SORPTION OF ZINC ON SUSPENDED PARTICLES ALONG A SALINITY GRADIENT: A LABORATORY STUDY USING ILLITE AND SUSPENDED MATTER FROM THE RIVER RHINE

W.J.M. HEGEMAN[1]*, C.H. VAN DER WEIJDEN[1] and J.J.G. ZWOLSMAN[2]

[1]*Department of Geochemistry, Institute of Earth Sciences, University of Utrecht, P.O. Box 80021, 3508 TA Utrecht, The Netherlands*

[2]*Delft Hydraulics, P.O. Box 177, 2600 MH Delft, The Netherlands*

ABSTRACT

The adsorption of zinc on suspended matter from the river Rhine has been studied. High rates of adsorption were apparent during the first hours of the experiments, but during the next few days adsorption kinetics were much slower. The adsorption could be described by a Freundlich isotherm, indicating surface heterogeneity. In subsequent experiments, desorption of previously adsorbed Zn was investigated in solutions of various salinities. These experiments showed that the largest desorption effect occurred in the low salinity range (S=0-5). The adsorption reaction was not completely reversible. Our results indicate that desorption of Zn is to be expected in an estuary due to the presence of a salinity gradient. In field measurements, however, adsorption of Zn is often observed. This apparent contradiction is caused by additional processes that are not taken into account in laboratory studies.

1. INTRODUCTION

In the Rhine river Zn is transported mainly in particulate form (VAN DER WEIJDEN & MIDDELBURG, 1989). In the Rhine estuary, the distribution of Zn among the dissolved and particulate phases changes due to gradients in ionic strength, pH and suspended matter concentrations. In addition, sedimentation, flocculation and the formation of new particulate material may affect the sorption properties of Zn. Only the net effect of all these parameters or processes can be determined in field studies.

In the literature conflicting evidence is presented on the behaviour of Zn in estuaries (MORRIS *et al.*, 1978; DUINKER, 1980; AHLF, 1983; ACKROYD *et al.*, 1986; CHURCH, 1986; NOLTING *et al.*, 1989). A field investigation by DUINKER & NOLTING (1978) showed that dissolved Zn is removed from solution in the upper Rhine estuary. On the other hand, laboratory studies have demonstrated that Zn is desorbed from suspended matter during estuarine mixing (VAN DER WEIJDEN *et al.*, 1977; CALMANO & LIESER, 1981; LI *et al.*, 1984). This apparent contradiction must be related to the sorption properties of suspended matter in the low salinity zone. In this context we have investigated the sorption properties of suspended matter from the Rhine river under simulated estuarine conditions, focusing on low salinities.

2. MATERIALS AND METHODS

Adsorption of Zn on illite and suspended matter from the Rhine collected at Lobith (hereafter referred to as Rhine Water suspended matter, RWSM), was studied in artificial river water (ARW) as a function of sorption time (1-12 days) and dissolved Zn concentrations (25 to 500 $\mu g \cdot dm^{-3}$). The Zn content of the suspended matter was 704 $\mu g \cdot g^{-1}$; further details on the composition can be found in COMANS (1987) and COMANS & VAN DIJK (1988). The ARW consisted of Ca^{2+}, HCO_3^- and NO_3^- (ionic strength=0.003 M, pH=7.85). All experiments were performed in duplicate.

* author to whom correspondence should be sent

The Zn solutions were prepared by dissolving $Zn(NO_3)_2$ (Merck, suprapur) in 80 cm^3 of artificial river water; these solutions were spiked with 100 mm^3 of a ^{65}Zn solution (3,7 to 37 $GBq \cdot mg^{-1}$ Zn, carrier free). Subsequently, dense suspensions (1 cm^3) of RWSM, equilibrated in ARW for 2 weeks, were added to these solutions (t=0). The final suspension concentration was 100 $mg \cdot dm^{-3}$. The solutions were continuously stirred in order to prevent the suspended matter from settling.

Adsorption was monitored by taking samples (2 cm^3) during a 12-day period. Samples were centrifuged for 30 min (at $2 \cdot 10^4$ g) in order to remove the solid phase. Centrifugation gave a better separation result than filtration through 0.2 μm membrane filters. The dissolved phase (supernatant) was collected and analysed for ^{65}Zn by gamma-counting.

