

Equilibrium Speciation Models for Hg, Cd, and Pb in the Gulf of Bothnia and its Catchment Area

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Equilibrium speciation models were established for Hg (II), Cd (II) and Pb (II) in bog-, river- and sea water having a composition corresponding to that of the Gulf of Bothnia (6‰ salinity). The calculations were performed using the computer program SOLGASWATER. The models were based on available thermodynamic data at 25°C and included the inorganic ligands OH⁻, Cl⁻, Br⁻, HPO₄²⁻ and CO₂ (aq). Furthermore, complex formation with organic substances originating from a bog water was considered, Mg (II) and Ca (II) were also included as competing cations. All water types were assumed to be oxic and in equilibrium with atmospheric carbon dioxide, 10^{-3.5} atm (32 Pa).

The calculations showed that the speciation of Hg (II) and Pb (II) in bog and river waters is dominated by complexation with the organic substance, except for lead (II), where the Pb²⁺-ion dominates at pH ≤ 5. In the Gulf of Bothnia, the chloro complexes HgCl₂ and HgCl₃⁻ becomes prevailing as the salinity increases. Besides Pb²⁺, the species PbCl⁺ and PbCO₃ become important upon increasing the salinity and pH. The dominating fraction of Cd (II) is Cd²⁺ in bog water, in river water and in waters of salinity lower than 4.5‰.

With increasing salinity CdCl⁺ and CdCl₂ predominate.

Introduction

The accumulation of toxic metals in the biosphere will continue to be a serious environmental problem, even if the immediate sources of pollution were to be removed in the near future. Thus leachates from waste deposits, transfers from contaminated sediments to the water column and releases due to ground and surface water acidification will cause continuing problems. For instance, mercury

levels in pikes caught in Swedish lakes still have a tendency to increase with time despite a considerable decrease in the direct release of mercury to water and air during the last 20 years (Andersson, Nilsson, Håkansson and Brydsten 1987).

To estimate the hazard of environmental damage and to present suitable steps for lowering the concentrations of toxic metals circulating in biota, it has become of urgent importance to understand the conversion, transport and bio-uptake of these metals. These processes are often closely related to the speciation of the elements, *i.e.* a characterization of the individual physico-chemical forms of the element that together make up its total concentration. It is now well established that a knowledge of the speciation of a metal is a necessity to be able to understand its toxicity as well as its transport in rivers and estuaries (Campbell and Tessier 1987). Measurements of the total concentration of a trace element provide no information about its bio-availability or its interactions with sediments and suspended particles.

Trace metal speciation in natural waters has been based on the use of two different techniques: experimental measurements and computer chemical modelling. The first approach is still limited by the lack of experimental techniques sufficiently sensitive and selective to detect individual species at the concentrations normally found in natural systems.

The computer modelling approach to trace metal speciation in waters involves the use of thermodynamic data, together with known concentrations of reacting components, to compute the equilibrium concentrations (or activities) of the various species. Computer modelling has made an important contribution towards an understanding of speciation in natural waters, and will continue to be an important technique as more accurate thermodynamic data becomes available.

Several equilibrium models for trace metal speciation in natural waters have been published, most of which have been calculated for sea water conditions, for example by Zirino and Yamamoto (1972) and by Dyrssen and Wedborg (1979). In a paper by Dyrssen and Wedborg (1979), trace metal speciation in fresh water and estuaries was calculated. However, metal-organic complexes which may be formed in low salinity waters with high contents of dissolved organic carbon (DOC) were neglected. Mantoura, Dickson and Riley (1978) included metal complexation with humic materials in their trace metal speciation model for fresh water, estuaries and sea water. However, the model was calculated for a relatively narrow pH-range ($7.5 \leq \text{pH} \leq 8.2$).

In the present study a scenario in which changes in the speciation of some heavy metals occur as they are transported from a bog water via river water out into the Gulf of Bothnia is presented. The water composition changes drastically through these water types and consequently, so does the complex forming capacity. Starting with the bog waters, they generally have low pH and ionic strength, but are rich in strongly complexing organic materials, the so-called humic substances. The organic content decreases in the rivers, and the pH is higher here. When the river water is mixed with the brackish water of the Gulf of Bothnia, there is a drastic increase in

the salinity besides a further increase in pH. This implies that inorganic complex forming ligands such as halogenides, hydroxide, carbonate and sulphate become more significant.

