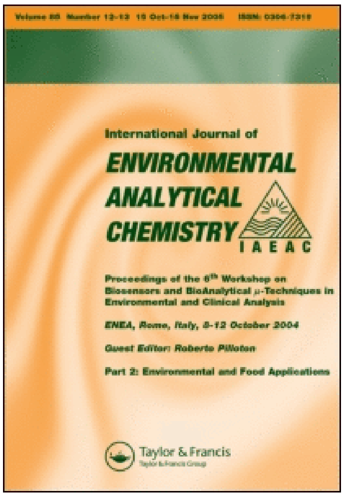

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STUDY OF A MODEL FOR THE INTERACTION BETWEEN HEAVY METALS AND SEDIMENTS OF THE PISUERGA RIVER

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We have applied a competitive model, first proposed by Mouvet and Bourg, to explain the interaction between the heavy metals zinc, cadmium, lead, nickel and cobalt and bottom sediments from the Pisuerga River. Two sampling sites were chosen, the first located on an urban sewer and the second downstream from the polluting zone. The calculated constants for the first sediment were always lower than those found for the second one. The validity of the model is demonstrated by the existence of a correlation between the calculated constants and the first hydrolysis constants of the metals examined. All metal determinations were made by means of voltammetric techniques.

KEY WORDS: Heavy metals, sediments, fluvial waters, voltammetry.

INTRODUCTION

Heavy metals have a great ecological significance due to their toxicity and accumulative behaviour.[1,2] Their environmental impact is enhanced by their non-biodegradability: heavy metals undergo a global eco-biological cycle[3] in which the fluvial systems play a main role as pathway. The impact of a given heavy metal on the biota will be a function of its mobility, which can be ascertained by means of the knowledge of its distribution between dissolved and particulate species, and for such a goal a theoretical model is essential.

Amongst the several mechanisms responsible for the exchange of trace metals across the interface water–solid matter,[4] adsorption/desorption is the most important one and can be described in terms of a heterogeneous complexation/dissociation of the metals with the surface of the particulate matter. Such a model was proposed by Mouvet and Bourg, who applied it to the Meuse river[5] and the Gironde estuary.[4]. The model implies a heterogeneous reaction between the heavy metals present in the dissolved state and on the active sites of the surface sediment:

$$(\text{S-OH})_n + \text{Me}^{2+} \rightleftharpoons (\text{S-O})_n\text{Me}^{(2-n)+} + n\text{H}^+. \tag{1}$$

The equilibrium constant can be written as:

$$\beta_a = \frac{[(\text{S-O})_n\text{Me}^{(2-n)+}][(\text{H}^+)^n]}{[(\text{S-OH})_n][\text{Me}^{n+}]} \tag{2}$$

The active sites of the surface sediments are assumed to be of the S-OH type, and can be protonated or deprotonated at extreme pH values, giving $(S\text{-}OH_2)^+$ (at low pH) and $(S\text{-}O)^-$ (at high pH), respectively. Therefore, the uptake of heavy metals by the sediment can be seen as a competition between H_3O^+ and the metals for the active sites. The values of β_a are determined by carrying out adsorption experiences of known amounts of the heavy metals at different pH values, measuring the pH and the metal concentration remaining in solution. The value of $[(S\text{-}OH)_n]$, i.e. the concentration of active sites of the sediment which is necessary for the calculation of β_a, is identified with the maximum surface charge of the sediment, σ_m, determined by means of acid-base titrations.[5]

In this paper we have applied the above model to the distribution of several heavy metals (zinc, cadmium, lead, nickel and cobalt) between the dissolved state and sediments of the Pisuerga River at its passage through the town of Valladolid, a zone already studied by us in previous work on speciation of heavy metals in waters[6] or sediments.[7]. The calculation of the stability constants is described, and the validity of the model is tested by correlating the β_a values of the interaction reaction and the first hydrolysis constant of the metals considered.[8,9]

EXPERIMENTAL

Sampling Zone

The town of Valladolid (ca. 400000 habitants) is the capital of the Comunidad of Castilla y León in central Spain, as well as the greatest industrial agglomeration of that region. The Pisuerga River flows through the town, and it is polluted by industrial and urban effluents (see Figure 1). In previous work,[6,7] we have already located a series of sampling sites covering several environmental situations. In this case we have chosen two points. Point 1 (Rosaleda) is located on an urban sewer, while Point 2 (Simancas) is 10 km downstream from the town, that is after all municipal and industrial residues have been collected. Bottom sediments were collected at these sites and analyzed, using standard methods[10] to determine the parameters shown in Table 1. As can be seen, the Rosaleda sediment has a greater loading of heavy metals, being more polluted than the Simancas one.