The extent of Zn adsorption was calculated by:

$$C_a = (1-F) \cdot C_0 \cdot m^{-1}$$

where:

C_a = adsorbed Zn concentration ($\mu g \cdot g^{-1}$)
C_0 = dissolved Zn concentration at t=0 ($\mu g \cdot dm^{-3}$)
F = fraction of dissolved Zn concentration remaining in solution, measured as the activity of the ^{65}Zn tracer at t=t divided by the activity of the added ^{65}Zn tracer at t=0.
m = suspended matter concentration (0.1 $g \cdot dm^{-3}$)

The distribution (partition) coefficient was calculated by:

$$Kd = C_a / C_d$$

where $C_d = F \cdot C_0$, C_d representing the dissolved Zn concentration at any time t.

After completion of the adsorption experiments (12 days), the suspensions were centrifuged. Subsequently, the supernatant (60 cm^3) was almost completely siphoned off leaving a concentrated suspension (3 cm^3). Thereafter, desorption experiments were performed by adding solutions (60 cm^3) of various salinities (0 to 35) to the concentrated suspensions. These solutions were prepared by mixing appropriate amounts of zinc-free ARW and Atlantic seawater (S=35, pH=8.1). Sampling and analysis were performed in a way similar to that described for the adsorption experiments. The results were corrected for the amount of Zn lost during the removal of the supernatant after the adsorption experiments.

All sorption experiments were performed in acid-cleaned 110-cm^3 Teflon (PTFE) reaction vessels. The Teflon material was found to adsorb less than 2% of the initial Zn concentration during a 12-day sorption period. Temperature was kept constant at 20 ($\pm$1)°C throughout all handling procedures. The recovery of

^{65}Zn in solution plus that in the suspended matter (as determined by leaching with 0.02 M HNO_3) was always $\geqslant$96% of the initially added activity of ^{65}Zn.

Throughout the experiments we used identical handling and separation procedures. Therefore, possible anomalous effects related to the presence of 'dissolved' colloids or particle-particle interaction or coagulation and disaggregation (MOREL & GSCHWEND, 1987; HONEYMAN & SANTSCHI, 1988, 1991) can be neglected or were constant during the experiments.

In laboratory experiments, where radiotracers are used to study the characteristics of natural suspended matter, isotopic exchange may interfere with the results. Therefore, the exchangeable Zn fraction present on the RWSM was determined by a weak acid leach (1 M NH_4OAc as used by TESSIER et al., 1979). The Zn concentration was measured by GFAAS (applying Zeeman-correction). The exchangeable Zn fraction of the RWSM was 60 $\mu g \cdot g^{-1}$. The RWSM concentration used was 0.1 $g \cdot dm^{-3}$ implying that at most 6 $\mu g \cdot dm^{-3}$ of Zn was involved in isotopic exchange. We conclude that only when the Zn concentration added was very low (25 $\mu g \cdot dm^{-3}$), that isotopic exchange might have changed the specific ^{65}Zn-activity significantly.

3. RESULTS AND DISCUSSION

3.1. ADSORPTION AND SURFACE HETEROGENEITY

The kinetics of Zn adsorption onto Rhine water suspended matter (during a 12-day period) are shown in Fig.1. Most of the Zn was adsorbed within a few hours; the uptake was much slower during the next hours and days. This can be attributed to quick sur-
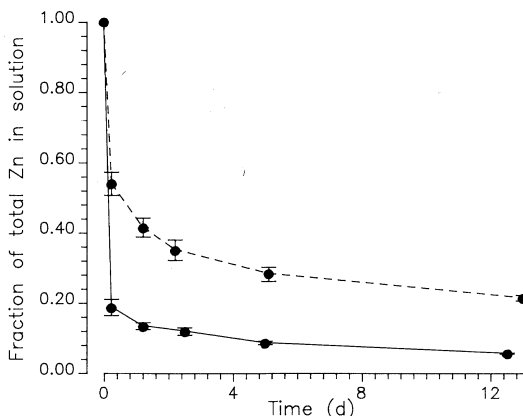

