The influence of salinity on the solubility of Zn and Cd sulphides in the Scheldt estuary

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Abstract

In the estuary of the river Scheldt, where an oxygen gradient exists in addition to the salinity gradient, redox processes will be of major importance for trace metal mobilisation. In this study, the influence of salinity and pH on the redox processes of dissolved Zn and Cd sulphides is investigated together with the effects on the ratio of the dissolved Zn and Cd concentrations. The speciation of these metals is calculated with the chemical equilibrium programme MINEQL + . Zn sulphides are oxidised at lower oxygen concentrations than Cd sulphides, due to lower stability constants, causing a sudden increase or peak in the dissolved Zn/Cd ratio. The formation of dissolved Cd chloride complexes when oxidation occurs at high salinities ($S = 15$) increases the mobility of Cd, causing a decrease in the Zn/Cd peak of the total dissolved concentrations. The peak is three to four times smaller at $S = 15$ than when oxidation occurs at $S = 2$. The simple model calculations compare very well with field data. The Scheldt estuary is suitable to illustrate these calculations. In the 1970s, the anoxic part of the estuary reached $S = $ 15–20, but since the early 1980s it has dropped to $S = 2$–10. Historic data on metals in the estuary from 1978, 1987 and the 1990s were used to compare with the equilibrium calculations. The increase of the dissolved Zn/Cd peak at low salinity as a consequence, of the decreasing anoxic region is confirmed well by the data. The good agreement between model calculations and field data is a proof of the extreme importance of redox processes for the solubility of Zn and Cd sulphides in the estuary. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The combination of Zn and Cd is a very interesting one since the ratio between the concentrations of these elements changes considerably between different geochemical phases. Elemental ratios of Zn/Cd of 600–900 are reported for igneous rocks and sediments. Ratios varying between 25 and 200 are found in coastal waters, ratios as low as 5–10 have been found in oceanic waters, and again ratios of 600–900 occur in deep-sea sediment (Chester, 1990; Nolting et al., 1999a). Apparently, major fractionations of Zn versus Cd occur in the geochemical pathway from weathering of continental rocks and soils, to streams and rivers, via estuaries into coastal seas and open oceans, and final burial in deep-sea sediments. As estuaries are the transition between fresh waters and seawater, an investigation of conceivable fractionations of Zn and Cd in estuaries is warranted. The Zn/Cd ratio of the dissolved concentrations in the Scheldt estuary changed considerably in the past,

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from 300 at $S = 20$ in 1978 to >3000 at $S = 2$–5 in the1990s.

Estuaries are complex systems. Bio-geo-chemical and physical processes all occur simultaneously, especially in the upper part of the estuary with low salinity. Mixing of river and seawater results in flocculation in the zone — therefore called high turbidity zone — where a large part of the dissolved metals supplied by the river is precipitated. Anoxia may occur through a combination of high organic matter content and a long residence time. This may be restricted to the sediment (Westerlund et al., 1986; Kerner and Wallmann, 1992; Zwolsman, 1999) but can also occur in the water column (Zwolsman et al., 1997; Shiller and Mao, 1999). Such anoxic conditions may induce the precipitation of sulphides of Zn and Cd. Due to oxidation in the more saline parts of the estuary, Zn and Cd are released into the water column, giving rise to a so-called mid-estuarine maximum of their dissolved concentrations (Sholkovitz, 1976; Duinker and Nolting, 1978; Duinker et al., 1983; Wollast, 1988; Regnier and Wollast, 1993; Chiffoleau et al., 1994; Paucot and Wollast, 1997).

The chemistry of Cd in estuaries and seawater has been studied carefully (Comans and van Dijk, 1988; Muller, 1996). With increasing salinity, Cd is released by the combination of the formation of dissolved chloride complexes and by competition with Ca for adsorption sites on suspended particles (Paalman et al., 1994). Organic complexation in the dissolved phase occurs, but to a lesser extent than for metals like Zn and Cu (Kozelka and Bruland, 1998; Baeyens et al., 1998c). For Zn, conclusions from the literature are less unambiguous, but flocculation, precipitation as sulphides and adsorption on particles are processes of its chemistry in the upper low-salinity estuary. Often, but not always, a release of Zn into the water phase is observed upon oxidation (Duinker et al., 1983; Zwolsman et al., 1997; Paucot and Wollast, 1997). Then, also Zn concentrations demonstrate a mid-estuarine maximum (Duinker et al., 1983) and its chemistry, as for Cd, can be explained by complexation with inorganic anions from seawater (Kraepiel et al., 1997). However, organic complexation of Zn plays an important role in Zn release in estuaries (Van den Berg et al., 1987). Sometimes no estuarine maximum for Zn is observed at all (Zwolsman et al., 1997; Baeyens et al., 1998a,b).

In this paper the influence of salinity on the oxidative dissolution of Zn and Cd is studied together with its influence on the dissolved Zn/Cd ratio. We restricted ourselves to the influence of the oxygen concentration, salinity and pH on the dissolution of Zn and Cd sulphides. Processes in the sediment were not considered. The sediment was assumed to be a solid phase, part of which may become dissolved. Equilibrium conditions in the water phase were assumed to exist in a kinetically controlled system (Emerson et. al., 1983; Landing and Lewis, 1991). The chemical equilibrium model MINEQL + (Secher and McAvoy, 1992) was used to calculate the equilibrium composition of the dissolved phase at $S = 2$ with pH = 7 and 8, and at $S = 15$ with pH = 7 and 8. The calculations were compared with data from the Scheldt estuary, for which a large and excellent data set is available. Interestingly, the conditions of this estuary have changed considerably during the past decades. Since the early 1980s, the extension of the anoxic zone has been decreasing due to improving water quality of the river Scheldt (Van Damme et al., 1995; Van Eck et al., 1998; Zwolsman, 1999). In the1970s, the anoxic zone reached to where $S = 15$–20, whereas since the mid-1980s oxidation normally occurs at $S = 2$–10. Only under extreme conditions (high temperatures and low river discharge) does anoxia reach further downstream towards higher salinities (Zwolsman et al., 1997). In the anoxic region the pH ranges between 7 and 8, or even higher, mainly due to nitrification (Frankignoulle et al., 1996; Zwolsman et al., 1997).

