 5% RSD of GF-AAS and ICP-AES measure-merits. However, they do not take into account the reproducibility of the step in which aliquots are withdrawn from the suspension. There is nevertheless evidence that the methodology followed overcomes such a source of error. Indeed, titration curves (pH vs. volume of HC1) and extraction curves (% metal released vs pH) are smooth and continuous. In addition no significant difference in pH was observed for the duplicate titrations of the Doel sediment. Therefore, the main source of errors is related to the measurements of trace element concentrations by GF-AAS and ICP-AES.

***Table 2**. Bulk concentration and HCl-reactive fraction of trace elements. The average analytical uncertainty is about 5% RSD.*

| | **Cd** | **Co** | **Cr** | **Cu** | **Pb** | **Zn** |
|---|---|---|---|---|---|---|
| BULK (ppm) | 16 | 13 | 206 | 111 | 155 | 707 |
| % HCl-reactive | 88 | 56 | 20 | 68 | 67 | 86 |

## 4. Discussion

Even if all the mineralogical phases can influence the pH during the acidimetric titration, only the dissolution of major mineralogical phases will have a strong control on how the pH is "buffered". Silicon is the most abundant element in the solid investigated and Al has a bulk concentration comparable to those of Ca and Fe, but these two major elements are leached from the solid in much smaller proportions (~0.8% and ~4.5%, respectively, for Si and Al). Compared to Al and Si, the acidimetric titration released more minor constituents such as Mn and Mg proportionally to their bulk concentration. In contrast, Ca and Fe constitute most of the dissolved major elements released in solution during the course of the titration. Therefore, these two elements must be associated with the mineralogical phases which control the evolution of the pH.

The behaviour of elements with respect to pH is fairly consistent with the results of Hatje et al. (2003), who considered interactions of natural suspended matter in contact with trace metal radiotracers as a function of pH. These authors interpreted the results as an effect of proton competition on adsorption sites of insoluble minerals.

In the present study the release of trace and major elements into solution cannot be fully attributed solely to such a process. Conversely, results of the acidimetric titration suggest that pH changes are controlled by acid-base reactions. Such reactions are stoichiometrically quantified and supported by min-eralogical observations using XRD and SEM.

***Fig. 4.*** *Acidimetric titrations of major elements (a) Ca, (b) Mg, (c) Mn, (d) Fe and (e) Al for the Doel surface sediment.*

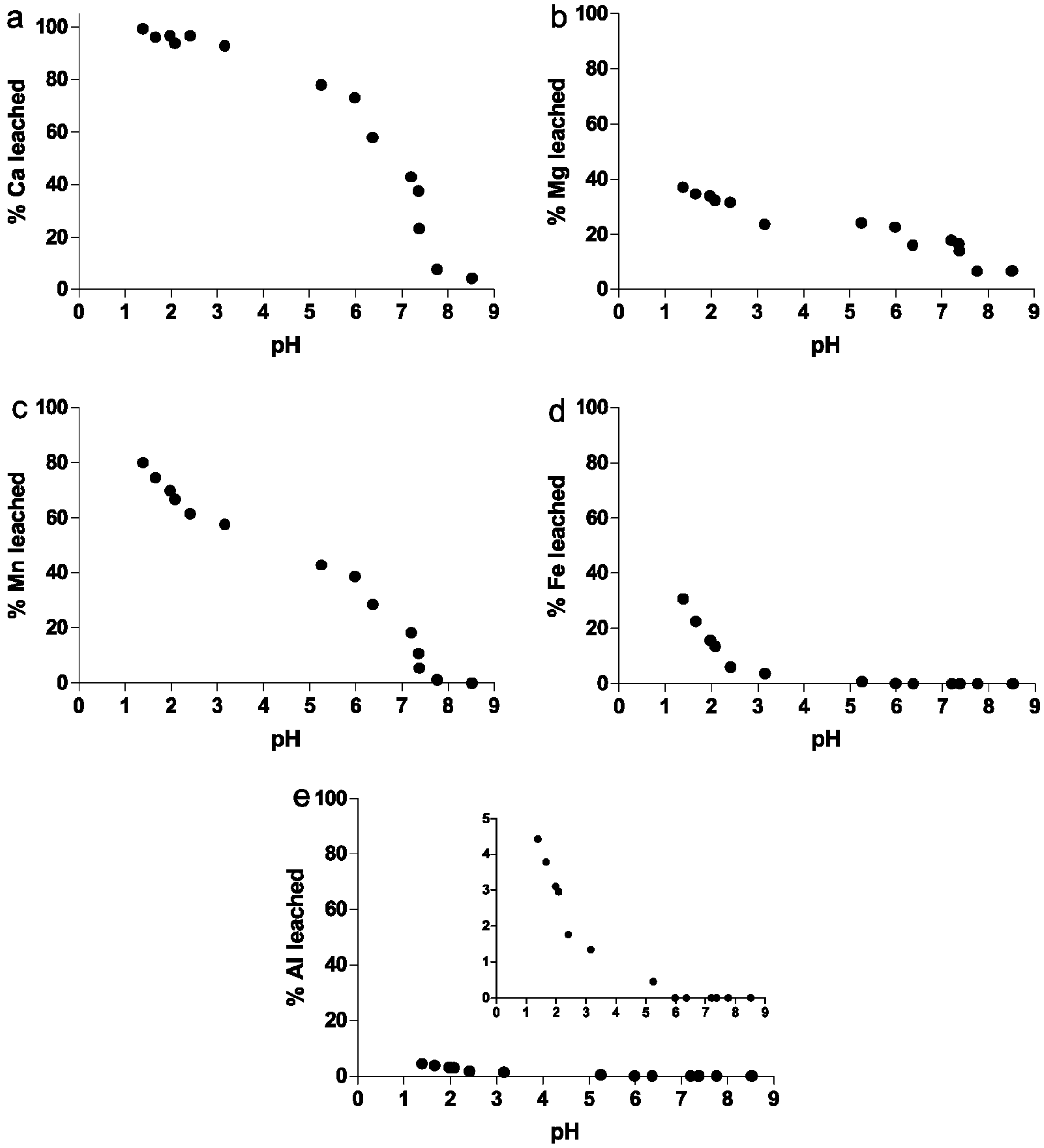
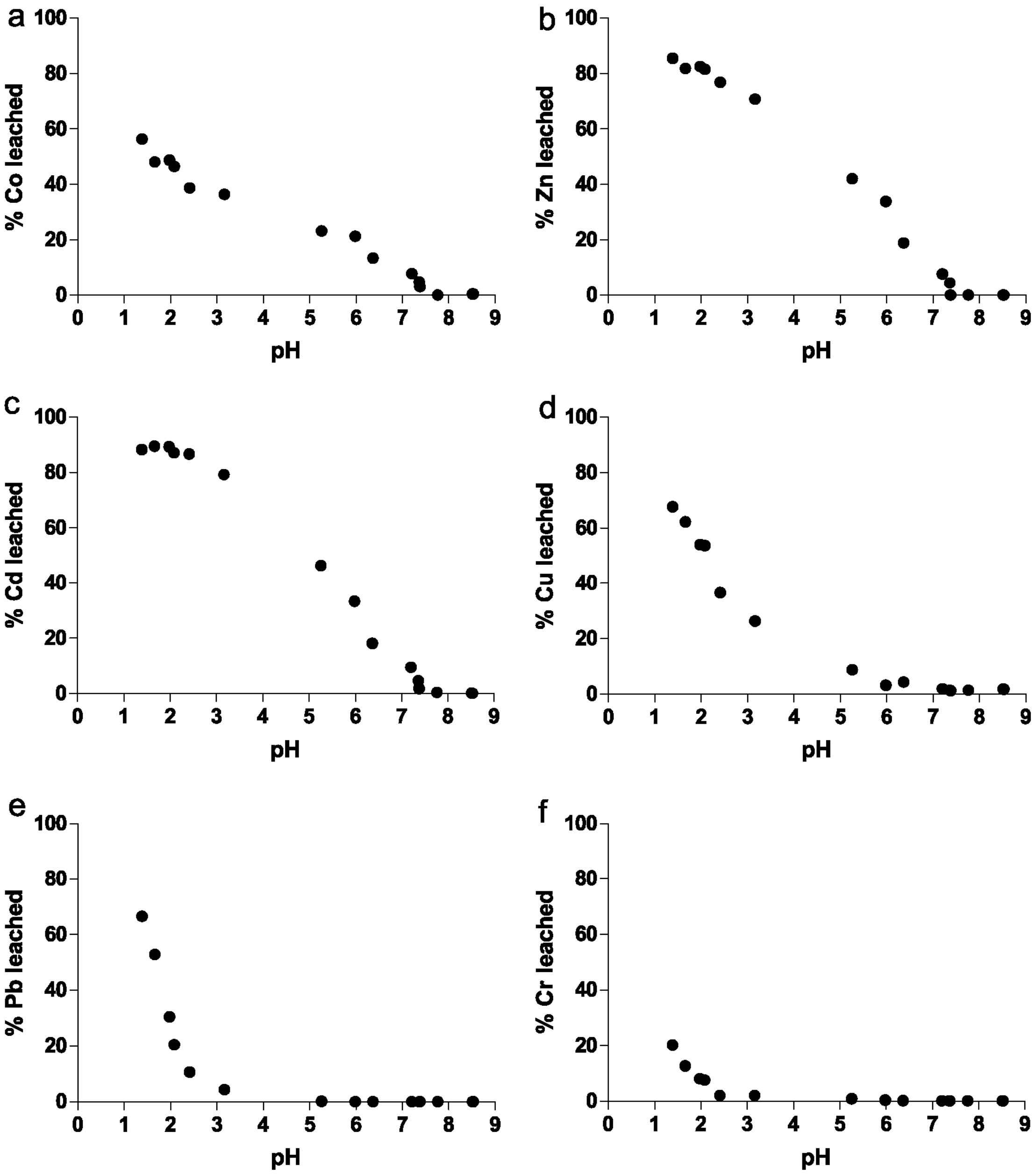