Fig. 1. Adsorption of Zn onto Rhine water suspended matter as a function of time. Initial Zn concentrations of 25 (solid line) and 500 $\mu g \cdot dm^{-3}$ (dashed line). Ionic strength=0.003 M, pH=7.8, suspended matter concentration=0.1 $g \cdot dm^{-3}$. Bars denote standard error of mean, n=6.
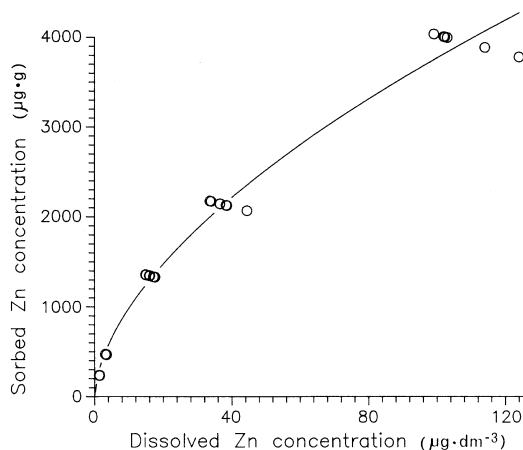
Fig. 2. Adsorption of Zn onto Rhine water suspended matter as a function of the dissolved Zn concentration. Initial Zn concentrations were 25, 75, 150, 250, 500 μg Zn·dm^{-3}, the sorption period was 12 days. Ionic strength=0.003 M, pH=7.8, suspended matter concentration=0.1 g·dm^{-3}, n=6. The solid curve represents a Freundlich isotherm: $C_a = k \, C_d^{1/m}$ calculated by non-linear regression (WILKINSON, 1988). Best fit: k=258, m=1.718.
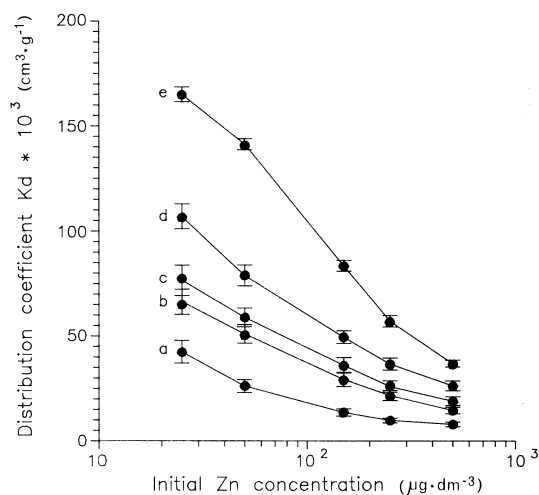

Fig. 3. Distribution coefficient as a function of initial Zn concentration after a sorption period of 0.2, 1.2, 2, 5, and 12 days (lines a-e, respectively). Ionic strength=0.003 M, pH=7.8, suspended matter concentration=0.1 g·dm^{-3}. Error bars denote standard error of mean, n=6.

face adsorption, followed by penetration of the inner surface (WEBER, 1984, VAN DE MEENT et al., 1990) or by a gradual occupation of the less reactive surface sites. Fig. 2 shows that adsorption of Zn onto Rhine suspended matter does not depend linearly on the dissolved Zn concentration. The adsorption could best be fitted by a Freundlich isotherm; Langmuir isotherms gave less satisfactory results. These observations indicate that the overall energy of adsorption decreases with increasing surface coverage (BENJAMIN & LECKIE, 1981; TESSIER et al., 1985). This apparent surface heterogeneity is caused by the presence of various components of the suspended matter which can act as substrates for Zn adsorption. The relative contribution of each of these substrates (hydrous oxides of iron and manganese, carbonates and organic matter) to the sorption of Zn depends on the (overall) surface coverage. Fig. 3 shows the partition (distribution) coefficient, Kd, as a function of the initial Zn concentration and sorption time. The Kd increases with time as more Zn becomes adsorbed onto the suspended matter. The Kd is inversely related to the initial Zn concentration, which is compatible with the surface heterogeneity mentioned before. The weak sorption sites on RWSM are more involved in the sorption of Zn at higher initial Zn concentrations. Therefore, adsorption onto a heterogeneous substrate such as RWSM cannot be described by a constant Kd. This parameter depends on the surface coverage (or the initial Zn concentration).