2. Materials and methods

The chemical equilibrium model MINEQL + , version 4 (Secher and McAvoy, 1992) was used for the calculations on the redox chemistry of the metals Zn and Cd as a function of salinity, pH and sulphide and oxygen concentrations. MINEQL + consists of a thermodynamic data base of formation constants of dissolved and solid constituents. Concentrations are entered, the program calculates via the transformation of concentration into activity whether solubility products are exceeded and solids formed, and it calculates the division of the elements over the dissolved complexes according to the strength of
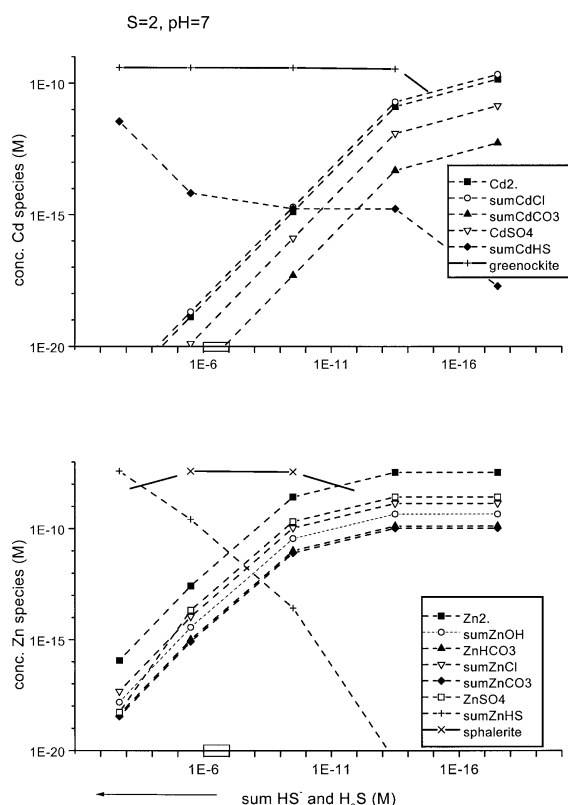
Fig. 1. The speciation of Cd, Zn at $S = 2$, pH = 7 as a function of the concentration of the sum of HS^- and H_2S ($\sum HS$). The calculation was performed with MINEQL +, version 4. The concentrations of the different chloride, carbonate, bicarbonate, hydroxide (including for Zn ZnOHCl) and the dissolved sulphide complexes were summed. The square at the x-axis denotes the sulphide concentrations as measured by Zwolsman et al. (1997) and Paucot and Wollast (October 1995, unpublished results).

formation constant and concentration of the ligand with which the complex is formed. This is all done assuming chemical equilibrium, i.e. without considering kinetics.

For verification purposes, data sets were used from October and November 1978 (Duinker et al., 1983; Nolting et al., 1999b), 1987 (Zwolsman and Van Eck, 1993; Zwolsman et al., 1997) and 1991–1995 (Paucot, 1997; Paucot and Wollast, 1997).

For the calculations two extreme salinities $S = 2$ and 15 were chosen at which oxygen is re-introduced into the Scheldt estuary. These situations are representative of the 1970s and mid-1980s until the

present, respectively. For pH, values of 7 and 8 were chosen to represent the influence of the pH on the chemistry of Zn and Cd. The water constituents were calculated as a dilution of standard seawater with standard river water for the two chosen salinities. The composition of this estuarine water, especially the sulphate compounds, were compared with data sets from the Scheldt estuary from Rijkswaterstaat (Van Eck), NIOZ (Nolting) and 'de Vlaamse Milieumaatschappij' (De Meyere, Belgium) and, where necessary, adapted to mean measured values.

The program MINEQL + allows the user to handle three methods to calculate redox problems by manipulating (i) oxygen concentration, (ii) redox potential or (iii) the ratio of the concentrations of a specific redox couple. The oxygen concentration was chosen in order to determine the redox conditions and only the sulphide/sulphate couple was incorporated in the calculations. Other redox processes such as for instance Fe(II)/Fe(III) were not considered. The CO_2 concentration was assumed to be in equilibrium with the atmosphere.

The ionic strength differed between the two salinities 2 and 15 ($S = 2$, pH = 7, $I = 0.0436$; $S = 2$, pH = 8, $I = 0.0415$; $S = 15$, pH = 7, $I = 0.285$; and $S = 15$, pH = 8, $I = 0.256$). We chose to ignore organic complexation of both metals and concentrated on the influence of redox processes, but we come back to this in the Discussion (Section 3).

The choice of stability constants (K) is crucial, especially those of the dissolved metal (poly-)-sulphides. For the sake of consistency the K values used in MINEQL + were chosen. The historic field data used here did not give any proof of considerable mobilisation by poly-sulphide complexation by either Zn or Cd.