***Fig. 5.*** *Acidimetric titrations of trace elements (a) Co, (b) Zn, (c) Cd, (d) Cu, (e) Pb and (f) Cr for the Doel surface sediment.*



*4.1. Speciation of major elements*

4.1.1. Carbonate phase

The titration of Ca (Fig. 4a) strongly suggests that calcite is readily dissolved at the beginning of the titration, between pH 8.5 and 6. XRD pattern and SEM observations (not shown) acquired on the filters at pH 6 indicate the absence of calcite at this pH. The complete dissolution of Ca is further attested by the sudden drop of about 2.5 pH units from pH 5.5 to pH 3 (Fig. 3). Magnesium titration (Fig. 4b) closely follows that of Ca and about 25% of Mg is leached in this pH range. Examination by SEM of the filter collected at pH 8.5 revealed the presence of calcite as shell debris, even though neoformation of Ca-Mg carbonates are evident from porewater data acquired on the Doel core (unpublished data). From a kinetic point of view, at pH 8, compared to calcite and aragonite the dissolution of dolomite is one order of magnitude slower and that of magnesite is three orders of magnitude slower (Chou et al., 1989). The authors therefore favour the existence of the magnesian calcite mineral, likely associated with calcite in the carbonate phase.

It is pinpointed that the acidimetric titration method allows the study of Mg speciation, which is an improvement over SESs in which $MgCl_2$ is used as a reagent, therefore cancelling the potential interest of studying Mg geochemistry.

Protons consumed by the dissolution of the magnesian calcite can be calculated from stoichiometry (Eqs. (1) and (2)).

$$(Ca_xMg_{1-x})CO_3 + H^+ \Rightarrow xCa^{2+} + (1-x)Mg^{2+} + HCO_3^- \text{ at neutral pH} \qquad (1)$$

$$(Ca_xMg_{1-x})CO_3 + 2H^+ \Rightarrow xCa^{2+} + (1-x)Mg^{2+} + H_2O + CO_2 \text{ at acidic pH} \qquad (2)$$

Magnesian calcite dissolution is responsible for the complete consumption of protons between pH 8.5 and pH 5.5 and for the majority of proton consumption during the entire titration, as evidenced in Fig. 6. As the "buffering" capacity of magnesian calcite is overcome, the pH drops abruptly from 5.5 to 3 at which pH a second "buffer" is responsible for an additional consumption of $H^+$ caused by the dissolution of another phase (see Section 4.1.2).

In addition to Mg, about 40% of the bulk Mn content is significantly leached from the solid between pH 8.5 and 6, simultaneously to Ca (Fig. 7). This proportion is consistent with the estimation of Zwolsman and van Eck (1999). The results of the acidimetric titration of Mn strongly suggest its association with carbonates. Manganese can occur either as "pure" rhodocrosite, or as a limited solid solution into (magnesian) calcite. The occurrence of the $Mn\text{-}CO_3$ chemical bound has been evidenced by Raman spectroscopy (Prof. Wartel, Universite des Sciences et des Technologies de Lille 1, Laboratoire de Chimie Analytique et Marine, pers. com.), however, this technique was not able to distinguish between rhodocrosite and crystallographically assimilated Mn into the magnesian calcite. Other studies have concluded that Mn is associated with carbonate minerals in anoxic estuarine sediments (e.g. Saulnier and Mucci, 2000) possibly as rhodochrosite.

