

# Heavy Metal Pollution in Rivers and Estuaries

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## 1 Introduction

The presentation given by Dr C. Ridgway at the opening of the Study Group detailed some of the processes that occur during the generation of electrical power. Recent legislation has led to a tightening of waste disposal restrictions. As a result Powergen is involved in modelling the emission of wastes and how these wastes are adsorbed into the environment. The company has a team modelling these physical processes using a sophisticated computer package called IMPAQT.

## 2 Dependence of the adsorption of heavy metal ions on pH

The IMPAQT computer code requires the input of certain physical values such as reaction coefficients and partition constants. These must be obtained experimentally.

It has been found that the adsorption of heavy metals into sediment has a strong dependence on the pH of the river. Since pH varies from river to river and also seasonally, it is desirable that, once experiments have been performed that determine how a metal is adsorbed under certain conditions, the data found may be used to describe adsorption under other conditions.

Experiments show that the percentage of a particular metal that is adsorbed follows an 'S' curve-like dependence on the pH as shown in Figure 1. We have developed a model to describe this dependence. We suppose that on the surface of sediment there are a number of sites,  $X^-$ , onto which aqueous metal ions,  $Me^{2+}$ , may bind. The metal ions are in competition for these sites with aqueous hydrogen ions,  $H^+$ . The relevant reactions may be written



Figure 2 schematically shows the process. If the reactions are in equilibrium we obtain

$$\alpha[H][X] = [HX], \quad (3)$$

$$\beta[Me][X]^2 = [MeX_2], \quad (4)$$

where  $\alpha$  and  $\beta$  are the partition coefficients for the two reactions. If there is a fixed concentration of binding sites then

$$[X] + 2[MeX_2] + [HX] = L_1, \quad (5)$$

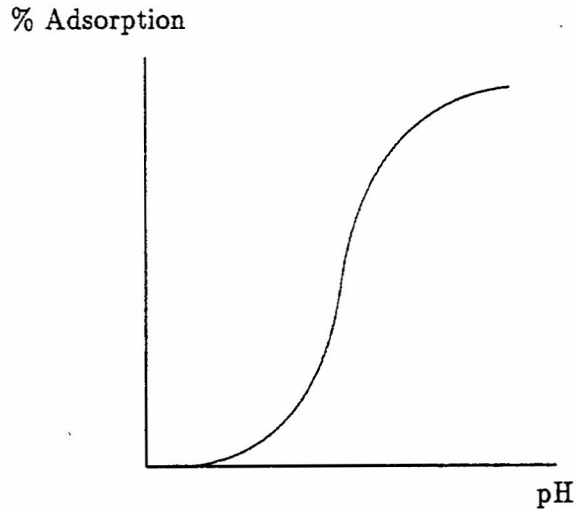


Figure 1: Adsorption vs pH (schematic)

and similarly the total amount of metal in the system is also conserved

$$[Me] + [MeX_2] = L_2. \quad (6)$$

The proportion of metal that has been adsorbed is given by  $[MeX_2]/L_2$ , and the concentration of hydrogen ions  $[H]$  is given by

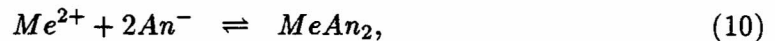
$$[H] = 10^{-pH}. \quad (7)$$

Expressions (3) to (6) are four equations with four unknowns ( $[H]$  is determined from the pH). The solution,  $[MeX_2]$  as a function of  $[H]$ , satisfies the cubic equation

$$\begin{aligned} \beta L_1^2 L_2 - (1 + 2\alpha[H] + \alpha^2[H]^2 + \beta L_1^2 + 4\beta L_1 L_2)[MeX_2] + \\ + (4\beta L_1 + 4\beta L_2)[MeX_2]^2 - 4\beta[MeX_2]^3 = 0. \end{aligned} \quad (8)$$

The dependence of the quantity adsorbed on the amount of sediment present is controlled through the parameter  $L_1$ .

As an aside we note that the dependence on the presence of anions, e.g.  $Cl^-$  may be modelled by the inclusion of two more reactions (and therefore two more reaction equilibrium expressions)



so that the sites are in competition with the anions for the metal and hydrogen ions.