In order to identify the respective changes between Zn and Cd, dissolved Zn/Cd ratios were calculated. To obtain a realistic Zn/Cd ratio outside the area of reducing conditions we chose a total dissolved Zn concentration of 40 nM and a total dissolved Cd concentration of 0.4 nM as input for the calculations. Between 1978 and 1995 values for the Zn/Cd ratio between 50 and 200 were found by Duinker et al. (1983), Zwolsman et al. (1997) and Paucot and Wollast (1997), respectively.
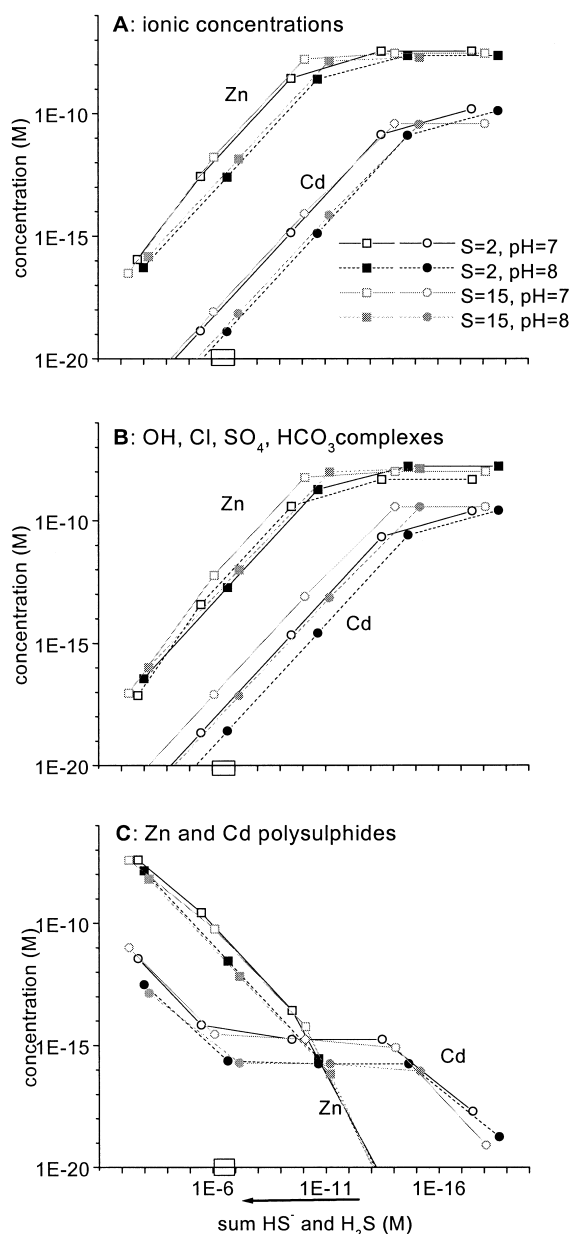
Fig. 2. Dissolution/oxidation of Zn and Cd sulphides as a function of the concentration of the sum of HS^- and H_2S at two salinities and two pH values, according to MINEQL + . (A) the ionic concentrations; (B) the concentrations of sum of the inorganic complexes at oxic conditions; (C) the concentrations of the poly-sulphide complexes. See Fig. 1 for Zn and Cd sulphide precipitates. Squares are used for Zn, circles for Cd. The square at the *x*-axis denotes the sulphide concentrations as measured by Zwolsman et al. (1997) and Paucot and Wollast (October 1995, unpublished results).

3. Results and discussion

3.1. MINEQL + *calculations*

The speciation of Zn and Cd as a function of the sulphide concentration at $S = 2$ and pH = 7 is given as example of the calculations with MINEQL + (Fig. 1). Figs. 2 and 3 are compilations of the calculations shown in Fig. 1 for all the four conditions (two salinities, two pH values). Sulphide concentrations in the anoxic part of the Scheldt estuary were measured by Zwolsman et al. (1997) and Paucot and Wollast (October 1995, unpublished results) and varied between 0.1 and 2 μM. According to the calculations the solid phases, Sphalerite and Greenockite, would be the predominant species (Fig. 1).

Cd is dissolved at lower sulphide (higher oxygen) concentrations than Zn due to the higher stability constants of Greenockite (CdS) (Dyrssen, 1988) (Figs. 1 and 2A–C). The inorganically complexed Cd has a higher concentration than the free ionic Cd even at $S = 2$, in contrast to the Zn species (Fig. 1). The influence of salinity is obvious by the large shift in inorganically complexed Cd, mainly chlorides, at both salinities, causing dissolution at lower oxygen concentrations at higher salinity. The inorganic side reaction coefficient, α_{inorg}, is the fraction of metal bound to inorganic ligands (L), like chlorides or hydroxides, and can be expressed as

$$\alpha_{inorg} = \sum K'_i [L]_i \tag{1}$$

where K'_i is the conditional stability constant and $[L]_i$ the concentration of an inorganic ligand i, not bound to the metal. At oxic conditions α_{inorg} of Cd changes from 1.8 to 9.3 between $S = 2$ and 15. Poly-sulphide complexes are formed at high sulphide concentrations (Fig. 2C). Under anoxic conditions the inorganic side reaction coefficient increases, due to poly-sulphide formation, by a factor of 24 from the minimal value of 602 at total sulphide concentration = 0.1 μM, $S = 15$, pH = 7, to a the maximum of 14326 at total sulphide concentration = 2 μM, $S = 2$, pH = 8. The coefficient α of the poly-sulphide complexes is much higher than that of the inorganic complexes at oxic conditions, whereas their concentrations are lower. This is because the concentrations of the Cd complexes also depend on the ionic Cd concentration. Due to the high solubility product of Greenockite, the
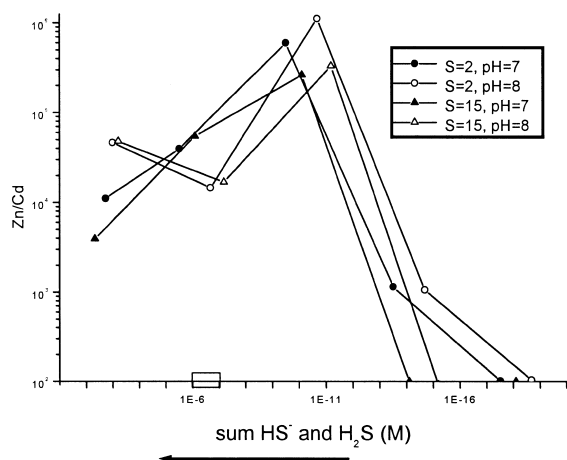
Fig. 3. The ratio of dissolved Zn/Cd according to the calculations with MINEQL + as a function of the concentration of the sum of HS$^-$ and H$_2$S. Total Cd and Zn concentrations are 0.4 and 40 nM. The square at the *x*-axis denotes the sulphide concentrations as measured by Zwolsman et al. (1997) and Paucot and Wollast (October 1995, unpublished results).

free Cd concentration in equilibrium with CdS is very low compared to oxic conditions, and therefore the Cd–poly-sulphide concentration is low compared to the inorganic complexes at oxic conditions too. The speciation of Cd is also influenced by pH. A pH change from 7 to 8 causes a similar shift of the concentrations of both free ionic and inorganically complexed species as the change in salinity from 2 to 15 (Fig. 2A and B). At oxic conditions the solubility product of CdCO$_3$ is exceeded, but only at low salinity ($S = 2$) and high pH (pH = 8).