### 4.1.2. Oxyhydroxide phase

Oxyhydroxides are known to be completely soluble in HC1 (Cooper and Morse, 1999) and should therefore account for the second consumption of protons occurring after the first abrupt drop in pH (Fig. 6). Indeed, this second consumption of protons is consistent with the beginning of the leaching of Al (Fig. 4e) and Fe (Fig. 4d) in the vicinity of pH 5 and becomes more pronounced at pH 3. In addition, the second consumption of protons below pH 3 is stoi-chiometrically balanced by the dissolution of the oxyhydroxide phases, composed for most part of a FeOOH polymorph and a smaller amount of $Al(OH)_3$ possibly as gibbsite, according to the following equations:

$$FeOOH + 3H^+ \Rightarrow Fe^{3+} + 2H_2O \qquad (3)$$

$$Al(OH)_3 + 3H^+ \Rightarrow Al^{3+} + 3H_2O \qquad (4)$$

Mass balance calculations performed on the last three steps of the acidimetric titration show that the molar ratio of the amount of Fe and Al leached from the sediment to protons consumed (in excess of those required to dissolve the magnesian calcite) is close to $(Fe^{3+}+Al^{3+})/H^+ \approx 0.3$, as shown in Table 3.

In general, the total consumption of $H^+$, calculated by adding up protons consumed by the dissolution of magnesian calcite, FeOOH and $Al(OH)_3$, agrees with the "measured consumption of $H^+$", calculated by the mean of the difference between the "theoretical" pH and the pH measured in the suspension (Fig. 6). These phases account for the near total consumption of protons and control how the acidity is "buffered" during the titration.

Together with 30% of Fe and 5% of Al, the second release of ~20% Mn apparently below pH 5.5 occurs simultaneously to the leaching of Fe (Fig. 8). This strongly suggests the occurrence of Mn sorbed onto or coprecipitated with Fe-oxyhydroxide.

***Fig. 6.*** *Calculation of the protons consumed during the course of the titration by the dissolution of magnesian calcite, FeOOH and $Al(OH)_3$, according to Eqs. (1 )-(4). The "total consumption of $H^+$" agrees with the "measured consumption of $H^+$", calculated from pH measurements.*

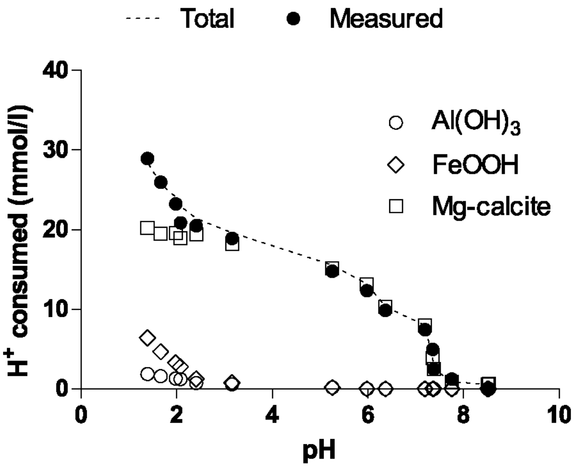
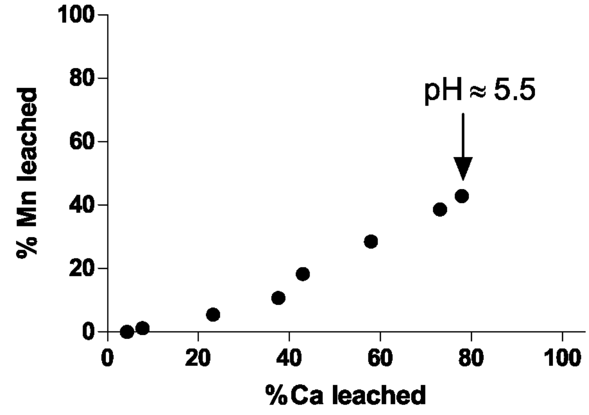


***Fig. 7.*** *% Mn leached as a function of % Ca leached during titration for pH values ranging from 8.5 to 5.5. The linear relationship indicates the association of Mn with the carbonate phase.*



In addition to Mn, the acidimetric titration of P, starting significantly at pH 3, is well correlated to that of Fe (Fig. 9), suggesting that P is partly bound to Fe-oxyhydroxides. The close relationship between P and Fe is in agreement with data from the upper section of sediment cores sampled on salt marshes of the Scheldt estuary in which Fe-oxyhydroxides were suggested to account for the P speciation (Zwolsman et al., 1993). The speciation of P with Fe-oxyhydroxides involves likely mineralized P as $PO_4^{3,-}$ instead of organic P and suggests that the sorption of P onto Fe-oxyhydroxide is a major sink for orthophosphate. This has the following implications: the existence of this P pool may retard the improvement of water quality in the future as nutrient reduction policies become implemented, since the reduction of external sources of P will result in the desorption of phosphate in order to reach sorption equilibrium (Zwolsman, 1994). In a recent study on P biogeochemistry, Van der Zee et al. (2007) determined the P speciation in the water column of the Scheldt estuary and found that desorption of $P0_4$ was the most important transformation process for P along the salinity gradient. The dissolved P pool increased and the particulate inorganic P pool decreased, while total P behaved conservatively during estuarine mixing. This pool of particulate P is likely to be long-lived in oxic freshwaters because it requires sufficiently low pH to become available. The HCl-reactive fraction of about 60% of total P is consistent with residual P present in the sediment, most likely bound to organic matter.

***Table 3**: Stoichiometric relationship between protons consumed and Fe and Al leached into solution. A ($Fe^{3+}$ + $Al^{3+}$)/$H^+$ ratio of ≈0.3 indicates that oxyhydroxides are dissolving at the end of the acidimetric titration.*

| pH | $H^+$(mmol/L) | Fe (mmol/L) | Al (mmol/L) | (Fe + Al)/$H^+$ |
|---|---|---|---|---|
| 1.98 | 3.69 | 1.09 | 0.44 | 0.36 |
| 1.67 | 6.50 | 1.56 | 0.53 | 0.30 |
| 1.39 | 8.73 | 2.13 | 0.62 | 0.30 |

***Fig. 8.** % Mn leached as a function of % Fe leached during titration for pH values ranging from 5.5 and 1.4. The linear relationship indicates the association of Mn with the oxyhydroxide phase.*

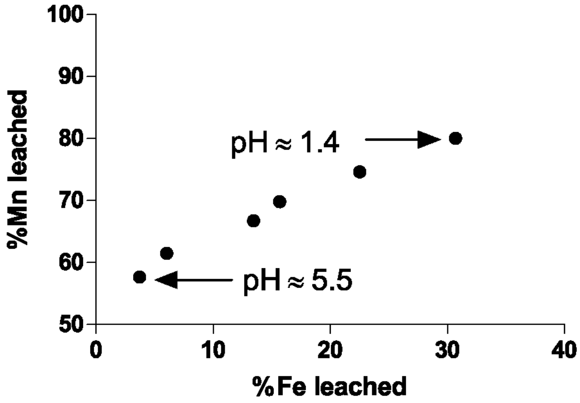
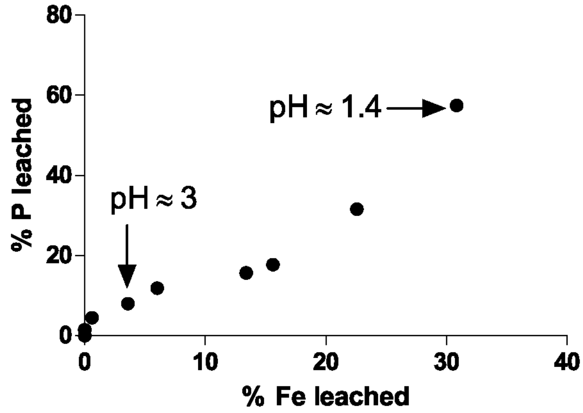


***Fig. 9**. % P leached as a function of % Fe leached during titration. The linear relationship indicates the occurrence of orthophosphates sorbed on Fe-oxyhydroxide.*



4.1.3. Organic matter and sulfides phases

*4.1.3.1. Organic matter.* A few preliminary tests carried out with $H_20_2$ or low temperature calcination on suspended matter have shown that only trace amounts of metals are released during the mineralization of organic matter. The results indicate that the trace metal content of the organic matter is very small, which may be surprising but has been confirmed by the application of the Tessier speciation method (LOCGE, unpublished data).