In order to simulate the speciation changes for aqueous Hg (II), Cd (II) and Pb (II), we have constructed an equilibrium model. The calculations were performed using the computer program SOLGASWATER (Eriksson 1979), which is well suited to modelling natural waters (Ingri 1978, Sjöberg 1983).

This work is a part of a project dealing with the speciation, adsorption and sedimentation processes of some toxic metals of environmental interest in the Gulf of Bothnia and its catchment area.

The Real Systems

Heavy Metal Concentrations

To represent the large range of water types spanned by the Gulf of Bothnia and its catchment area we have examined the changes in metal speciation due to variations in the composition of three distinct water types: i) bog water, ii) river water, and iii) Gulf of Bothnia water. For Hg (II), Cd (II) and Pb (II) no data for total concentrations in these waters were available. However, the total concentrations of these metals in all natural waters are extremely low, ranging from 10^{-12} mol \times dm $^{-3}$ to 10^{-8} mol \times dm $^{-3}$, and variations within these ranges will thereby not influence the speciation significantly, because of the high ratio ligand concentration/metal concentration.

Mean values for the total concentrations of Cd and Pb in sea and fresh waters were taken from Garrels and MacKenzie (1973). The concentration of Hg (II) was as obtained from measurements in the Baltic Sea (Lindström 1986). The concentrations of components in the aqueous phase used in this study are summarized in Table 1.

i) Bog-Water

The bog waters in the Gulf of Bothnia catchment area are characterized by low pH (pH \approx 4-5) and high content of organic substance. Both dissolved and colloidal organics are strong complex formers, and consequently of great importance for metal speciation in this type of water. Bog water concentrations were taken from Lövgren, Hedlund, Öhman and Sjöberg (1987).

ii) River Water

A large number of Swedish rivers have been sampled monthly within the "Programme for environmental quality control", administered by the national Swedish Environment Protection Board (SNV), and analyzed for a number of chemical and physical parameters. In this investigation mean values of relevant data were used for the rivers with outlets into the Gulf of Bothnia.

Table 1 - Mean concentrations of some elements and ligands in the different water types. All concentrations are given in $\text{mol} \times \text{dm}^{-3}$, except the Total Organic Carbon (TOC) values which are given in $\text{mg carbon} \times \text{dm}^{-3}$. Alk represents the alkalinity and arises mainly from the HCO_3^- concentration. Org.H^+ denotes the concentration of organic acidic groups in the bog water. The TOC values for the river water have been estimated from KMnO_4 consumption

	Bog-water		River water		Gulf of Bothnia (S = 6‰)
pH	4.4	1)	6.9	2)	7.9
Alk	-		2.2×10^{-4}	2)	1.0×10^{-3}
org.H ⁺	1.5×10^{-4}	1)	-		-
TOC	26.0	1)	10.7	2)	5.0
[Cl ⁻]	1.5×10^{-5}	1)	4.5×10^{-5}	2)	0.0932
[SO ₄ ²⁻]	1.6×10^{-5}	1)	1.0×10^{-4}	2)	0.0049
[Br ⁻]	2.5×10^{-7}	6)	2.5×10^{-7}	6)	1.4×10^{-4}
[HPO ₄ ²⁻]	8.0×10^{-8}	1)	3.0×10^{-8}	2)	1.0×10^{-7}
[Ca(II)]	3.0×10^{-5}	1)	2.6×10^{-4}	2)	0.0022
[Mg(II)]	2.4×10^{-5}	1)	7.1×10^{-5}	2)	0.0091
[Hg(II)]	2.5×10^{-11}	7)	2.5×10^{-11}	7)	2.5×10^{-11}
[Cd(II)]	1.0×10^{-9}	6)	1.0×10^{-9}	6)	1.0×10^{-9}
[Pb(II)]	1.5×10^{-8}	6)	1.5×10^{-8}	6)	1.5×10^{-9}

1) Lövgren and Sjöberg (1987).

2) Values obtained from the "Programme for environmental quality control" administered by the National Swedish Environment Protection Board (SNV).

3) Pietikäinen *et al.* (1978).

4) Kremling (1970).

5) Grasshof and Voipio (1981).

6) Garrels *et al.* (1973).

7) Lindeström (1986).