3.2. SALINITY EFFECTS AND SPECIATION

In this section we will discuss the results of the desorption experiments performed with RWSM which had been exposed to 25 μg Zn·dm^{-3} for 12 days. Similar results were obtained in all other desorption experiments (initially added Zn concentrations up to 500 μg Zn·dm^{-3}). The effect of salinity
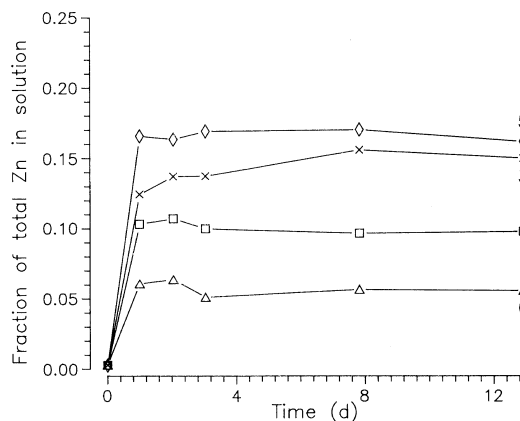

Fig. 4. Desorption of previously adsorbed Zn from Rhine water suspended matter as a function of time and salinity (S=0, 1, 3, 5). Initial sorption concentration was 25 μg·dm^{-3}. Suspended matter concentration: 0.1 g·dm^{-3}; pH=7.8 - 8.1, depending on salinity.

on the desorption process is shown in Fig. 4. The Zn concentration in solution reaches an apparent equilibrium level within a few days. Thereafter, a small decrease in dissolved Zn occurs, which may be due to adsorption onto unsaturated sorption sites on the inner surface of the suspended particles (E.A. Jenne, pers. comm.). Fig. 5 shows the Kd determined after a desorption time of 2 days, which corresponds with the residence time of water in the Rhine estuary (DUINKER et al., 1979). A large decrease in Kd is observed in the low salinity range (0-5). Although the small increase in pH during estuarine mixing (from 7.8 to 8.1) tends to enhance the adsorption of Zn, net desorption is observed due to the combined effects of increasing ionic strength, complexation with inorganic ligands and competition with Ca and Mg for adsorption sites (BOURG, 1983; LI et al., 1984). For instance, Table 1 shows that the activity of the free Zn^{2+}-species decreases sharply during the first stages of estuarine mixing. This is mainly due to the rapid decrease in ion activity coefficients with increasing ionic strength (BOURG, 1983). The extent of Zn adsorption will be reduced accordingly, leading to a decreasing Kd during the first stages of estuarine mixing.

3.3. IRREVERSIBILITY AND SPECIATION EFFECTS

The sorption characteristics of Zn on illite and RWSM are shown in Figs 6a and 6b. It is obvious that the adsorption and desorption isotherms recorded in the same ionic medium (ARW) do not coincide, indicat-
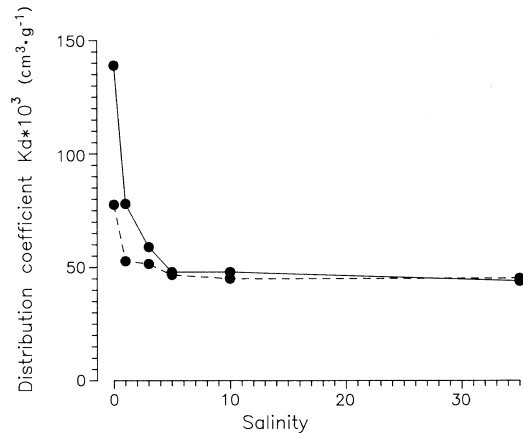

Fig. 5. Distribution coefficient Kd determined after a desorption time of 2 days as a function of salinity. Initially adsorbed Zn concentration 25 (solid line) and 500 μg Zn·dm^{-3} (dashed line), pH=7.8 - 8.1, suspended matter concentration=0.1 g·dm^{-3}.

ing that sorption behaviour is irreversible. In fact, the extent of desorption is less than that of adsorption over the same time scale, implying that Zn becomes more strongly bound to the suspended matter with increasing time. Similar observations have been reported previously by SALOMONS (1980).

Fig. 6a shows that the Zn concentration sorbed by illite decreases steadily with increasing salinity. As mentioned, this is due to the decrease in the activity

TABLE 1

Stability constants used in the Zn-speciation model (VAN GAANS, 1989; PLUMMER et al., 1976) and calculated Zn speciation at different salinities.