*4.1.3.2. Sulfides.* Chemical reactions involving Fe, S and trace metals are likely to occur by the precipitation of amorphous acid volatile sulfides (AVS) that play an active role in coprecititation/sorption of trace metals. Maturation of these sulfides involves the formation of pyrite framboids of nearly pure chemical composition (Large et al., 2001). Trace elements associated with the AVS can be released and redistributed during their transformation to pyrite (Elderfield et al., 1979; Large et al., 2001) to form pure sulfide precipitates such as CuS, ZnS, CdS, NiS, PbS, etc. The overall replacement of AVS to pyrite during early diagenesis may enhance the reactivity of trace metals (Burton et al., 2006).

Sulfides in the Doel sample observed by SEM consist in different kinds of polycrystalline aggregates of authigenic pyrite (Petit, 2000). They occur in various sizes but are recognized and distinguished from other Fe sulfides by their well developed {1 1 1} and {1 0 0} crystal faces. Observations were acquired from an unacidified aliquot (pH 8.5, Fig. 10a) of the top centimetre sample from the Doel sediment core and from the most acidic aliquot (pH 1.4, Fig. 10b) of that sample. The occurrence of pyrite in both ali-quots, the absence of alteration features, and its pure chemical composition suggest that pyrite is not dissolved during the titration and is not an important scavenger for trace metals, in agreement with Cooper and Morse (1999), Large et al. (2001) and Huerta-Diaz et al. (1998). Interestingly, the presence of a thin coating around the framboids observed at pH 8.5, is not observed at pH 1.4. This thin coating, slightly transparent to electrons, is likely made of a freshly precipitated mineral (possibly Fe-oxyhydroxide) that may play an important role in scavenging trace metals.

The titration of S (Fig. 11), together with Fe, Zn and Cd was performed on a separate aliquot of the same sample following an adaptation of the experimental protocol from Molinero et al. (1996). As a consequence, the acidimetric titration of S cannot be quantitatively implemented in calculations with the data presented in this study. However, it can be compared qualitatively to those of major elements and trace metals. Clearly, the behaviour of S during the titration, with a very rapid release at pH 7 (at which no Fe is yet leached), together with the inconsistent relative proportion of Fe and S (molar Fe/S = 12 at the end of the titration), is not in favour of the occurrence of Fe monosulfides. Fe was indeed stoichiometrically consistent with the dissolution of Fe-oxyhy-droxides as discussed in the previous section.

Instead of suggesting the absence of Fe monosulfides in the sample, the authors favour the hypothesis of its rapid dissolution in the presence of HC1, at moderate to low pH closely followed by a process of reprecipitation/adsorption onto Fe-oxyhydroxides. The overall reaction should take less than 16 h - the contact time of the leaching. Such a process is naturally occurring in estuarine environments in less than 1 h (Saulnier and Mucci, 2000). At this point, additional experiments to better constrain the chemical composition and the mineralogy of the sulfides has not been performed.

Data on S suggest that AVS are present in too small amounts to have an important control on the buffering of pH during the titration, in any case, for the sample studied.

### 4.1.4. Residual phase

The residual phase is operationally defined as the fraction of elements not released to solution at the end of the acidimetric titration. It consists of ~99% of the total Si, ~95% of the total Al, ~70% of total Fe and ~60% of the total Mg, suggesting that the residual fraction is predominantly composed of silicates. XRD indeed revealed clay minerals, quartz, microcline and albite, as well as a minor amount of glauconite. At high temperature well ordered tectosilicates such as albite are not expected to dissolve during the experiment due to their extremely low dissolution rate at room temperature (Chou and Wollast, 1985). Further, XRD performed for clay minerals showed that the clay fraction is composed of about 90% of dioctahedral clay minerals (smectite, illite and kaolinite) and 10% of trioctahedral clay minerals (chlorite), i.e. as a whole, clay minerals are richer in Al than in Mg and Fe. In this respect, Fe is also expected to be incorporated into high temperature detrital oxides such as ilmenite or spinels (black diamagnetic grains observed under the binoculars), even though authigenic pyrite was also observed by SEM and recognized to be residual.

### *4.2. Speciation of particulate trace elements*

This section compares the titrations of trace elements to those of major/minor elements in order to better understand how they are associated within the particulate phase. Moreover, for each trace element, a residual fraction can be defined and presumably associated to minerals present in the sediments that are not dissolved during the titration. According to the amount leached at the end of the titration, a potential mobility can be established for each element.

***Fig. 10.*** *Micrographs of framboidal pyrites observed by SEM (a) framboid observed from the aliquot at pH ~8.5 showing a thin electron transparent coating and (b) framboid observed from the most acidic aliquot of the titration (pH ~1.4) occurring as polycrystalline aggregates of well formed complex crystal shapes showing octahedral and minor cubic faces. Note the absence of alteration features.*

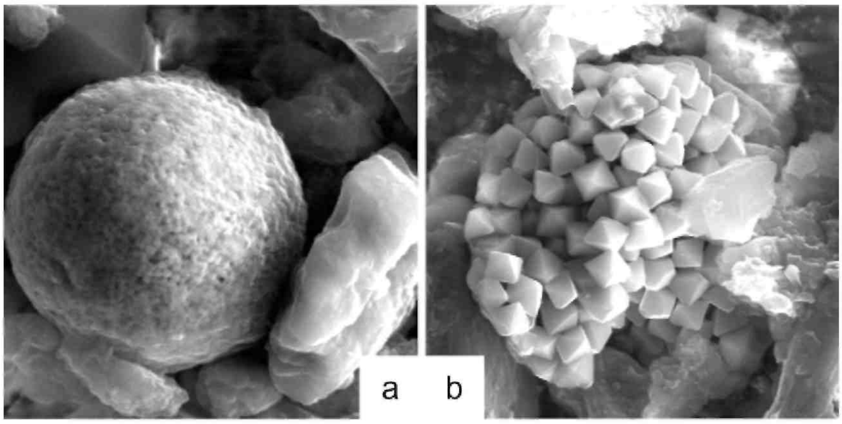
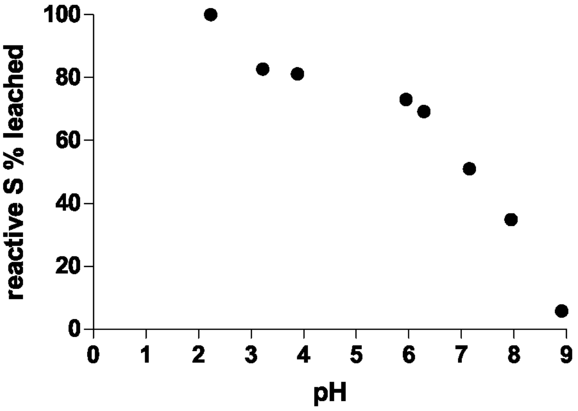