Apparatus

Heavy metals were always determined by voltammetric techniques, using a Polarecord Metrohm E506 in combination with a Metrohm VA663 electrode stand, and a Metrohm E608 control unit used to control the parameters of the stripping steps. A HMDE was the working electrode with a Pt counter-electrode and a AgCl/Ag reference electrode. The pH was measured with a Metrohm 654 pH meter and a Metrohm 6.0202.000 combined glass electrode.

Reagents

Carlo Erba RPE ACS grade standard solutions of 1000 mg/l were used for the

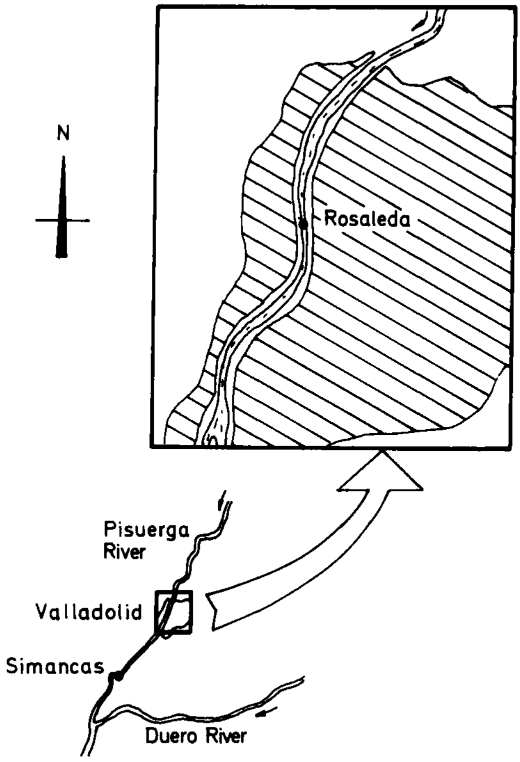

Figure 1 Map of the area studied showing the sampling sites.

Table 1 Analysis of the sediments

Sediment	H_2O^a	*800 °C*^{a}	$CaCO_3^a$	*Org. C*^{a}	*Org. N*^{a}	*Zn*^{b}	*Cd*^{b}	*Pb*^{b}	*Ni*^{b}	*Co*^{b}
Rosaleda	73.81	22.12	14.22	5.11	1.70	429.1	2.2	30.2	92.1	85.8
Simancas	38.02	5.86	7.89	2.60	1.99	182.7	0.2	13.6	18.1	5.7

[a] Percentage refers to dried sample.
[b] μg/g of dried sample.

heavy metals. Less concentrated solutions were made by dilution, using a GILSON 100 μl micropipette. The other reagents were of analytical-grade quality; de-ionized water was used throughout.

Procedures

Sediment conditioning After collection, the sediments were washed with a mixture of 0.1 M EDTA and 0.1 M HNO_3, and then rinsed with de-ionized water until constant pH of the supernatant liquid. In this way, the heavy metals present at the sediment surface are eliminated: the active sites are in the R-SOH form—the sediment becomes "activated".

Determination of the active site concentration Different samples all containing 50 mg of conditioned sediments, were equilibrated for 36 h in 50 ml of solutions of varying pH, obtained by adding the necessary amount of HNO_3 (C_a) or KOH (C_b) standard solutions, and measuring the final pH of the solution. The curve was calculated according to Eq. (5) below by using the values of both C_a (or C_b) and final pH, and taking into account that the sediment was present in a concentration of 1 g/l.

Adsorption experiments Different 50 mg samples of the sediment were mixed with 50 ml of solutions containing 5.10^{-6} M concentrations of all five metals studied, as well as the necessary amounts of KOH or HNO_3 to give a pH value of between 1 and 12. The resulting suspensions were equilibrated for 36 h and the sediments filtered off, after which the pH and the metal concentrations left in solution were measured.

All equilibrations were made with continuous stirring and the ionic strength of the solutions was always adjusted to 0.0091, the mean value of the Pisuerga River, with KNO_3. Wet sediments were used to avoid variations of the surface characteristics; however, all results are given related to dried samples.