No analyses of total organic carbon (TOC) were given in this compilation, but the cited average chemical oxygen demand (COD), ($29 \text{ mg KMnO}_4 \times \text{dm}^{-3}$), was used to estimate the TOC value. Using an empirical derived ratio COD ($\text{mg KMnO}_4 \times \text{dm}^{-3}$)/TOC ($\text{mg} \times \text{dm}^{-3}$) of 2.7 from a study by Gjessing (1976), a mean value of $10.7 \text{ mg} \times \text{dm}^{-3}$ is obtained for the Bothnian rivers.

iii) The Gulf of Bothnia Water

The Gulf of Bothnia, as a part of the Baltic Sea, has been characterized regarding several of its chemical parameters (Voipio 1981).

The salinity in the Gulf of Bothnia gradually increases from north to south and reaches a maximum of about 6‰ for surface waters and 7‰ for deep water in the southern Gulf of Bothnia. The pH also increases from north to south. Each of these characteristics is a result of the mixing between incoming humic-rich river

water from the north and Baltic sea water from the south. pH varies significantly with depth in the summer due to biological processes, and reaches a maximum around 8.2 in the surface water in the south of the Gulf of Bothnia (Pitkänen 1978). In winter no such depth dependence has been reported. Maximum pH in the south then is about 7.6 (Pietikäinen, Niemi, Tulkki and Aurimaa 1978).

The concentrations of Cl^- , Br^- , Mg^{2+} , Ca^{2+} and SO_4^{2-} are related to the salinity, as has been reported by Kremling (1970). The phosphate concentration is generally below $10^{-7} \text{ mol} \times \text{dm}^{-3}$ but increases with depth (Grasshof and Voipio 1979). No TOC values for the Gulf of Bothnia could be found, but for the Baltic Sea generally, Grasshof and Voipio (1979) presents DOC (dissolved organic carbon) values reaching from 3 to 13 $\text{mg} \times \text{dm}^{-3}$ in their discussion of the subject. They also conclude that reported DOC and TOC values are nearly the same, since the particulate material usually is much less than 10 % of the TOC. From these data a TOC value of 5 $\text{mg} \times \text{dm}^{-3}$ was estimated for the southern part of the Gulf of Bothnia.

The Model Systems

The transport of water from its source via the river system and estuaries into the Gulf of Bothnia involves large changes in the main component concentrations. This will result in a gradual change in metal speciation. To simulate these changes two gradient model systems were calculated for each metal.

- 1) A fresh water gradient. This simulates the change in composition between bog water and river water, and involves gradually altering the pH and the concentrations of the model organic substance (H_2L), Cl^- , SO_4^{2-} , Mg^{2+} and Ca^{2+} .
- 2) A salt water gradient. This describes the change in composition from a river mouth to Bothnian sea water (*i.e.* an estuarine water). Many concentration changes are known to occur exponentially due to mixing with sea water. The concentration variations were therefore made on a logarithmic scale, except for the organic component which was decreased more moderately.

Components

As model components we selected those inorganic substances in natural waters which are known to form strong complexes with the metals studied or which exist in higher concentrations: H^+ , HCO_3^- , Cl^- , Br^- , HPO_4^{2-} and SO_4^{2-} . It should be noted that the ligand HPO_4^{2-} was excluded from speciation studies of Cd (II) and Pb (II) since no relevant data for these complexes could be found. Mg (II) and Ca (II) were included in the models. Both are weak complex formers but are present in relatively high concentrations, especially in the Gulf of Bothnia and competes with other complex forming cations. This effect is consequently most pronounced for Cd (II) which is a weak complex former.

As a model organic substance, we have used the soluble organic content of a bog water. It has previously been studied with respect to acid-base properties and complexation to several metal ions (Al (III), Hg (II), Cd (II), Cu (II)) (Lövgren *et al.* 1987; Lövgren and Sjöberg 1989).

In the characterizations of their bog water concentrate, Lövgren *et al.* (1987) found no pronounced polyelectronic acid-base behaviour, instead a good fit to the experimental data was obtained by introducing a di-protic acid into the model (H₂L). This model organic substance was used for both fresh water system and salt water systems.

Concentrations

Values for the concentration of organic substances in the river water and Gulf of Bothnia water have been estimated by applying the bog water data by Lövgren *et al.* (1987) for TOC and concentration of organic acidic groups. From these concentrations a value of about 1 H₂L group/ 30 carbon atoms were derived. The mean TOC value of 10.7 mg carbon × dm⁻³ in the rivers then results in the concentration of 30 μmol × dm⁻³ H₂L, and the DOC value in the Gulf of Bothnia 5 mg carbon × dm⁻³, results in 15 μmol × dm⁻³.

The concentrations used in the calculations are summarized in Table 3. For all types of water the assumption was made that the water is in equilibrium with air, P_{CO₂} = 10^{-3.5} atm (32 Pa).