***Fig. 11.*** *Acidimetric titration of HCl-reactive S for the Doel surface sediment. Since bulk S concentration was not measured, the% S leached is expressed relative to the total S leached at the end of the titration rather than to the bulk S concentration in the sample.*



4.2.1. Cobalt (and Manganese)

Owing to very similar electronic configurations, Mn and Co are obviously strongly correlated in nature, and are, indeed, closely linked together in the Scheldt estuary. Previous studies related to the geochemistry of Co and Mn in the bulk particulate phase have already suggested a close relationship in cored sediments from salt marshes (Zwolsman et al., 1993) as well as in suspended particulate matter of the lower Scheldt estuary (Zwolsman et al., 1999). Kinetic experiments on the sorption of Co and Mn by natural particles have demonstrated that they have the same behaviour with respect to pH, salinity and particle loading (Hatje et al., 2003; Ciff-roy et al., 2003). Therefore, the speciation of Mn and Co inferred from the acidimetric titration method agrees with what is commonly found in the literature. This constitutes additional support for its efficiency to assess trace metals speciation.

Manganese speciation has already been addressed in Sections 4.1.1 and 4.1.2 (see also Figs. 7 and 8). The acidimetric titration of Co shows a strong correlation with Mn, across the entire pH range (Fig. 12). Cobalt is therefore associated with both the carbonate phase (about 25 to 30% of bulk Co) and the Fe/Mn-oxyhydrox-ides phase (about 30% to 35% of bulk Co).

The very high HCl-reactive fractions suggest that the bulk Mn may be attributed to *in situ* precipitation of rhodocrosite and/or Mn-oxyhydroxides. In the case of Co, the large residual fraction of 40%, close to what was suggested by Zwolsman et al. (1993), strongly favours the occurrence of a detrital phase such as a high temperature well crystallized oxides (e.g. ilmenite, magnetite or spinel), likely related to the amount of residual Fe of up to 70% of the bulk Fe content.

### 4.2.2. Cadmium and zinc

Cadmium and Zn exhibit a very strong correlation across the entire pH range of the acidimetric titration (Fig. 13a), suggesting that they are closely bound to the same phase. The close relationship between Cd and Zn has been previously established by Hatje et al. (2003) under varying conditions (pH, salinity and particle loading), as well as by Ciffroy et al. (2003) in their kinetic studies on trace metal desorption during *in vitro* mixing of fresh and brackish waters from the Loire estuary.

The leaching of Cd and Zn from the solid starts at pH 7.5 at which about 40% of Ca is already released into solution by the dissolution of calcite (Fig. 13b). This offset rules out the association of Cd and Zn with carbonate minerals, in agreement with thermodynamic calculations of Gerringa et al. (2001). These findings are in disagreement with older studies by Zachara et al. (1989), Fuller and Davis (1987) and Davis et al. (1987), as well as with SESs (Section 4.4), which attributed the speciation of Cd and Zn to the carbonate phase. The leaching of Fe (and Al) starts when about 40% of Zn and 45% of Cd are already leached into solution (Fig. 13c). In addition, Cd and Zn titrations do not show a second release below pH 3 as is the case for Mn and Co. These two features suggest that Cd and Zn are not associated with the oxyhydroxide phase.

The remaining possibilities for the speciation of Cd and Zn are the sulfides and organic matter. Surprisingly the latter seems to be associated with a very small amount of trace metals (LOCGE, unpublished data). In contrast to Ca, Fe and Al, the titration of S more closely resembles those of Zn and Cd, suggesting that Zn and Cd are associated with the sulfide phase. Owing to identical electronic configuration, Cd may be incorporated into ZnS as a partial solid solution. Results from the acidimetric titration agree with conclusions found in different publications. The *in vitro* experiments by Cooper and Morse (1999) support the occurrence of a Zn sulfide fully soluble in HC1 (synthetic makinawite exposed to trace metal solutions). AVS measurements by Allen et al. (1993) showed that unlike Cu, Cd and Zn are fully associated with sulfides in the sediments. Geochemical modelling of dissolved Cd and Zn in the Scheldt estuary by Gerringa et al. (2001) was consistent with the dissolution of CdS and ZnS occurring as two pure minerals (ZnS being more soluble than CdS).

Both Cd and Zn undergo a nearly complete leaching at the end of the titration. Hydrochloric acid-reactive Cd and Zn fractions represent 90% and 85%, respectively, of the bulk concentrations in the sediment.

***Fig. 12.*** *Acidimetric titration of Co as a function of the acidimetric titration of Mn. Cobalt is associated with the carbonate phase as well as the oxyhydroxide phase.*

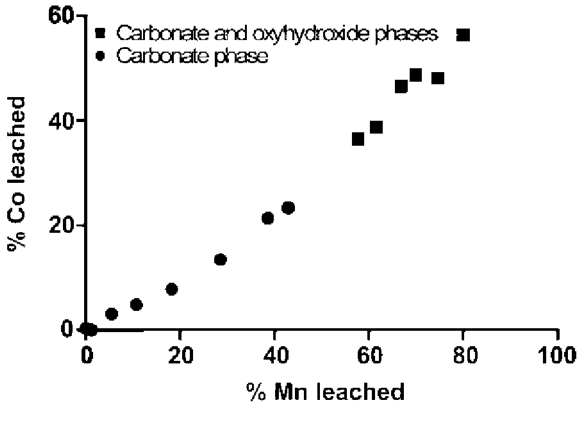
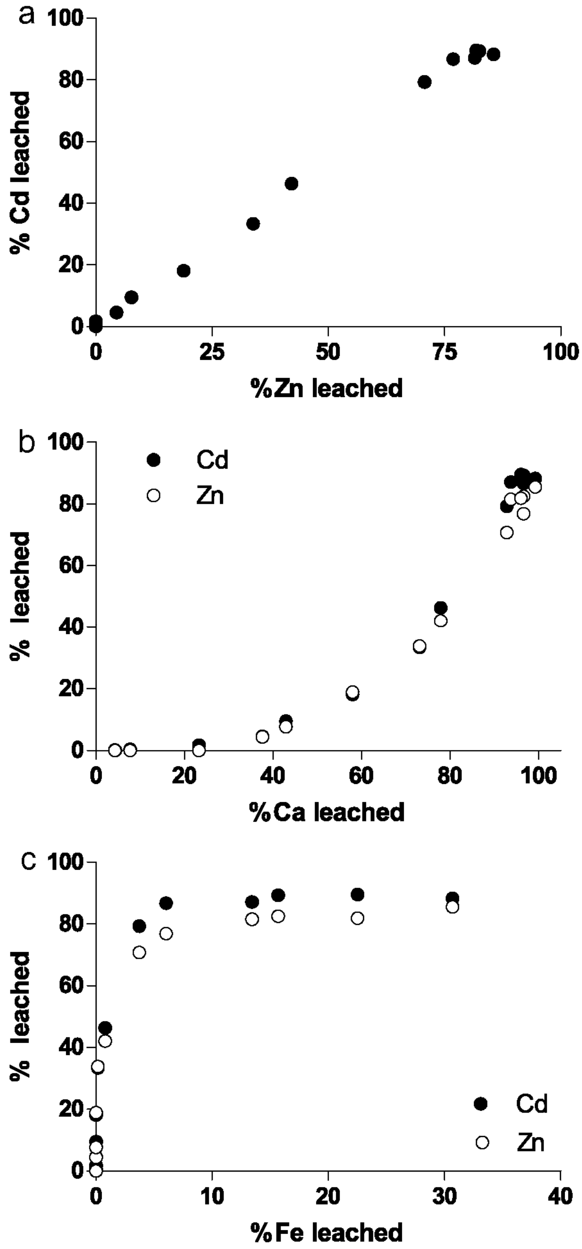