* % species=activity species/total dissolved Zn(II) concentration.
** From TURNER et al. (1981), unless otherwise indicated.
*** Calculated from the formation constant of zinc bicarbonate given by STANLEY & BYRNE (1990). The following species were also considered but made no significant contributions to the results: $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$, ZnF^+ ZnF_2, $Zn(SO_4)_3^{4-}$, $Zn(SO_4)_4^{6-}$, $Zn(CO_3)$ (s) and $Zn(OH)_2$ (s).
**** From WEAST & ASTLE (1984).

| Reaction		logK**	Salinity 0 / pH 7.85	1 / 7.86	3 / 7.93	5 / 7.96	10 / 7.96	35 / 8.11
Zn^{2+} +	$= Zn^{2+}$	-	93	50.5	35.7	29.7	23.0	15.0
Zn^{2+} + OH^-	$= Zn(OH)^+$	5.04	4.4	2.7	2.3	2.0	1.6	1.4
Zn^{2+} + $2OH^-$	$= Zn(OH)_2$	11.1	2.2	1.6	1.5	1.4	1.1	1.4
Zn^{2+} + Cl^-	$= ZnCl^+$	0.49	-	2.2	4.3	5.6	8.1	16.5
Zn^{2+} + $2Cl^-$	$= ZnCl_2$	0.62	-	-	0.2	0.5	1.3	8.0
Zn^{2+} + $3Cl^-$	$= ZnCl_3^-$	0.51	-	-	-	-	0.1	2.2
Zn^{2+} + $4Cl^-$	$= ZnCl_4^{2-}$	0.20	-	-	-	-	-	0.4
Zn^{2+} + SO_4^{2-}	$= ZnSO_4$	2.36	-	5.0	7.4	8.3	9.0	7.8
Zn^{2+} + $2SO_4^{2-}$	$= Zn(SO_4)_2^{2-}$	3.63	-	-	0.1	0.2	0.3	0.3
Zn^{2+} + HCO_3^-	$= ZnHCO_3^+$	1.49***	-	0.1	0.2	0.2	0.3	0.5
Zn^{2+} + CO_3^{2-}	$= Zn(CO_3)^0$	4.75****	-	0.5	1.1	1.5	2.1	4.7
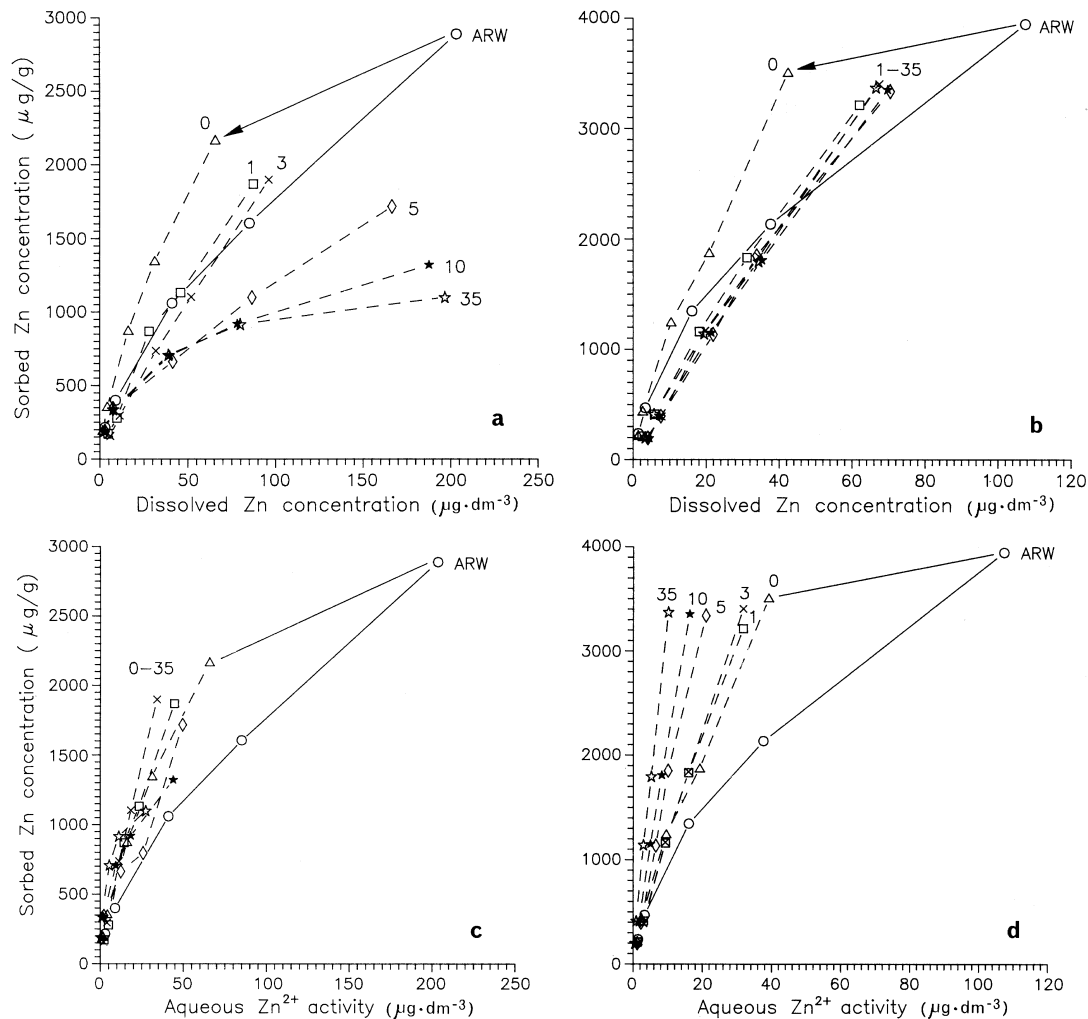
Fig. 6. (a). Adsorption of Zn on illite in artificial river water (ARW), determined after a period of 12 days (solid line). In subsequent experiments the fresh water was displaced by solutions of various salinities and desorption isotherms were recorded after 12 days (dashed lines, S=0-35). The arrow indicates hysteresis between the adsorption and desorption isotherms recorded in ARW. pH=7.8 - 8.1, suspended matter concentration=0.1 g·dm^{-3}. (b). Sorption characteristics of Rhine water suspended matter. Experimental conditions as in Fig. 6a. (c). Sorption of Zn on illite as a function of free Zn^{2+} activity (recalculated from Fig. 6a). (d). Sorption of Zn on Rhine water suspended matter as a function of free Zn^{2+} activity (recalculated from Fig. 6b).