The predominant form of Zn is free ionic (Figs. 1 and 2A, B). At oxic conditions the influence of salinity cannot be seen; indeed α_{inorg} remains constant (0.62) according to the calculations. The distribution over the species, inorganically complexed and free ionic, is influenced by pH, especially at $S = 2$. Logically, the carbonates and hydroxides become more important at pH = 8 with respect to the sulphate complex. The influence of pH on Zn dissolution is less obvious than on its speciation (Fig. 2A and B). At anoxic conditions the inorganic side reaction co-efficient, due to poly-sulphide formation, increases by a factor of 100 from the minimal value of 2 at total sulphide concentration = 0.1 μM, $S = 15$, pH = 7, to a the maximum of 203 at total sulphide

concentration = 2 μM, $S = 2$, pH = 8. The increase is four times larger than for Cd and the resulting larger increase of Zn poly-sulphides is shown in Fig. 2C. Due to the lower solubility product of Sphalerite compared to Greenockite, a factor of 10^4, the ionic Zn concentration in equilibrium with Sphalerite is larger. At sulphide concentrations of 1 μM the concentration of Zn poly-sulphides comes close to the nanomolar level. The Zn and Cd concentrations used for the calculation of the Zn/Cd ratio include all their dissolved species (Fig. 3), ignoring at $S = 2$, pH = 8 the possible formation of CdCO$_3$(s). The peak in the dissolved Zn/Cd ratio is formed when both metals are precipitated due to the higher solubility product of ZnS(s) than of CdS(s). Due to the formation of Zn poly-sulphide complexes dissolution of ZnS(s) results in an increase of the Zn/Cd ratio at high sulphide concentrations (Fig. 3). The vertical log scale of Fig. 3 magnifies this feature.

The dissolved Zn/Cd ratio of the peak is three to four times higher at $S = 2$ than at $S = 15$. This is caused by the increasing formation of dissolved Cd chloride complexes at higher salinity. Salinity also plays an indirect role here, since at higher salinities more sulphate is present as a source for sulphides. Due to our choice of stability constants of the dissolved metal (poly-)sulphides, hardly any mobilisation of Cd is observed under anoxic conditions by the formation of dissolved sulphide complexes. Emerson et al. (1983) used log K^I ($I = 1$) values for dissolved Cd sulphide complexes (log K^ICd(HS)$_2 = 14.6$) which are lower than those in MINEQL + (log $K^I = 15.7$). They, therefore, calculated the mobilisation of Cd by formation of these dissolved sulphide complexes when high sulphide concentrations were reached. Such high sulphide concentrations were not measured in the Scheldt estuary (Zwolsman et al., 1997; Paucot and Wollast (unpublished results)). Landing and Lewis (1991) calculated Black Sea data with MINEQL + and used higher log K^I values than ours for the mentioned sulphide complexes and they found precipitation of Cd and Zn sulphides, which were not released in solution at higher sulphide concentrations.

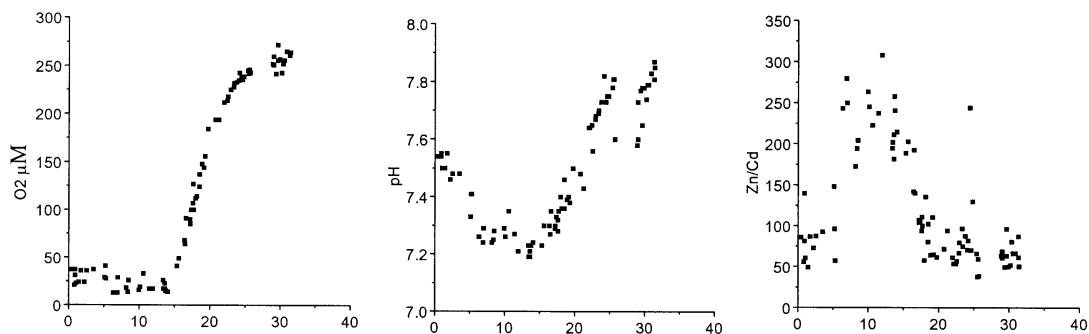### 3.2. Comparison with field data from the Scheldt estuary
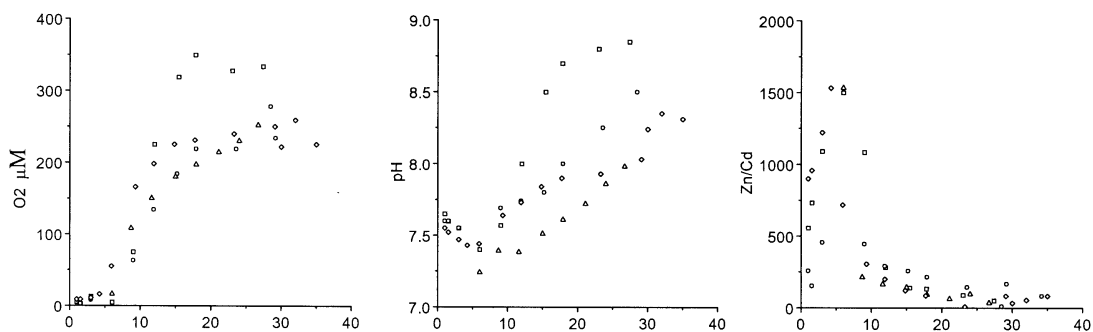
In the Scheldt estuary, as well as in other estuaries