***Fig. 13.** (a) Acidimetric titration of Cd as a function of the acidimetric titration of Zn. Acidimetric titrations of Cd and Zn as a function of (b) Ca and (c) Fe. (b) and (c) show that neither the carbonates nor the oxyhydroxides are responsible for Cd and Zn speciation.*

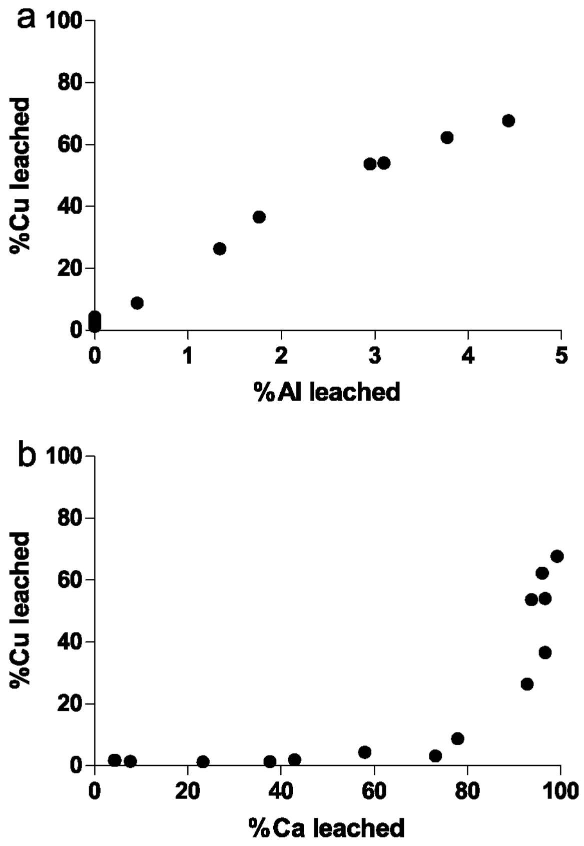


### 4.2.3. Copper

Like Cr and Pb, Cu is strongly bound to the particulate phase. Its titration resembles that of Pb and Cr but is initiated at a higher pH. Copper cannot be associated with the carbonate minerals because its leaching starts when about 80% of Ca is already dissolved (Fig. 14b). Moreover, Cu titration is significantly offset from S titration which starts at pH 7, suggesting that Cu does not occur as a sulfide in the sediment. AVS studies, such as the one conducted by Allen et al. (1993) show that, in contrast to Ni and Zn, there is no relationship between Cu and the concentration of AVS. They suggest, with Ankley et al. (1992) that Cu is linked to phases other than sulfides in the sediment.

The speciation of Cu is more likely related to the oxyhydroxide phase. The leaching of Cu starts at a pH closer to that for Al (Fig. 14a) than that for Fe, suggesting that Cu is preferentially adsorbed onto gibbsite. The close relationship between Cu and Al, as evidenced from the acidimetric titration results, has been addressed in the literature (Kinninburgh et al., 1976; McBride and Blasiak, 1979; Pickering, 1979; Weesner and Bleam 1997; Cheah et al., 1998; Martinez and McBride, 2000). Again, this argues in favour of the acidimetric titration method to be an efficient means of assessing trace metal speciation.

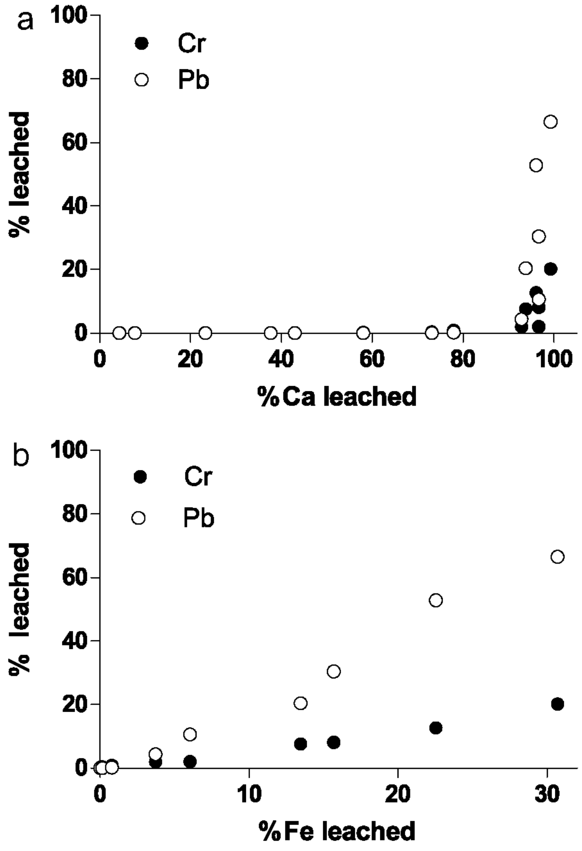
***Fig. 14.*** *Acidimetric titration of Cu as a function of the acidimetric titrations of (a) Al and (b) Ca. (a) Shows that Cu speciation is controlled by the oxyhydroxide phase, possibly coprecipitated with gibbsite and (b) indicates that the speciation of Cu cannot be attributed to the carbonate phase.*