Thermodynamic Data

The thermodynamic data used are valid at 25°C and 1 atm (1.01 × 10⁵ Pa).

In the adjustment of published stability constants to the correct ionic strength, an extended Debye-Hückel expression was used. Davies (1962) proposed the equation

$$\log \beta_{pqr} = \log \beta_{pqr}^0 + a_i \left(\frac{I^{1/2}}{1+I^{1/2}} \right) - 0.3 I \quad (1)$$

for calculation of stability constants at different ionic strengths. In this equation β⁰_{pqr} is the stability constant at zero ionic strength, and β_{pqr} the stability constant at the ionic strength *I*. *a_i* = *S*Δ*Z*² where *S* denotes the Debye-Hückel limiting slope (0.51 M^{-1/2}) and Δ*Z*² is the square of the charge on each species summed over the formation reaction. This equation has been found to be relevant for ionic strengths below 0.1 mol × dm⁻³ which corresponds to a salinity around 6‰. For some of the data for Hg²⁺ complexes, recalculations using Davies equations from ionic strengths greater than 0.1 mol × dm⁻³ have to be made in order to cover the formation of all possible species, as has been indicated in Table 2a.

To be able to compute bog water (H₂L) interactions with Pb (II), Ca (II) and Mg (II), the corresponding formation constants had to be estimated. According to Lövgren and Sjöberg (1989), oxalate forms a metal-oxalate complex with Cd, Hg and Cu that is slightly weaker than the corresponding bog water complex (MeL).

Speciation Models for Hg, Cd and Pb

Table 2a = Thermodynamic data used in the calculations. All log β_{pqr} values are valid at 25°C and zero ionic strength or have been recalculated to zero ionic strength using Davies equation (1962)

Species	Metals/log β_{pqr}				
	Hg (II)	Cd (II)	Pb (II)	Mg (II)	Ca (II)
MeOH ⁺	- 3.40 ^a	-10.08 ^a	- 7.71 ^a	-11.44 ^a	-12.85 ^a
Me(OH) ₂ (aq)	- 6.17 ^a	-20.35 ^a	-17.12	-	-
Me(OH) ₃ ⁻	-21.10 ^a	-	-28.06 ^a	-	-
Me ₂ (OH) ₃ ⁺	- 3.33 ^a	-	-	-	-
Me ₃ (OH) ₃ ³⁺	- 6.42 ^a	-	-	-	-
Me ₃ (OH) ₄ ²⁺	-	-	-23.88	-	-
Me(OH)CO ₃ ⁻	-11.88 ^{b1}	-	-	-	-
MeHCO ₃ ⁺	- 0.53 ^{b1}	- 4.25 ^c	- 2.90 ^c	- 5.40 ^d	- 5.35 ^d
MeCO ₃ (aq)	- 4.60 ^{b1}	-12.58 ^c	-10.43 ^e	-13.80 ^d	-13.54 ^d
Me(CO ₃) ₂ ²⁻	-17.78 ^{b1}	-	-23.91 ^e	-	-
MeCl ⁺	7.21 ^a	1.98 ^{f1}	1.59 ^{f1}	-	-
MeCl ₂ (aq)	13.98 ^a	2.60 ^{f1}	1.80 ^{f1}	-	-
MeCl ₃ ⁻	15.06 ^a	2.40 ^{f1}	1.70 ^{f1}	-	-
MeCl ₄ ⁻²	15.42 ^a	1.70 ^{f1}	1.40 ^{f1}	-	-
MeOHCl(aq)	4.06 ^a	-	-	-	-
MeBr ⁺	9.54 ^{f2}	2.14 ^{f1}	1.77 ^{f1}	-	-
MeBr ₂ (aq)	17.91 ^{f2}	3.00 ^{f1}	2.60 ^{f1}	-	-
MeBr ₃ ⁻	0.21 ^{f2}	3.00 ^{f1}	3.00 ^{f1}	-	-
MeBr ₄ ²⁻	21.54 ^{f2}	2.90 ^{f1}	2.30 ^{f1}	-	-
MeClBr(aq)	16.63 ^g	-	-	-	-
MeCl ₂ Br ⁻	17.19 ^g	-	-	-	-
MeCl ₃ Br ²⁻	17.65 ^g	-	-	-	-
MeClBr ₂ ⁻	19.08 ^g	-	-	-	-
MeClBr ₃ ²⁻	0.62 ^g	-	-	-	-
MeCl ₂ Br ₂ ²⁻	19.14 ^g	-	-	-	-
MeHPO ₄ (aq)	7.72 ^{b2}	-	-	-	-
MePO ₄ ⁻	2.44 ^{b2}	-	-	-	-
MeSO ₄ (aq)	2.41 ^{f2}	2.46 ^{f1}	2.62 ^{h1}	2.23 ^d	2.31 ^d
Me(SO ₄) ₂ ²⁻	3.47 ^{f2}	-	-	-	-
MeL(aq)	2.73 ⁱ	- 5.16 ⁱ	- 4.14 ^j	- 5.62 ^j	- 6.05 ^j
Me(H ₋₁ L) ⁻	- 1.77 ⁱ	-	-	-	-
Me(COO) ₂ (aq)	-	- 1.59 ^{f1}	- 0.57 ^{f1}	- 2.05 ^{f1}	- 2.48 ^{f1}