of the free Zn^{2+} species with increasing salinity. If it is assumed that Zn^{2+} is the only species to be adsorbed, the sorption isotherms can be recalculated as a function of the actual free Zn^{2+} activity. The salinity-corrected isotherms, calculated using the speciation model Wateqx (Table 1), are presented in Fig. 6c. The recalculated isotherms coincide approximately with the desorption isotherm recorded in ARW (S=0). This indicates that the effect of salinity

on the sorptive behaviour of Zn (Fig. 6a) can be largely explained by the decrease of Zn^{2+} activity with increasing ionic strength.

The effect of salinity on the desorption isotherms of Zn is less pronounced for RWSM (Fig. 6b) than it is for illite (Fig. 6a). Actually, this effect can only be demonstrated in the very low salinity range (S=0-1). There is no shift in the desorption isotherms at higher salinities (S=1-35), although the aqueous Zn specia-

tion is subject to continuous changes over this salinity range (Table 1). If the Zn-concentrations in Fig. 6b are converted to free Zn^{2+} activities, as done for Zn adsorption on illite, the isotherms diverge (Fig. 6d). The fact that the uncorrected isotherms for S=1-35 practically coincide (Fig. 6b) means that they are determined by Zn concentrations rather than by free Zn^{2+} activities.

The different sorption behaviour of Zn on illite and RWSM is presumably related to the heterogeneous composition of the RWSM. Easily reducible iron and manganese oxides, as well as organic matter, are the major carriers of Zn in Rhine sediments (SALOMONS & FÖRSTNER, 1984). The affinity of hydrous iron and manganese oxides for Zn in seawater was found to be much higher than that of illite (VAN DER WEIJDEN, 1975). A similar high affinity for Zn might apply to organic matter, which has effective binding sites like amide and carbonyl functional groups (DUGAS & PENNEY, 1981; LION et al., 1982). Therefore, RWSM has a higher Zn adsorption capacity than illite, as observed in our experiments.

The recalculated isotherms for Zn adsorption on illite at different salinities coincide with the isotherm measured in ARW (Fig. 6c), whereas those for RWSM do not (Fig. 6d). This indicates that Zn^{2+} is the only species to be adsorbed by illite. However, if several inorganic complexes are adsorbed too, as seems to be the case for RWSM, then adsorption will effectively compete with complex formation in solution. This can explain why the complexation of Zn in solution hardly affects the sorption isotherms (Fig. 6b). In addition, strong salinity gradients in estuaries can result in ion-exchange reactions on particles. In fresh water most sediments are negatively charged. According to DUINKER (1980), surface charge transitions occur at salinity values that characterize the early stages of mixing. This could explain the discrepancy in sorption behaviour of RWSM between 0 and 1-35 salinity.