4.2.4. Lead and chromium

Among all the trace elements investigated for speciation, Pb, Cr are the most strongly bound to the particulate phase. Their leaching starts at pH 3 but they are significantly leached only at pH < 3, ruling out their association with the carbonate phase, which is completely dissolved at pH 6. Moreover, the leaching of S being initiated at pH 8, well above the pH at which Pb and Cr start to be leached, indicates that no significant Pb and Cr sulfides are present in the sediments. In contrast, Cr and Pb closely follow the titration of Fe, suggesting that adsorption/coprecipitation with Fe-oxyhydrox-ides is the dominant process controlling the speciation of Pb and Cr (Fig. 15). The acidimetric titration of Al suggests a possible role of gibbsite in the speciation of Cr and Pb because Al leaching starts in the vicinity of these elements, but, however, is offset towards higher pH. Again, the results from the acidimetric titration agree with what is commonly found in the literature. Lead speciation has been attributed to Fe-oxyhydroxides by Bargar et al. (1997a,b) and Caet-ano et al. (2003). The sorption studies of Kinninburgh et al. (1976) and Pickering (1979) are consistent with a stronger affinity of Pb for Fe oxides than for Al oxides. Sorption studies of Cr(VI) as a function of pH onto natural or synthetic pure sorbants have already addressed the preferential sorption of Cr(VI) to Fe oxide and oxyhydroxide in soils rather than (in a decreasing order of affinity) Al oxide, kaolinite and montmorillonite (Zachara et al., 1989). Available data on Cr(III) suggest also a stronger affinity of this metal for Fe hydroxides (Bradl, 2004). The preferential affinity of Cr for Fe was also demonstrated by Hatje et al. (2003) in kinetic experiments performed on natural suspended particulate matter exposed to solution of trace metal radiotracers.

***Fig. 15**. Acidimetric titrations of Cr (filled circles) and Pb (open circles) as a function of the acidimetric titrations of (a) Ca and (b) Fe, suggesting the association of both trace metals with the oxyhydroxide phase.*



Although both are scavenged on FeOOH, Cr and Pb differ in their HCl-reactive fraction: ~20% of total Cr and ~70% of total Pb are leached at the end of the titration. The smaller HCl-reactive fraction of Cr indicates that the residual mineralogical assemblage is composed of a detrital phase, likely a high temperature well crystallized oxide such as ilmenite or chromite. The occurrence of Cr in detrital minerals is consistent with the data of Astrδm (1997). Compared to other surface sediments collected along the estuarine transect (data not shown), the Doel surface sediment exhibits one of the highest HCl-reactive fractions for all trace metals including Cr, indicating that Cr is bound to fresh Fe-oxyhydroxide formed in the upper estuary, either settled from the water column or precipitated *in situ* at the oxic-suboxic layer in the sediments. Compared to Cr, the higher HCl-reactive fraction for Pb suggests that its speciation is controlled by authigenic precipitation, with the possible occurrence of a detrital phase accounting for 20-30% of total Pb in the residual phase.

### *4.3. Reactivity and mobility of major and trace elements*

If SESs may bring insights to trace metal speciation, they fail to provide relevant information on the mobility of trace metals with respect to changes in environmental conditions.

One can consider that the acidimetric titration of a sample material mimics the response of that sample to changes in pH that may result from chemical disequilibrium between the mineral phases it contains and the changing conditions of its surrounding environment. In this respect, once that sample material is characterized by an acidimetric titration, the pH may be used as a proxy to assess the risks resulting from the release of trace metals owing to changes in pH that are to affect that sample material (e.g. when they are to be dredged and dumped ashore or discharged into technical burial sites).

For this purpose, the data obtained from the acidimetric titration have been interpolated. Table 4 summarizes the results showing how the acidimetric titration data can be used to predict the effect of pH on the mobility of trace metals, sorted here by decreasing reactivity, as defined earlier.

Comparison of Co and Cd, as well as Cr and Pb, indicates that there is no clear relationship between mobility and reactivity. This is not surprising since the chemical composition of detrital minerals is acquired in high temperature environments, whereas the chemical composition of HCl-reactive minerals is more likely determined by low temperature equilibrium occurring in anthro-pogenically perturbed systems. Therefore, the potential threat of a polluted material is strongly dependant on the relative proportion of the so-called "residual fraction", which must represent as near as possible the "background assemblage" of phases not involved in biogeochemical or low temperature processes affecting trace element speciation and mobility. The chemical technique of defining its composition is of paramount importance to address the potential hazard of a contaminated solid material. For instance, Tessier's protocol predicts that 70% of Cr is environmentally mobile against only 20% determined by the acidimetric titration in this study.

### *4.4. Comparison of acidimetric titration and sequential extraction*

The speciation of Fe, Mn, Al, Cd, Cu, Co and Cr determined by the SES of Tessier et al. (1979) is compared to the speciation determined by the acidimetric titration method in Table 5, for the Doel surface sediments.

The two methods show rather poor agreement. The acidimetric titration and the SES are not consistent with respect to the specia-tion of Cd. Moreover, the SES proposes more complex schemes of speciation for Fe, Cr Al, and more importantly for Cu. Some degree of consistency between the two methods is observed for Mn and Co that are predominantly associated with carbonates and oxyhy-droxides (Section 4.2.1), as well as for Cr, Fe and Al, (Sections 4.1.2, 4.1.4 and 4.2.4) associated with the oxyhydroxides and the residual phases by the acidimetric titration method and accounting for their highest proportions in the same phases of the SES.

The acidimetric titration method gives a higher proportion for residual fractions than the SES (with the exception of Cd, which is very mobile). Since the residual fraction was defined earlier as the amount of trace metals not leached at the end of the HC1 titration, it is expected to represent a larger proportion in the speciation of elements than the residual fraction defined by Tessier et al. (1979), obtained by a HF/aqua regia dissolution.

The exchangeable fraction designated by Tessier et al. (1979) to release very mobile trace elements/freshly precipitated minerals, should have a chemical composition fairly close to the elements partially leached in the early stage of the titration (pH 8.5-7). Surprisingly, it shows insignificant amounts of Cd, Co and Mn which are among the most mobile elements and as much as 10% of Cu, whose leaching is offset by two units to a lower pH than Cd (Fig. 4c and d).

Most of the disagreement between the two methods is related to the evaluation of the composition of the carbonate phase. The acidimetric titration method provides very reliable information on the composition of the carbonate phase because the dissolution of calcite exerts a strong control on the buffering of pH (Section 4.1.1), which allowed the stepwise monitoring of its dissolution. Compared to the acidimetric titration, Tessier's protocol predicts systematically higher proportions in the carbonate phase for all elements, all of them being more or less significantly associated with carbonates. Tessier's protocol predicts that 50% Cu is present in the carbonate phase. However, the acidimetric titration of Cu starts when Ca is almost entirely leached due to the complete dissolution of calcite, as shown in Fig. 14b. In addition, Al, Cr and Fe which are present in the carbonate phase of Tessier's protocol in proportions of 1%, 6% and 10%, respectively, are not leached until nearly complete dissolution of calcite (Fig. 15a for Cr). Cadmium, whose leaching starts only when 40% of Ca is already dissolved (Fig. 14b), is likely to undergo a significant mobilization from a phase reacting with acetic acid designed to trigger the dissolution of carbonates. This overestimation of the carbonate fraction by the SES can be attributed to the non-selectivity of $H^+$ inherent in the use of acetic acid which acts to dissolve fully or partially carbonates, oxyhydroxides and possibly (acid volatile) sulfides and also to compete with trace metals for adsorption sites.