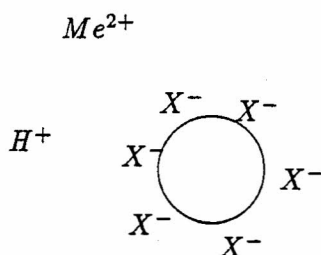


Figure 2: Competition of metal and hydrogen ions for surface sites (schematic)

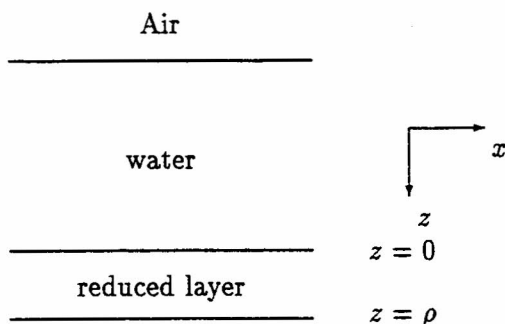


Figure 3: Schematic of river

### 3 Generalised Model

In this section we perform analysis that describes the steady state behaviour of the IMPAQT model. However we will ignore the presence of the oxidized layer and assume that there is only one reduced layer as shown in Figure 3. We present a general model that describes the movement of  $N$  mobile species (including dissolved ions, complexes and emulsions). We assume, however, that all mobile species have the same diffusivities and the same rate of transfer  $k$  between the water column and the reduced layer. In common with the IMPAQT model we assume that the water column is well mixed vertically so that the concentration of species within the water column is independent of depth. The variable  $x$  denotes the position downstream of the outflow and  $z$  the position measured from the top of the reduced layer. We assume that the reduced layer is of constant depth  $\rho$  and that the water is flowing downstream with constant velocity  $v$ .

We introduce the following notation

$$c_i(t, x) = \text{Concentration of species } i \text{ in water column,}$$

$$b_i(t, x, z) = \text{Concentration of species } i \text{ in reduced layer,}$$

and choose the units of  $c_i$  and  $b_i$  so that they have equal activity at the interface. The conversion (reaction) between the species in the water column and the species in the reduced layer is then described by  $c_i(t, x) = b_i(t, x, 0)$  for each  $i = 1, \dots, N$ .

The movement of species  $i$  within the river, the reaction with other species and the exchange with the reduced layer is then described by

$$\frac{\partial c_i}{\partial t} = D \frac{\partial^2 c_i}{\partial x^2} - v \frac{\partial c_i}{\partial x} + R_i(\tilde{c}) - k(c_i - b_i(t, x, 0)), \quad (11)$$

where  $D$  is the diffusivity of the species within the water column and  $R_i$  is the gain or loss of species  $i$  due to generation or removal due to reaction with or by other species.

Movement within the reduced layer is described by

$$\frac{\partial b_i}{\partial t} = d \frac{\partial^2 b_i}{\partial z^2} + r_i(\tilde{b}) + \hat{d} \frac{\partial^2 b_i}{\partial x^2} - v_i \frac{\partial b_i}{\partial x}, \quad (12)$$

where  $d$  is the diffusivity in the  $z$  direction,  $\hat{d}$  is the diffusivity in the  $x$  direction and  $v_i$  represents convection in the  $x$  direction due to flow effects caused by the motion of the water in the water column. We neglect the last two terms in equation (12) since diffusion and advection in the water column will dominate movement of species in the  $x$  direction.

The boundary conditions for equations (11) and (12) are given by

$$c_i = c_i^{dump} \text{ at } x=0, \quad (13)$$

$$-d \frac{\partial b_i}{\partial z} = k(c_i - b_i) \text{ at } z=0, \quad (14)$$

$$\frac{\partial b_i}{\partial z} = 0 \text{ at } z=\rho. \quad (15)$$

In the water the reactions are fast and are therefore in equilibrium. To understand how the various species diffuse and convect it is necessary to take combinations of the equations which cancel the reaction terms. The appropriate form of the model is then, say,  $J$  diffusion equations and  $N - J$  reaction equilibrium expressions. There are  $J$  constant linearly independent vectors  $\tilde{\mathbf{n}}_j \in R^N$  such that

$$\tilde{\mathbf{n}}_j \cdot \tilde{\mathbf{R}} = 0 \text{ for } j = 1, \dots, J \text{ and all } c. \quad (16)$$