* The formation constants, β_{pqr} are defined according to the general equilibrium: $pA + qB + rC + \dots = A_p B_q C_r \dots$;

$$\beta_{pqr} = \frac{[A]^p [B]^q [C]^r \dots}{[A]^p [B]^q [C]^r \dots}$$

A, B, C, ... are the main components in the model: H⁺, CO₂(aq), Cl⁻, Br⁻, HPO₄²⁻, SO₄²⁻, H₂L, Mg²⁺, Ca²⁺, Hg²⁺, Cd²⁺, Pb²⁺. H₂L represents the protonated organic substance used in the calculations.

Table 2b – Thermodynamic data used in the calculations. All $\log \beta_{pqr}$ values are valid at 25°C and zero ionic strength or have been recalculated to zero ionic strength using Davies equation (1962)

Species	$\log \beta_{pqr}$	species	$\log \beta_{pqr}$
HCO_3^-	- 6.35 ^{f1}	CO_3^{2-}	-16.68 ^{f1}
HL^-	- 3.65 ⁱ	L^{2-}	- 8.81 ⁱ
OH^-	-14.00 ^{f1}	H_2PO_4^-	+ 7.20 ^{f1}
HSO_4^-	+ 1.99 ^{f1}		

- a) Baes and Mesmer (1976)
- b1) Clever *et al.* (1985). Recalculated from $I \equiv 0.5 \text{ mol} \times \text{dm}^{-3}$
- b2) Clever *et al.* (1985). Recalculated from $I \equiv 3.0 \text{ mol} \times \text{dm}^{-3}$
- c) Zirino and Yamamoto (1972)
- d) Dyrssen and Wedborg (1974)
- e) Mean values of data reported by Bilinski *et al.* (1976). Recalculated from $I = 0.1 \text{ mol} \times \text{dm}^{-3}$
- f1) Smith and Martell (1976)
- f2) Smith and Martell (1976). Recalculated from $I \equiv 0.5 \text{ mol} \times \text{dm}^{-3}$
- g) Dyrssen and Wedborg (1979). Recalculated from $I \equiv 0.7 \text{ mol} \times \text{dm}^{-3}$
- h) Lindsay (1979)
- i) Lövgren and Sjöberg (1989). Recalculation from $I \equiv 0.1 \text{ mol} \times \text{dm}^{-3}$
- j) Estimated from the oxalate complex stability

The values of the stability constants for the different bog water complexes K (MeL), (Me = Pb (II), Ca (II), Mg (II)) were calculated by adding the difference between $\log K(\text{CdL})$ and $\log K(\text{CdOx})$ to the different $\log K(\text{MeOx})$ - values.

For modelling system 1), the fresh water gradient, the equilibrium constants used were those valid at zero ionic strength; the ionic strength in these fresh waters is usually below $10^{-4} \text{ mol} \times \text{dm}^{-3}$. For system 2), the salt water gradient, the ionic strength varies from around $10^{-4} \text{ mol} \times \text{dm}^{-3}$ at the river mouth to $0.1 \text{ mol} \times \text{dm}^{-3}$ in the southern Gulf of Bothnia. All equilibrium constants for this system were recalculated to $0.01 \text{ mol} \times \text{dm}^{-3}$ and $0.1 \text{ mol} \times \text{dm}^{-3}$. Composition matrices with species and formation constants valid at zero ionic strength are given in Tables 2a and 2b.

Results and Discussion

The results of the various calculations are presented as distribution diagrams in Figs. 1-3. Species formed in fractions less than 2% of the total metal concentrations have been omitted.