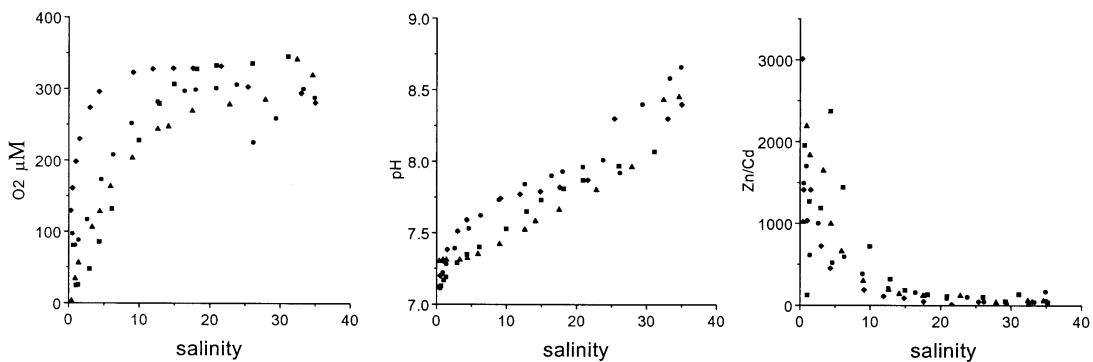# oxygen   pH   Zn/Cd

Duinker Oct-Nov 1978

Zwolsman summer 1987

Zwolsman winter 1987

and basins with anoxia, the pH varies between 7 and 8 in the zone where the system turns from anoxic to oxic (Figs. 4 and 5) (Kremling, 1983; Landing and Lewis, 1991; Frankignoulle et al., 1996). Sulphide concentrations in the anoxic part of the Scheldt estuary measured by Zwolsman et al. (1997) and Paucot and Wollast (October 1995, unpublished results) varied between 0.1 and 2 μM. According to the MINEQL + calculations, Cd and Zn are precipitated as sulphides and mobilisation of poly-sulphides starts to occur for Zn at these sulphide concentrations (Figs. 1 and 2C).

The assumption in our calculations that CO_2 is in equilibrium with the atmosphere is not true at low salinity ($S = 0–5$). Frankignoulle et al. (1996) found a large oversaturation of CO_2 with respect to the atmosphere due to the combination of a long residence time of the water in this part of the estuary and an intense bacterial respiration resulting in high pH and total alkalinity concentrations. This combination of a relatively high pH (7.6–7.4) and high alkalinity (5.5–4 mM) favours the precipitation of $CdCO_3(s)$. According to MINEQL + calculations at oxic conditions and $S = 2$, Cd is precipitated as a carbonate (Otavite) for 85% at pH = 7.6 and alkalinity 6 mM but only for 16% at pH = 7.4 and total alkalinity is 4 mM. However, these conditions of relatively high pH and high alkalinity prevail when the oxygen concentration is low, which is close to the region where precipitation of Greenockite (CdS) occurs. According to MINEQL + , CdS(s) precipitates in favour of $CdCO_3(s)$ as soon as the sulphide concentration is high enough. At higher salinities, however, these conditions do not result in carbonate precipitation, but instead dissolved Cd chloride complexes are formed. The influence of carbonate precipitation on the Cd chemistry is relatively small since precipitation can only occur in a small zone of low salinity, and relatively high oxygen concentration. This is illustrated, as shown above, by the fact that
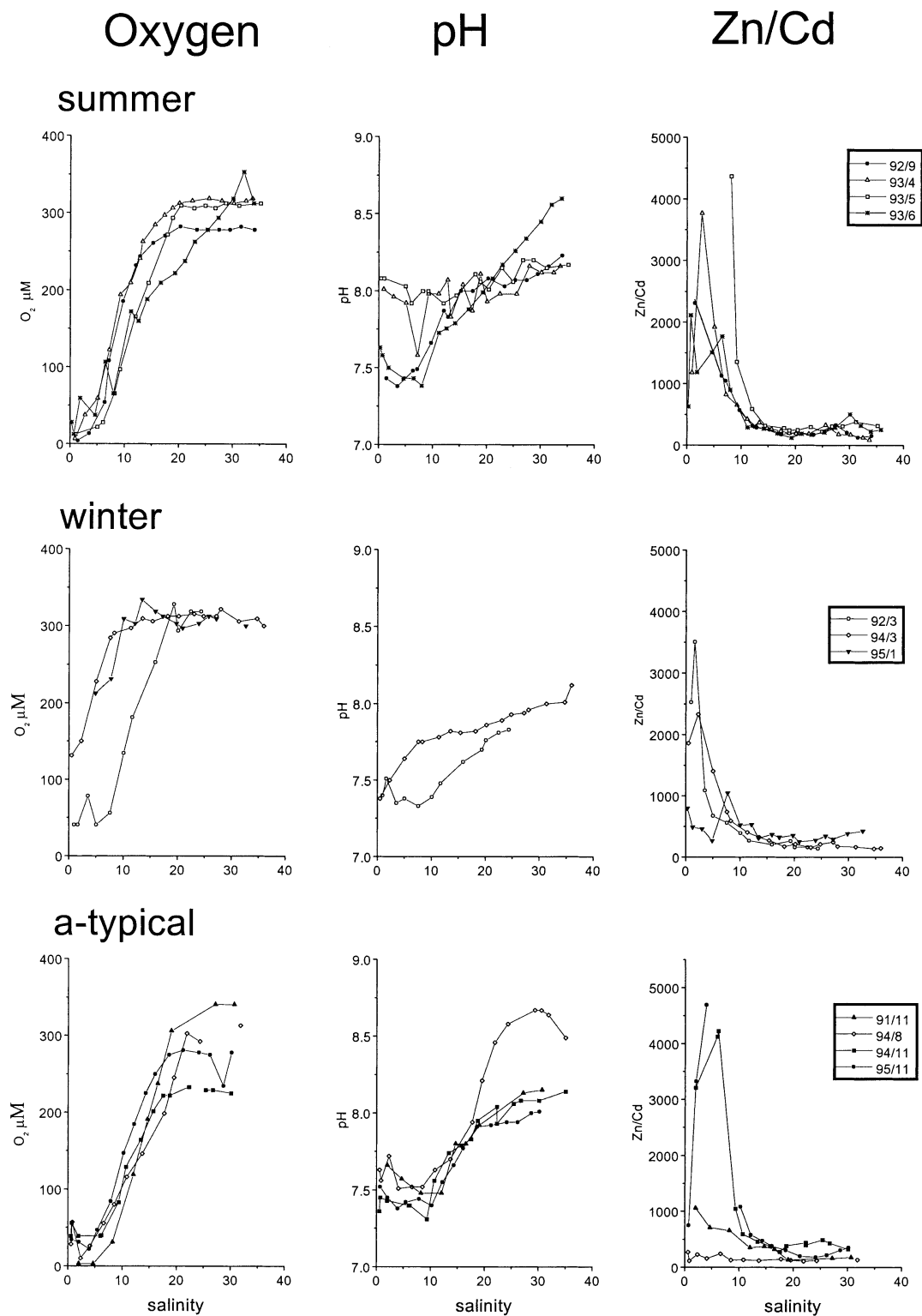
small differences in the observed concentrations (pH = 7.6, total alkalinity = 6 mM versus pH = 7.4 total alkalinity = 4 mM) have large effects on the percentages of Cd, 85–16% of the total dissolved concentration, which is precipitated.