Since Tessier's protocol overestimates the proportions of elements in the carbonate phase, the proportion of the elements would be underestimated by the next steps of the sequential extraction. This effect may be seen for Mn, by comparing its relative proportions in the carbonate and oxyhydroxide phases inferred by both methods, as well as for Cu, which shows the strongest overestimation and exhibits a much smaller proportion than that expected in the oxyhydroxide phase. Cumulated proportions of Fe in the carbonates and in the Fe/Mn oxyhydroxide phases from the SES protocol yield twice as much Fe as the HCl-reactive fraction. This suggests either that the acidimetric titration of Fe was not complete at pH 1.4, or that the specific reagent used in the SES dissolves a Fe mineral other than FeOOH, which could contain additional amounts of Co, Cr and Mn. However, while the acidimetric titrations of Co, Cr and Fe are consistent with the occurrence of a residual mineral, the titration of Mn is generally very close to completion (for other samples studied). This implies that, if the SES speciation method targets an additional Fe mineral, this mineral contains insignificant amounts of Mn.

Specific dissolution of sulfides/organic matter by the SES mobilizes small proportions (in increasing order) of Mn, Cd, Al, Co, Fe, Cu and Cr. In contrast to Cu, Cd, Co and Fe, elements such as Al and Cr are not prone to form sulfides. Cadmium titration is tentatively attributed to the dissolution of sulfides (Section 4.2.3) but these sulfides are predicted to account for ~2% of Cd by the SES. Such a small proportion is, again, likely attributed to the lack of selectivity of the carbonate phase reagent. Other sulfides, if they truly occur in the sediments, are likely associated with the residual fraction of the acidimetric titration. Iron in the sulfides/organic matter phase of the SES may be attributed to pyrite because amorphous Fe sulfides, if present, are likely to dissolve during the acidimetric titration.

***Table 4****: Interpolation of data from the acidimetric titration experiment. Such a table can be used to assess the risk of trace metal remobilisation due to pH change in the surrounding environment.*

| pH | **% Cd leached** | **% Zn leached** | **% Co leached** | **% Cu leached** | **% Cr leached** | **% Pb leached** |
|---|---|---|---|---|---|---|
| 8.50 | 0.4 | 0.0 | 0.1 | 1.6 | 0.1 | 0.0 |
| 7.00 | 12 | 10 | 10 | 2.5 | 0.1 | 0.0 |
| 6.00 | 33 | 33 | 21 | 3.3 | 0.3 | 0.0 |
| 5.00 | 51 | 46 | 25 | 11 | 1.0 | 0.7 |
| 4.00 | 66 | 56 | 31 | 19 | 1.6 | 2.7 |
| 3.00 | 81 | 72 | 37 | 29 | 2.0 | 5.7 |
| 2.00 | 89 | 82 | 48 | 54 | 8.0 | 28 |
| 1.50 | 89 | 86 | 56 | 68 | 20 | 67 |

***Table 5****: Comparison between Tessier (SES) and acidimetric titration (AT) methods applied to the Doel surface sediment.*

| | **Cd** | | **Cu** | | **Cr** | | **Co** | | **Mn** | | **Fe** | | **Al** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **SES** | **AT** | **SES** | **AT** | **SES** | **AT** | **SES** | **AT** | **SES** | **AT** | **SES** | **AT** | **SES** | **AT** |
| Exchangeable | 0 | - | 9 | - | 0 | - | 0 | - | 0 | - | 0 | - | 0 | - |
| Carbonates | 88 | 0 | 47 | 0 | 6 | 0 | 41 | 23 | 80 | 43 | 10 | 0 | 1 | 0 |
| Oxyhydroxides | 0 | 0 | 27 | 68 | 47 | 20 | 35 | 33 | 15 | 37 | 49 | 31 | 10 | 5 |
| Sulfides/organic matter | 2 | 88 | 13 | 0 | 17 | 0 | 6 | 0 | 1 | 0 | 9 | 0 | 3 | 0 |
| Residual | 10 | 12 | 4 | 32 | 30 | 80 | 17 | 44 | 4 | 20 | 32 | 69 | 86 | 95 |

## 5. Conclusions

The acidimetric titration is a simple and efficient method for the study of speciation, mobility and reactivity of trace elements. Its successful application to sediments from the Scheldt estuary demonstrates the elemental speciation within the carbonate phase (for Ca, Mg, Mn, Co), the Fe/Mn-oxyhydroxides as a FeOOH polymorph (Fe, Mn, P, Co, Pb, Cr,) and gibbsite (Al and Cu). These phases have the strongest control on the buffering of pH: consumption of proton by their dissolution is verified by acid-base reactions stoichi-ometry. Other trace elements, whose titrations resemble none of the above elements, are attributed to less abundant minerals such as sulfides (Cd and Zn). Some trace elements appear to be associated to a single HCl-reactive phase such as Cr, Pb, Cu, and P or Cd and Zn, which is apparently not the case for Mn and Co, partitioned between carbonates and Fe-oxyhydroxides.

This simple approach of speciation, performed by comparing shapes of pH titration curves, pH values at which leaching initiates and basic stoichiometric calculations, is fairly straightforward. The results obtained in this study agree with what is commonly found in the literature related to the speciation of trace metals in soils and sediments. Data acquired by the acidimetric titration method may be more easily implemented in sophisticated models for speciation because it uses a simple and unique reagent. This approach may be relevant for assessing in more detail the speciation of elements which have little control on the buffering of pH.

The acidimetric titration is potentially useful to estimate the reactivity and the mobility of trace metals under changing conditions of pH. The data obtained are consistent with respect to the relative mobility of trace elements. The order of mobility for trace elements agrees roughly with a general trend of affinity for different kinds of synthetic and pure sorbants. In contrast, the composition of the so-called exchangeable fraction of SES (Tessier et al., 1979) is poorly consistent with this general trend of affinity: it does not contain very mobile elements such as Cd and Co but contains instead significant amounts of rather poorly mobile elements such as Cu. In addition, the SES predicts that Cu and Cd are importantly scavenged onto the carbonate phase despite their different mobility and speciation inferred from acidimetric titration.

The acidimetric titration method has the potential to circumvent several limitations of selective extraction schemes (e.g. complexity of reagents, problems of selectivity, phases that are operationally defined and reagent/sample ratio, etc.). This new technique yields low blanks and is faster and easier to perform than SESs. The authors believe that it can be applied to any kind of material, with little or no changes in the protocol. Further development should focus on a more comprehensive assessment of fractions associated with sulfides and organic matter. The acidimetric titration method has the merit of being considered as an alternative to the BCR/SM&T protocol for trace metal speciation widely used in environmental and regulation studies dealing with soils and sediments.

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