Mercury (II) – speciation – As can be seen from Fig. 1a, nearly 90% of the

mercury is complexed to organic substances in the bog water at pH = 4. With increasing pH a deprotonation of the organic HgL-complex takes place and the corresponding complex is formed almost to 100 %.

This should be compared with the calculations of Mantoura *et al.* (1978) which were performed with pH 7.5-8.0. They found that more than 90 % of the mercury was complexed by humic materials in freshwaters.

In the estuarine environment a gradual change in the speciation takes place. According to Fig. 1b, the Hg (II)-organic complex is mainly transformed to various halide complexes.

In the southern part of Gulf of Bothnia in which the salinity has reached 6‰ the main species are HgCl_2 and HgCl_3^- , both formed to about 30 % of the total mercury. It can also be noted that the mixed HgClBr complex is calculated to form in significant amounts ($\approx 30\%$ at $S = 5\%$; $\text{pH} = 7.7$). In sea water ($S = 35\%$; $\text{pH} = 8.2$) the high chloride concentration implies that HgCl_4^{2-} and HgCl_3^- prevail, whereas bromo and mixed chloro-bromo complexes are formed in minor amounts, $\leq 5\%$ (Mantoura *et al.* 1978).

Cadmium (II) – speciation – It is well known that Cd (II) forms weak complexes with organic ligands in comparison with Hg (II) (Mantoura 1978; Bahan 1978). This fact is clearly shown in Fig. 2a, where the CdL complex never exceeds 15 % of total Cd (II) in the bog water/fresh water system. Instead the Cd^{2+} -ion predominates provided that the chloride concentration is low. In the estuary (*c.f.* Fig. 2b) a change in the speciation is noticed with increasing salinity. Similar to the mercury (II) system, chloro complexes become important with CdCl^+ prevailing at $S \geq 5\%$.

Lead (II) – speciation – Besides the Pb^{2+} -ion which predominates in bog water at $\text{pH} < 5.0$, the PbL complexes become important in the river water (*c.f.* Fig. 3a) with an optimum amount formed at $\text{pH} \approx 6$ (= 75 % of total Pb (II)). Besides forming quite stable chloro complexes, lead also form carbonato and bicarbonato complexes, the former becoming important as pH increase. Consequently, PbCl^+ and PbCO_3 are formed as the salinity and pH respectively is increased in the estuary (*c.f.* Fig. 3b).

In the Gulf of Bothnia, the fraction of lead complexed to the model organic ligand can be neglected, whereas PbCl^+ and PbCO_3 are formed to 28 and 24 % respectively. In the oceans, the corresponding figures are 11 and 83 % (Florence 1982).

Limitations of the models – The temperature in the Gulf of Bothnia and its catchment area usually varies between 0 and 20°C. Since most thermodynamic data of interest for this work are valid at 25°C, it became necessary to consider recalculation of the stability constants. However, the necessary data for these calculations were generally not available. Furthermore, temperature effects on logK are probably small in this narrow temperature range, and negligible compared with the uncertainties in the model.

Table 3 – The ranges of concentrations used in the model systems. Variations were made step-wise and simultaneously over 90 points. All concentrations are in mol dm⁻³ or -log₁₀ (mol×dm⁻³)

Component	Concentration (mol×dm ⁻³)	
	Fresh water gradients	Salt water gradient
Salinity	0	0-6‰
pH	4-7	7.0-7.9
[CO ₂ (aq)]*	10.7×10 ⁻⁶	10.7×10 ⁻⁶
[H ₂ L]	75-30×10 ⁻⁶	30-15×10 ⁻⁶
[Cl ⁻]	15-45×10 ⁻⁶	4.36-1.03**
[Br ⁻]	2.5×10 ⁻⁷	6.63-3.84**
[SO ₄ ²⁻]	15-105×10 ⁻⁶	4.02-2.31**
[HPO ₄ ²⁻]	5×10 ⁻⁸	1×10 ⁻⁷
[Mg(II)]	25-70×10 ⁻⁶	4.14-2.04**
[Ca(II)]	25-265×10 ⁻⁶	3.58-2.65**
[Hg(II)]	2.5×10 ⁻¹¹	2.5×10 ⁻¹¹
[Cd(II)]	1.0×10 ⁻⁹	1.0×10 ⁻⁹
[Pb(II)]	1.5×10 ⁻⁸	1.5×10 ⁻⁹

*) Equilibrium concentration of the species. **) -log₁₀ (mol×dm⁻³)