Both Zn and Cd belong to the same type of metal cations (STUMM & MORGAN, 1981); the stability of ion complexes is a result of covalent and coulombic interactions. Therefore, similar sorption behaviour should be expected. However, completely reversible sorption behaviour has been observed for Cd on RWSM (COMANS & VAN DIJK, 1988). This can be explained by the strong complexation of Cd with chlorides, which is much weaker for Zn. Consequently the suspended matter has a higher affinity for Zn than Cd in seawater. VAN DER WEIJDEN (1975) found experimentally that the adsorbed Zn/Cd ratio on clays at pH 8 was 9/1 in artificial freshwater and 25/1 in seawater.

3.4. COMPARISON BETWEEN LABORATORY AND FIELD STUDIES

The experimental conditions used in this study approach those encountered in the Rhine estuary. However, desorption of Zn from suspended matter, as predicted by our laboratory studies, is not commonly observed in the field. On the contrary, DUINKER & NOLTING (1978) found rapid removal of dissolved Zn in the low salinity zone of the Rhine estuary, as shown in Fig. 7. This apparent contradiction can only be explained by additional processes not taken into account in laboratory studies. For instance, it is known that small reactive particles are formed in the low salinity zone of the Rhine estuary (EISMA et al., 1980).

Another feature of many estuaries which is overlooked in laboratory studies is the transport of (uncontaminated) marine suspended matter to the low salinity zone by estuarine circulation processes (e.g. ALLEN et al., 1980). Both the 'in situ' formation of new reactive surfaces and the introduction of metal-depleted marine particles in the low salinity zone favour adsorption of Zn. Since many field studies show that Zn is removed from solution in estuaries it would seem that these processes offset the desorption effect of salinity. Thus, the discrepancy between laboratory and field observations may be explained by the complex dynamics of suspended matter in estuaries, which cannot be simulated adequately in laboratory experiments. Nevertheless, laboratory ex-
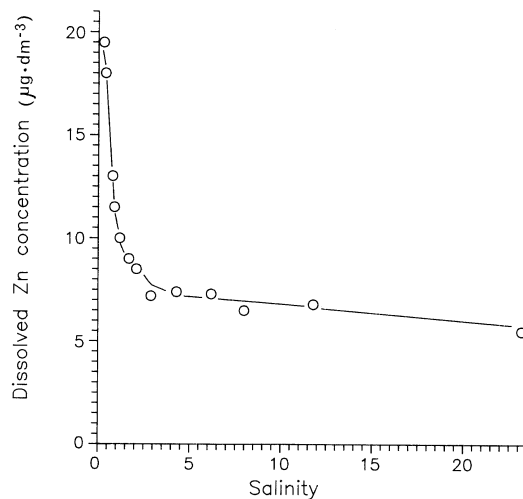

Fig. 7. Dissolved zinc concentration in the Rhine estuary as a function of salinity. Redrawn from DUINKER & NOLTING (1978).

periments are useful for elucidating the individual effect of the various parameters that control trace metal adsorption in estuaries (SALOMONS, 1980; BOURG, 1983).

4. CONCLUSIONS

Adsorption of Zn onto Rhine Water Suspended Matter (RWSM) was studied in laboratory experiments. During the first few hours the particle surfaces became covered with Zn. Thereafter the adsorption of Zn slowed down because Zn penetrated into the particles and/or because it occupied less reactive surface sites.

Sorption onto Rhine water suspended matter shows a Freundlich behaviour, indicating surface heterogeneity. Subsequent desorption experiments performed over a salinity range show that from 0-3 salinity the distribution coefficient decreases rapidly. In our experiments the net result of increasing salinity is desorption of Zn. Speciation calculations show that this is due primarily to decreasing Zn^{2+} activity with increasing salinity. The sorption process is not completely reversible on the time scale considered (12 days). Contradictions between these results and field investigations (DUINKER & NOLTING, 1978) can be attributed to particle dynamics which can cause scavenging of Zn and other heavy metals under natural conditions. These additional processes are not taken into account in laboratory studies.

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