In 1978, in the Scheldt estuary anoxia extended as far as $S = 15$. Between 1978 and 1987 the anoxic zone receded upstream to $S < 5$ (Duinker et al., 1983; Zwolsman and Van Eck, 1993; Zwolsman et al., 1997; Nolting et al., 1999b) (Fig. 4). Moreover, the oxygen penetration into the riverine section of the estuary depends on the season, as described in detail by Zwolsman et al. (1997). In spring/summer, high microbial activity is responsible for increased oxygen consumption, and the extension of the anoxic zone reaches $S = 2–5$, as compared to $S = 0–2$ in winter/autumn (Fig. 4). The 1991–1995 data of Paucot and Wollast (1997) and Paucot (1997) (Fig. 5) show the same extension of anoxia as in 1987. Similar observations were reported by Van Damme et al. (1995) and Van Eck et al. (1998).

The dissolved Zn/Cd ratio shows a peak when the sulphide concentration is between the values poising the solubility products of solid Zn and Cd sulphides. Going from anoxic to oxic conditions, Zn sulphides dissolve first and the dissolved Zn/Cd ratio increases. At higher oxygen concentrations (i.e. lower sulphide concentrations), Cd sulphide(s) also dissolve and the dissolved Zn/Cd ratio decreases again. This is confirmed by observations in the anoxic basins of the Baltic where the vertical Cd and Zn profiles indicate mobilisation of Zn at lower oxygen concentrations than Cd, which results in a peak in the dissolved Zn/Cd ratio at depth in the water column (Kremling, 1983).

In the Scheldt estuary the change of the position of the peak in the dissolved Zn/Cd ratio reflects the shift of the anoxic–oxic boundary in the estuary between 1978 and 1987. The oxygen concentration increased as the organic loading of the river decreased due to

Fig. 4. Field data from 1978 (Duinker et al., 1983; Nolting et al., 1999b) and 1987 (Zwolsman and Van Eck, 1993; Zwolsman et al., 1997). Note the different scales between the studies. Different fieldtrips of Zwolsman are denoted by different symbols. Closed symbols indicate conditions without an anoxic zone, mostly in winter (87/2, 87/4, 87/12, 88/2), open symbols denote an anoxic zone, in spring, summer and early autumn (87/5, 87/7 87/8, 87/10). The lower range of values (20–40 μM) of dissolved O_2 are considered upper estimates due to conceivable contamination with atmospheric O_2 during sampling and analysis (Codispoti et al., 1991) as the special low level method (Broenkow and Cline, 1969) was not used in the above studies. Moreover for anoxic waters this contamination may lead to rapid oxidative loss of sulphide (Millero, 1991) such that measured values of $[H_2S]$ are less than the original in situ concentrations.

Oxygen

pH

Zn/Cd

summer

winter

a-typical

improved wastewater treatment (Van Damme et al., 1995; Van Eck et al., 1998). The position of the peak in the ratio of dissolved Zn/Cd shifted from $S = 13$–15 in 1978 to $S = 5$ in the summer and $S = 2$ in the winter of 1987. The height of the peak was 250–300 in 1978 and 600–1600 (summer) and 2000 (winter) in 1987. Thus, over one decade the dissolved Zn/Cd ratio changed by a factor 6–8. Yet, in the oxic part of the estuary the ratio decreased to values between 50 and 70 in both 1978 and 1987. About half of the difference in peak heights between 1978 and 1987 is explained by the different salinities (Fig. 3). Precipitation of $CdCO_3(s)$, as previously described, could be a further explanation. $CdCO_3(s)$ precipitation can occur under oxic conditions and will increase the Zn/Cd ratio. Another explanation may be kinetics. In case of relatively fast dissolution kinetics of Zn compared to Cd at low salinities, the dissolved Zn/Cd would increase. Such a difference in dissolution kinetics was found by Kerner and Wallmann (1992) in experiments with Elbe sediments. Their experiments were performed with water of low salinity and their explanation was that Cd was re-adsorbed on sediment particles. Relatively quick kinetics of Zn dissolution in the freshwater part of the river at the present minimal extension of the anoxic zone may well explain the rarely observed Zn maximum in the Scheldt estuary (Zwolsman et al., 1997; Baeyens et al., 1998a,b).

Oxidation at high salinities leads to relatively quicker dissolution kinetics of Cd because its dissolution is stimulated by chloride-complex formation and adsorption sites are already filled with Ca, thus preventing re-adsorption. This is the reason why, even when no Zn maximum is found in the estuary, the dissolved Zn/Cd ratio may still exhibit a peak (Fig. 4 data of 1987).

The 'a-typical' data sets (Fig. 5) have in common that there is no anoxia but only low oxygen concentrations restricted to a narrow zone at very low salinity. When, even in summer, anoxia does not occur in the estuary, the anoxic region moves up to the Rupel river (Van Damme et al., 1995). Then of course dissolution of Cd and Zn in the estuary cannot be explained by oxidation chemistry alone.

Ignoring organic complexation in the MINEQL + calculations was allowed only because at the chosen total dissolved concentrations solubility products were not exceeded at oxic conditions, with the exception of $CdCO_3$ at high pH and low salinity. Especially for Zn, organic complexation may be very important and the dissolved Zn concentration is normally determined by the ligand concentration (Van den Berg et al., 1987). In reality, the inorganic species do not have such high concentrations as calculated (Fig. 1). The organic ligands compete with the inorganic ligands for the distribution of the metals (Me) according to Eq. (2)

$$[Me] = \text{organic dissolved metal}$$

$$+ \text{ inorganic dissolved metal}$$

$$= [Me^{2+}] + \alpha_0[Me^{2+}] + \alpha_{inorg}[Me^{2+}]$$

$$= [Me^{2+}](1 + \alpha_0 + \alpha_{inorg}) \quad (2)$$

α_0 is defined, like the inorganic side reaction coefficient α_{inorg} in Eq. (1), as the product of the conditional binding constant (K'_L) and free ligand concentration ($[L^{x-}]$).