Fig. 1a

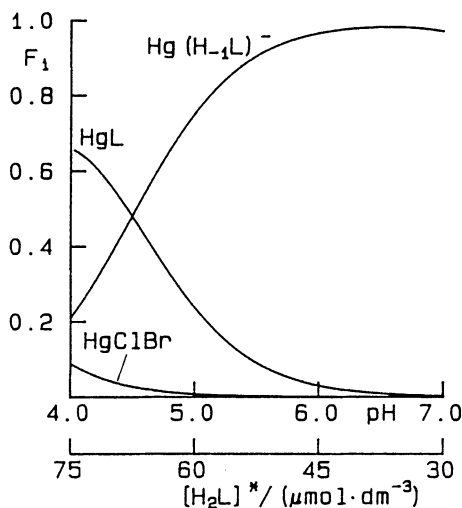


Fig. 1b

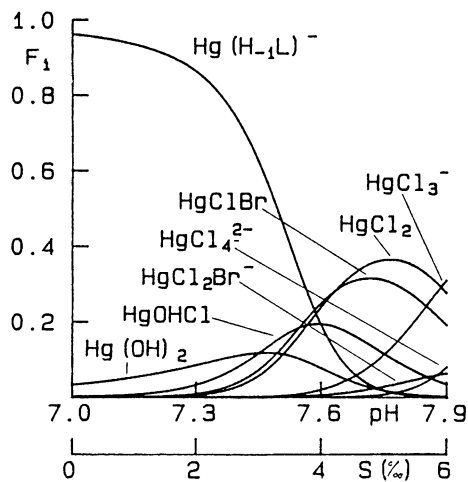


Fig. 1a, 2a and 3a. Distribution diagrams showing Hg (II), Cd (II) and Pb (II) speciation in a freshwater gradient. These diagrams are based on the changes in water composition from a bog-water to a river water. 6 parameters have been varied simultaneously through the diagram according to Table 3. The two most important of these, pH and the total concentration of the model organic ligand ([H₂L]*) are illustrated in the diagram. The equilibrium constants used in the calculations are valid at 0 mol×dm⁻³ ionic strength