Metal determination Zn, Cd and Pb were determined by means of differential pulse anodic stripping voltammetry (DPASV) at pH 4.7. The experimental parameters were: deposition potential, −1.2 V; deposition time, 60 s (with stirring) plus 30 s (rest time); superimposed potential, −50 mV. For Co and Ni differential pulse adsortive stripping voltammetry was used (DPAdSV) at pH 9.3 in the presence of 10^{-4} M dimethylglyoxim. The experimental parameters were: deposition potential, −0.6 V; deposition time as above; superimposed potential, 50 mV. All determinations were made at 25 °C after de-aeration with nitrogen for 10 min. No further treatment of the sample (apart from the filtration step indicated above) was necessary, but to avoid any problems deriving from differences in the analytical matrix of the solutions, an automated standard addition method was used.[11]

RESULTS AND DISCUSSION

Concentration of Active Sites

As was indicated above, in order to calculate the β_a values (see Eq. (2)), the total concentration of active sites in the sediment surface, C_0,, must be known. This determination is carried out by means of batch acid-base titrations as indicated in the Procedures section. The assumption of the identity between C_0 and the maximum surface charge, σ_m, is based upon the following considerations:

If we assume that the active sites of the sediments are of the S-OH type, a charge balance in our acid-base titrations leads to the expression:

$$[H_3O^+]+[K^+]+[S\text{-}OH_2^+]=[OH^-]+[NO_3^-]+[S\text{-}O^-] \qquad (3)$$

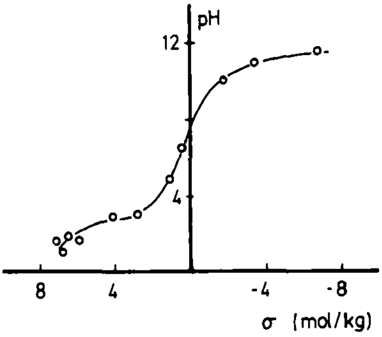

Figure 2 σ vs. pH plot for the Rosaleda sediment.

since K^+ and NO_3^- are the only ions added (as KOH or HNO_3, to adjust the ionic strength and to change the pH). At low pH values, $[OH^-]$ and $[S\text{-}O^-]$ are negligible, $[K^+]$ equals $[KNO_3]$ added to adjust the ionic strength, while $[NO_3^-]$ equals the sum of $[KNO_3]$ and $[HNO_3]$ added to reach the final pH. That is, $[S\text{-}OH_2^+]$ can be identified with the total concentration of active sites, C_0, and the above equation is simplified to:

$$C_0 = C_a - [H_3O^+] \tag{4}$$

C_a being the HNO_3 concentration added and $[H_3O^+]$ the equilibrium acidity obtained from the pH measurement.

The calculation of σ, the surface charge of the sediment, is based upon similar assumptions, giving:[12]

$$\sigma = C_a - C_b - [H_3O^+] + [OH^-] \tag{5}$$

which is identical to Eq. (4) at low pH when no base is added (and therefore $C_b = 0$), showing the validity of the identity initially made. Equation 5 gives a result in moles/l, that is converted to moles/kg by taking into account the concentration of the sediment in the solution (1 g/l) and its water content.

Figure 2 shows an example of a σ vs. pH curve for the Rosaleda sediment. The maximum value found for σ is taken as a measurement of C_0. The mean values of 4 replicates were 7.3 mol/kg for the Rosaleda sediment, and 6.8 mol/kg for the Simancas sediment. These values are high, at least when compared with that given by Mouvet and Bourg for the Meuse river (1.3 mol/kg), but these authors increased that value to 8.0 mol/kg to achieve better agreement between calculated and observed values for the distribution of trace metals between the dissolved and particulate state.[5] The increase is justified by the authors on the basis of dissolution of the active superficial coating of the sediments caused by the washing

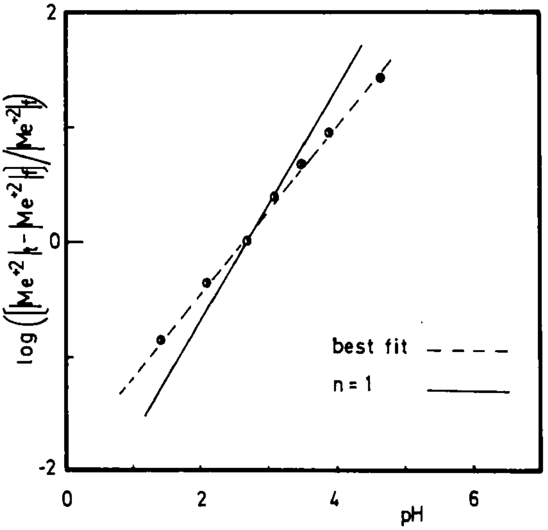

Figure 3 Plot of $\log\{([Me^{2+}]_t - [Me^{2+}]_f)/[Me^{2+}]_f\}$ vs. pH for lead adsorption on the Rosaleda sediment.

acids used in the conditioning step; that is, we can suppose that such a dissolution process does not take place in our case.