Baeyens et al. (1998c) used Kd values (concentration in the particulate phase divided by the concentration in the dissolved phase) and concentrations of dissolved labile metals in a model to calculate the conditional stability constants of metal–organic complexes. They found almost similar K' values for Zn and Cd, ranging from 10^7 to $10^{9.1}$ for Zn, in agreement with the results of Van den Berg et al. (1987), and from $10^{6.9}$ to $10^{8.9}$ for Cd. Since the ligand concentrations are always close to the metal concentrations, at least the same order of magnitude (Van den Berg et al., 1987; Bruland, 1989, 1992; Kozelka and Bruland, 1998), we assume equal dissolved ligand concentrations as dissolved Zn and Cd, 40 and 0.4

Fig. 5. Field data from the period between 1991 and 1995 (Paucot, 1997; Paucot and Wollast, 1997). Closed symbols are winter samples, open symbols represent summer samples: (summer) a sequence from autumn (92/9) into spring (93/4, 93/5) and summer without an anoxic zone (93/6); (winter) typical winter conditions with no anoxia (92/3, 94/3, 95/1); ('a-typical') 'a-typical' samples (91/11, 94/8, 94/11, 95/11). See caption of Fig. 4 for caution regarding low O_2 values.

nequiv. of metal, respectively. Using the maximum K^I values of Baeyens et al. (1998c) we obtain a maximum α_0 of 50.4 for Zn and 0.8 for Cd. The values for α_{inorg} are 0.62 for Zn and 1.8 ($S = 2$) and 9.3 ($S = 15$) for Cd. Thus, according to Eq. (2) 3% of the dissolved Zn (including the ionic fraction), and 50 and 93% of the dissolved Cd is inorganic at $S = 2$ and 15, respectively. The distribution over the dissolved species of Zn is heavily influenced by organic ligands; for Cd this influence is minor at higher salinities and of moderate importance at low salinity in agreement with the conclusions of Van den Berg et al. (1987) and Baeyens et al. (1998c), and others. Van den Berg et al. (1987), one of the first to point out the importance of organic complexation for metals in solution, concentrated their investigation on the middle and lower estuary, while they had only two data points at $9 < S < 15$. Their low salinity data suggest a Zn/ligand ratio >1. The model of Baeyens et al. (1998c) produces at low salinities, $S < 12.5$, ligand concentrations (the sum of two ligand groups) which for Zn are lower than the dissolved Zn concentrations. For Cd, the sum of the concentrations of the two ligand groups remains larger than the metal concentrations, even at $S = 1$ and 3.5. Paucot and Wollast (1997) concluded from changing Kd values an important mobilisation of Zn and Cd with increasing salinities due to formation of chloride complexes for Cd, desorption of exchangeable metals due to increasing concentration of major ions and formation of dissolved organic complexes. However, with these processes, the mobilisation could not be explained and an additional phenomenon was needed to explain the Kd values at constant ionic strength and varying oxygen concentrations. Our calculations suggest that in the upper estuary of the Scheldt river, redox processes determine the mobility of Zn and Cd, rather than organic complexation.

Our initial working hypothesis of major fractionation of Zn and Cd within an estuary was confirmed for the river Scheldt. However, in the context of the global Zn/Cd fractionation this mid-estuarine dissolved Zn/Cd maximum appears to be only a transient feature.

References

Baeyens, W., Elskens, M., Gillain, G., Goeyens, L., 1998a. Biogeochemical behaviour of Cd, Cu, Pb and Zn in the Scheldt estuary during the period 1981–1983. Hydrobiologia 366, 15–44.

Baeyens, W., Parmentier, K., Goeyens, L., Ducastel, G., De Gieter, M., Leermakers, M., 1998b. The biogeochemical behaviour of Cd, Cu, Pb and Zn in the Scheldt estuary: results of the 1995 surveys. Hydrobiologia 366, 45–62.

Baeyens, W., Goeyens, L., Monteny, F., Elskens, M., 1998c. Effect of organic complexation on the behaviour of dissolved Cd, Cu and Zn in the Scheldt estuary. Hydrobiologia 366, 81–90.

Broenkow, W.W., Cline, J.D., 1969. Colorimetric determination of dissolved oxygen at low concentrations. Limnol. Oceanogr. 14, 450–454.

Bruland, K.W., 1989. Complexation of zinc by natural organic ligands in the central North Pacific. Limnol. Oceanogr. 34, 269–285.

Bruland, K.W., 1992. Complexation of cadmium by natural organic ligands in the central North Pacific. Limnol. Oceanogr. 37, 1008–1017.

Chester, R., 1990. The transport of material to the oceans: the river pathway. In: Chester, R. (Ed.). Marine Geochemistry. Unwin Hymand Ltd, London, pp. 14–82.

Chiffoleau, J.-F., Cossa, D., Auger, D., Truquet, I., 1994. Trace metal distribution, partition and fluxes in the Seine estuary (France) in low discharge regime. Mar. Chem. 47, 145–158.

Codispoti, L.A., Friederich, G.E., Murray, J.W., Sakamoto, C.M., 1991. Chemical variability in the Black Sea: implications of continuous vertical profiles that penetrated the oxic/anoxic interface. Deep-Sea Res. 38 (S2), 691–710.

Comans, R.N.J., Van Dijk, C.P.J., 1988. Role of complexation processes in cadmium mobilization during estuarine mixing. Nature 336, 151–154.

Duinker, J.C., Nolting, R.F., 1978. Mixing, removal and mobilisation of trace metals in the Rhine estuary. Neth. J. Sea Res. 12, 205–223.