Speciation Models for Hg, Cd and Pb

Fig. 2a

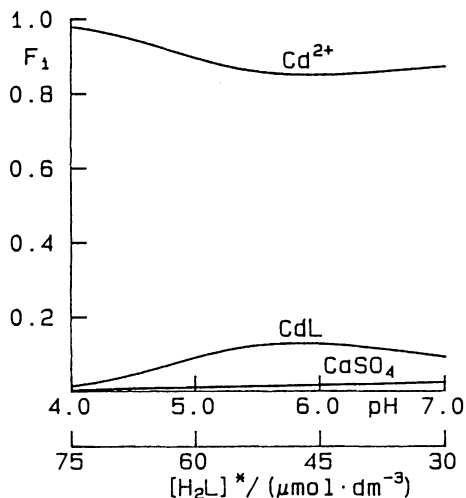


Fig. 2b

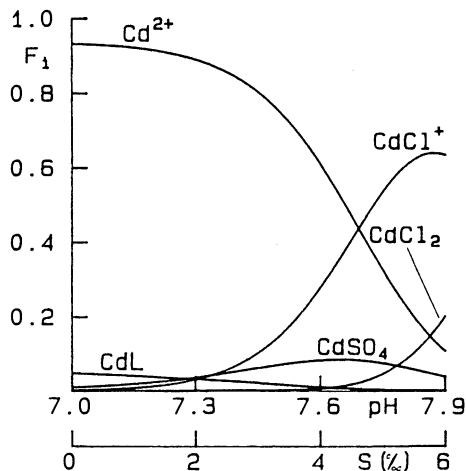


Fig. 3a

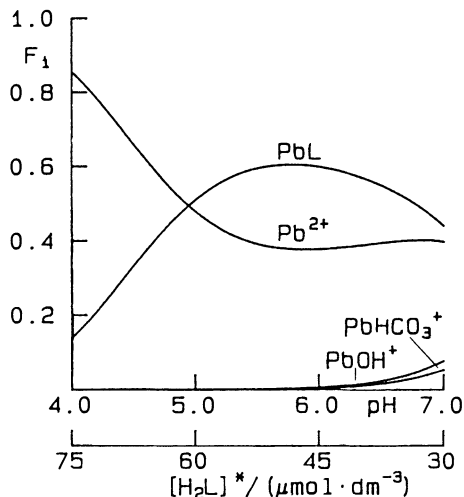


Fig. 3b

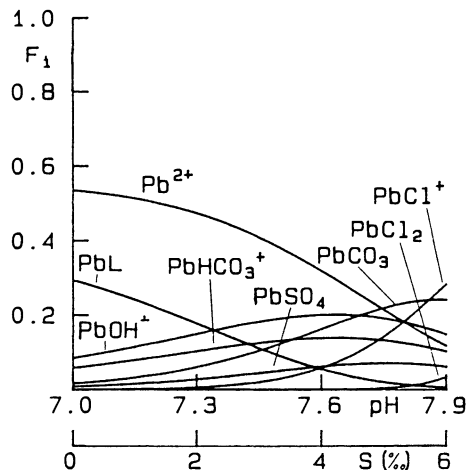


Fig. 1b, 2b and 3b. Distribution diagrams showing Hg (II), Cd (II) and Pb (II) speciation in an estuary of the Gulf of Bothnia. The salinity is varied from 0 to 6‰. The diagrams are based on the changes in water composition when river water runs into and mixes with water of the Gulf of Bothnia. 7 parameters have been varied simultaneously according to Table 3. The 2 most important, pH and salinity are illustrated in the diagram. The equilibrium constants used in the calculations are valid at 0.01 mol × dm⁻³ ionic strength.

Byrne, Kump and Cantrell (1988) have estimated the magnitude of these temperature effects for metal speciation in sea water. They found them to be small for the metal ions extensively complexed with chloride ions (< 0.5 %). However, for metal ions that are strongly hydrolyzed or which form stable carbonate complexes speciation is more influenced by temperature (1-2 % and up to 20 % respectively). The most pronounced effect was found for the fraction of PbCO_3 in sea water, which was calculated to decrease from 69 % at 25°C, to 50 % at 5°C.

This means that the only substantial temperature dependence for the speciation would be shown by Pb (II) in the estuary system. In this system, the formation of PbCO_3 is calculated to account for about 25 % of total Pb (II) concentration in the Gulf of Bothnia (pH = 7.9), but at lower temperatures this figure would then decrease.

In the present calculations, equilibrium with carbon dioxide pressure in air ($\text{CO}_2 = 10^{-3.5}$ atm) was assumed. This is an approximation because natural waters are often under or over saturated with CO_2 (aq) as a result of biological activity. It can therefore be expected that the carbonate complexes may be formed less or more extensively than indicated by these calculations. These effects would mainly affect the calculations made for the salt water gradient.

The stability constants for the salt water system were recalculated to $0.01 \text{ mol} \times \text{dm}^{-3}$ ionic strength. In the real system however, the ionic strength varies from about $0 \text{ mol} \times \text{dm}^{-3}$, up to $0.1 \text{ mol} \times \text{dm}^{-3}$ ($S \approx 6\text{‰}$). The deviations from the calculated models resulting from ionic strength effects are relatively small, but most pronounced at the endpoints in the system ($S \approx 0\text{‰}$ and $S \approx 6\text{‰}$). Generally, the equilibria will change so that higher charged species will be favoured by increasing ionic strength as a consequence of Davies equation. To quantify these effects for the endpoint of the salt water system ($S \approx 6\text{‰}$), a model calculation were performed with the equilibrium constants recalculated to $0.1 \text{ mol} \times \text{dm}^{-3}$ ionic strength.

For Hg (II) the relative amount of the species HgCl_4^{2-} will increase about 2 %, with minor effects on the other species. For Cd (II) the species Cd^{2+} will increase by 7 %, CdCl_2 and CdCl^+ decrease by 5 % and 1 %, respectively. The Pb (II) speciation will change so that the fraction of Pb^{2+} will increase 5 % and PbCl^+ decrease 5 %. The effects on the amounts of the other species are small.

The acid-base and metal complexing characteristics of the organic substance originating from bog water have been extrapolated to river waters and the Gulf of Bothnia. For the river waters, this is probably a good approximation since a large part of the organic materials in river waters is of a similar type, or originates from bog-waters. This assumption can be more questioned for the Gulf of Bothnia, since here some of the organic substances are due to algal and bacterial production, but the influence of river water is still significant (Pietikäinen 1978). There is a possibility that the complexing capacity from organic material of this origin should deviate significantly from the bog waters. This is probably of minor importance, since the

organic complexes are calculated to be nearly totally replaced by inorganic complexes in the southern Gulf of Bothnia (6‰), where the fraction organics of algal/bacterial origin would be largest.

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