Determination of the Constants

Simple rewriting of Eq. (2) gives:

$$\log\frac{[(S\text{-}O)_nMe^{(2-n)}]}{[Me(II)]} = \log(\beta_a * [(S\text{-}OH)_n]) + n\,pH \tag{6}$$

As $[(S\text{-}O)_nMe^{(2-n)}]$ is the metal concentration not remaining in solution, the above expression can be written as:

$$\log\frac{[Me^{+2}]_t - [Me^{+2}]_f}{[Me^{+2}]_f} = \log(\beta_a * [(S\text{-}OH)_n]) + n\,pH \tag{7}$$

where $[Me^{+2}]_t$ is the total metal concentration added and $[Me^{+2}]_f$ the free metal present in the dissolved state. By preparing different solutions with the same total metal concentration, $[Me^{2+}]_t$, and different pH values, as indicated in the Procedures section, the determination of both the pH and $[Me^{2+}]_f$ permits to calculate the l.h.s. of Eq. (6), so we can find the values of $\log(\beta_a * [(S\text{-}OH)_n])$ and n by means of a least-squares fit of the term vs. pH. Although this "free" adjustment will lead to an optimum n value, its chemical significance will be zero. Mouvet and Bourg[5] noted this problem and consequently only adjusted their experimental data to integer values of n. In our case, as can be seen from Figure 3, which shows a

Table 2 Values of the adsorption and hydrolysis constants

		log β_a	
Metal	*log k_{OH}*	*Rosaleda*	*Simancas*
Zinc	−9.0	−2.85	−2.73
Cadmium	−10.1	−3.35	−3.05
Lead	−7.7	−0.57	−0.40
Nickel	−9.9	−3.16	−2.56
Cobalt	−9.7	−1.96	−1.61

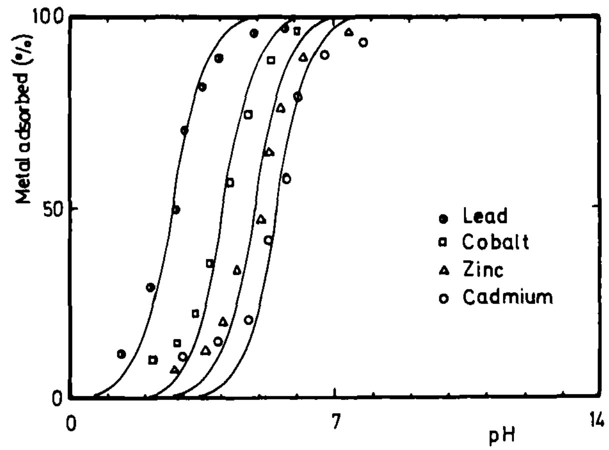

Figure 4 Adsorption of heavy metals by the Rosaleda sediment (curves are calculated values; nickel data are not shown for the sake of clarity).

plot of the l.h.s. of Eq. (7) vs. pH for an adsorption experiment of lead and the Rosaleda sediment, a "free" least-squares fit always leads to *n* values smaller than unity. Amongst the integer *n* values tested by us, the best results were obtained with $n=1$, so this value was consequently adopted in all cases (see Figure 3).

Table 2 shows the $\log\beta_a$ values (mean of 3 determinations) as well as data for $\log k_{OH}$, the first hydrolysis constant of the heavy metals.[13] Figure 4 shows the experimentally determined percentages of metal adsorbed by the sediment at different pH values, as well as the theoretical adsorption behaviour expected from the use of the β_a and C_0 values given in Table 2. As can be observed, the values for both sediments are similar, although the results for the Simancas sediment are, on an average, two-fold higher than those for Rosaleda, indicating that the latter sediment will retain the heavy metals to a lesser extent.