Duinker, J.C., Nolting, R.F., Michel, D., 1983. Effects of salinity, pH and redox conditions on the behaviour of Cd, Zn, Ni and Mn in the Scheldt Estuary. Thalassia Jugosl. 18, 191–201.

Dyrssen, D., 1988. Sulfide complexation in surface seawater. Mar. Chem. 24, 143–153.

Emerson, S., Jacobs, L., Tebo, B., 1983. The behaviour of trace metals in marine anoxic waters: solubilities at the oxygen–hydrogen sulphide interface. In: Wong, C.S., Boyle, E., Bruland, K.W., Bruland, J.D., Goldberg, E.D. (Eds.). Trace Metals in Sea Water. Plenum Press, New York, pp. 579–608.

Frankignoulle, M., Bourge, I., Wollast, R., 1996. Atmospheric CO_2 fluxes in a highly polluted estuary (the Scheldt). Limnol. Oceanogr. 41, 365–369.

Kerner, M., Wallmann, K., 1992. Remobilization events involving Cd and Zn from intertidal flat sediments in the Elbe estuary during the tidal cycle. Estuar. Coastal Shelf Sci. 35, 371–393.

Kozelka, P.B., Bruland, K.W., 1998. Chemical speciation of dissolved Cu, Zn, Cd, Pb, in Narragansett Bay, Rhode Island. Mar. Chem. 60, 267–282.

Kraepiel, A.M.L., Chiffoleau, J-F., Martin, J-M., Morel, F.M.M., 1997. Geochemistry of trace metals in the Gironde estuary. Geochim. Cosmochim. Acta 61, 1421–1436.

Kremling, K., 1983. The behavior of Zn, Cd, Cu, Ni, Co, Fe and Mn in anoxic Baltic waters. Mar. Chem. 13, 87–108.

Landing, W,M., Lewis, B.L., 1991. Thermodynamic modelling of trace metal speciation in the Black Sea. In: Izdar, E., Murray, J.W. (Eds.). Black Sea Oceanography. Kluwer Academic Publishers, Dordrecht, pp. 125–160.

Millero, F.J., 1991. The oxidation of H_2S in Black Sea waters. Deep-Sea Res. 38 (S2), 1139–1150.

Muller, F.L.L., 1996. Interactions of copper, lead and cadmium with the dissolved, colloidal and particulate components of estuarine and coastal waters. Mar. Chem. 52, 245–268.

Nolting, R.F., De Baar, H.J.W., Timmermans, K.R., Bakker, K., 1999a. Chemical fractionation of zinc versus cadmium among other metals nickel, copper and lead in the northern North Sea. Mar. Chem. 67, 267–287.

Nolting, R.F., Helder, W., De Baar, H.J.W., Gerringa, L.J.A., 1999b. Contrasting behaviour of trace metals in the Scheldt estuary: implications for Kd values. J. Sea Res. 42, 275–290.

Paalman, M.A.A., Van der Weijden, C.H., Loch, J.P.G., 1994. Sorption of Cd on suspended matter under estuarine conditions: competition and complexation with major sea-water ions. Water Air Soil Pollut. 73, 49–60.

Paucot, H., 1997. Distribution and biogeochemical behaviour of trace metals in particulate matter of marine systems. PhD Thesis, Université Libre de Bruxelles, Brussels, 232 pp. (in French).

Paucot, H., Wollast, R., 1997. Transport and transformation of trace metals in the Scheldt estuary. Mar. Chem. 58, 229–244.

Regnier, P., Wollast, R., 1993. Distribution of trace metals in suspended matter of the Scheldt estuary. Mar. Chem. 43, 3–19.

Secher, W.D., McAvoy, D.C., 1992. MINEQL + : A software environment for chemical equilibrium modelling. Comput. Environm. Urban Syst. 16, 65–76.

Shiller, A.M., Mao, L., 1999. Dissolved vanadium on the Louisiana Shelf: effect of oxygen depletion. Cont. Shelf Res. 19, 1007–1020.

Sholkovitz, E.R., 1976. Flocculation of dissolved organic and inorganic matter during the mixing of river and seawater. Geochim. Cosmochim. Acta 40, 831–845.

Van Damme, S., Meire, P., Maeckelberghe, H., Verdievel, M., Bourgoing, L., Taverniers, E., Ysebaert, T., Wattel, G., 1995. De waterkwaliteit van de Zeeschelde: Evolutie in de voorbije dertig jaar. Water 85, 244–256.

Van den Berg, C.M.G., Merks, A.G.A., Duursma, E.K., 1987. Organic complexation and its control of the dissolved concentrations of copper and zinc in the Scheldt estuary. Estuar. Coastal Shelf Sci. 24, 785–797.

Van Eck, G.T.M., De Bruijkere, F.L.G., De Meyer, E.W., Maeckelberghe, H., 1998. Naar een schone Schelde. Water 102, 293–303.

Westerlund, S.F.G., Anderson, L.G., Hall, P.O.J., Iverfeldt, A., Rutgers van der Loeff, M.M., Sundby, B., 1986. Benthic fluxes of cadmium, copper, nickel, zinc and lead in the coastal environment. Geochim. Cosmochim. Acta 50, 1289–1296.

Wollast, R., 1988. The Scheldt Estuary. In: Salomons, W., Bayne, B.L., Duursma, E.K., Förstner, U. (Eds.). Pollution of the North Sea, an Assessment. Springer, Berlin, pp. 183–194.

Zwolsman, J.J.G., 1999. Geochemistry of trace metals in the Scheldt estuary. PhD Thesis, no. 171 of 'Mededelingen van de Faculteit Aardwetenschappen Universiteit Utrecht', 183 pp.

Zwolsman, J.J.G., Van Eck, G.T.M., 1993. Dissolved and particulate trace metal geochemistry in the Scheldt estuary, S.W. Netherlands (water column and sediments). Neth. J. Aquat. Ecol. 27, 287–300.

Zwolsman, J.J.G., Van Eck, G.T.M., Van der Weijden, C.H., 1997. Geochemistry of dissolved trace metals (cadmium, copper, zinc) in the Scheldt estuary, southwestern Netherlands: impact of seasonal variability. Geochim. Cosmochim. Acta 61, 1635–1652.