Validity of the Model

For a given solid surface, there exists a correlation[4,5,8,9] between the formation

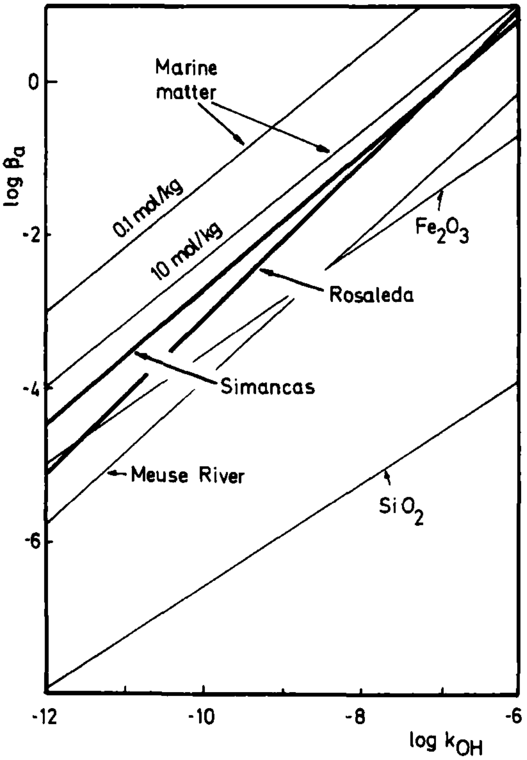

Figure 5 Correlations between surface stability constants and first hydrolysis constants of the metals (SiO_2 from ref. 8; Fe_2O_3 and marine matter from ref. 9; Meuse sediments from ref. 4).

constants of the metal surface complexes, and the first hydrolysis constants[13] of the same metals. In our case we have found a good correlation for the two sediments examined, the values of the fit being:

$$\text{Rosaleda sediment: } \log \beta_a = 1.006 \log k_{OH} + 6.96$$

$$\text{Simancas sediment: } \log \beta_a = 0.884 \log k_{OH} + 6.14.$$

Figure 5 shows the regression lines obtained, as well as other fits found in the literature for different metallic oxides,[8] marine particulate matter[8] and Meuse river sediments.[4] The values for the Pisuerga River agree well with those given by other authors. The regression equations found add to the credibility of the model proposed by Mouvet and Bourg, and permits an estimate of the $\log \beta_a$ value for other heavy metals not studied here.

CONCLUSIONS

We can conclude that the interaction between heavy metals and sediments from the Pisuerga River can be explained by means of a model based on a competitive reaction between H_3O^+ and the metals present in the dissolved state, for the active sites of the sediment surface. The correlation found between the constants of the model and the first hydrolysis constants of the metals studied will permit a prediction of β_a values for other metals.

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References

1. G. G. Leppard (Ed.), *Trace Element Speciation in Surface Waters* (Plenum Press, New York, 1983).
2. D. Purves, *Trace Element Contamination of the Environment* (Elsevier, Amsterdam, 1985).
3. H. W. Nürnberg, in: *Electrochemistry in Research and Development* (R. Kalvoda and R, Parsons, eds.) (Plenum Press, New York, 1985), p. 121.
4. A. C. M. Bourg and C. Mouvet, in: *Complexation of Trace Metals in Natural Waters* (C. J. M. Jramer and J. C. Duinker, eds.) (Martinus Nijhoff/Dr W. Junk Publishers, The Hague, 1984).
5. C. Mouvet and A. C. M. Bourg, *Water Res.*, **17**, 641 (1983).
6. R. Pardo E. Barrado, A. Arranz, J. M. Pérez and M. Vega, *Intern. J. Environ. Anal. Chem.*, **37**, 117 (1989).
7. R. Pardo, E. Barrado, L. Pérez and M. Vega, *Water Res.*, **24**, 373 (1990).
8. P. W. Schindler, B. Fuerst, R. Dick and P. U. Wolf, *Colloid. Jnterface Sci.*, **55**, 469 (1976).
9. L. Balistrieri, P. G. Brewer and J. W. Murray, *Deep-Sea Res.*, **28A**, 101 (1981).
10. Commission of the European Communities. Workshop on Standardization of Analytical Methods for Manure, Soils, Plants and Waters. Gent, 1978.
11. R. Pardo, E. Barrado, M. L. Tascón and M. D. Vázquez, *Quim. Anal.*, **8**, 121 (1989).
12. J. A. Davis, R. O. James and J. O. Leckie, *J. Colloid. Interface Sci.*, **63**, 480 (1978).
13. R. M. Smith and A. E. Martell, *Critical Stability Constants*, vol. 4, *Inorganic Complexes* (Plenum Press, New York, 1976).