We then introduce  $J$  new variables  $X_j$  which are given by

$$X_j = \tilde{\mathbf{n}}_j \cdot \tilde{\mathbf{c}} \text{ for } j = 1, \dots, J. \quad (17)$$

The equilibrium expressions transform in the same way

$$c_i = c_i^{eq}(\tilde{\mathbf{X}}), \quad X_j^{eq} \equiv \tilde{\mathbf{n}}_j \cdot \tilde{\mathbf{c}}^{eq}(\tilde{\mathbf{X}}) = X_j, \quad (18)$$

where  $\tilde{\mathbf{c}}^{eq}(\tilde{\mathbf{X}})$  is the equilibrium value of  $c_j$  at concentration  $X_j$ . The model in the water column may thus be written

$$\frac{\partial X_j}{\partial t} = D \frac{\partial^2 X_j}{\partial x^2} - v \frac{\partial X_j}{\partial x} - k(X_j - B_j(t, x, 0)), \quad (19)$$

$$X_j = X_j^{dump} \text{ at } x = 0, \quad (20)$$

where

$$B_j = \tilde{n}_j \cdot \tilde{\mathbf{b}} \quad (21)$$

for  $j = 1, \dots, J$ . We choose the rest of the  $\tilde{n}_j$ 's for  $j = J + 1, \dots, N$  to be linearly independent, and let

$$B_j = \tilde{n}_j \cdot \tilde{\mathbf{b}} \quad (22)$$

for  $j = J + 1, \dots, N$ . The governing equations in the reduced layer may now be written

$$\frac{\partial B_j}{\partial t} = d \frac{\partial^2 B_j}{\partial z^2} + \tilde{r}_j(\tilde{\mathbf{B}}) \text{ for } 0 < z < \rho, \quad (23)$$

with boundary conditions

$$-d \frac{\partial B_j}{\partial z} = k(c_j^{eq}(\tilde{\mathbf{X}}) - B_j) \text{ at } z = 0, \quad (24)$$

$$\frac{\partial B_j}{\partial z} = 0 \text{ at } z = \rho, \quad (25)$$

where

$$c_j^{eq}(\tilde{\mathbf{X}}) = \tilde{n}_j \cdot \tilde{\mathbf{c}}^{eq}(\tilde{\mathbf{X}}) = \begin{cases} X_j & j = 1, \dots, J, \\ \text{complicated} & j = J + 1, \dots, N. \end{cases} \quad (26)$$

We now look at some limiting cases of the above model.

### 3.1 Fast vertical transport through reduced layer

In this case there is no  $z$  dependence in the reduced layer and we obtain (to leading order)

$$B_j(t, x, z) = B_j(t, x), \quad (27)$$

$$\frac{\partial B_j}{\partial t} = \frac{k}{\rho} (c_j^{eq}(\tilde{\mathbf{X}}) - B_j) \text{ for } j = 1, \dots, N, \quad (28)$$

$$\frac{\partial X_j}{\partial t} = D \frac{\partial^2 X_j}{\partial x^2} - v \frac{\partial X_j}{\partial x} - k(X_j - B_j) \text{ for } x > 0, j = 1, \dots, J. \quad (29)$$

Over long timescales we can expect (29) to come to a steady state whereas (28) will evolve. If we neglect diffusion, behaviour on this timescale in the water column may be written

$$\frac{\partial X_j}{\partial x} = -\frac{k}{v} (X_j - B_j) \text{ with } X_j = X_j^{dump} \text{ at } x = 0. \quad (30)$$

### 3.2 Fast reaction in reduced layer

If the reactions in the sediment are also in equilibrium then we change the equations into conservation form (in the same way as we did for those in the water column). We have

$$B_j = B_j^{eq}(Y_1, Y_2, \dots, Y_s), \quad (31)$$

$$Y_s = \tilde{\mathbf{m}}_s \cdot \tilde{\mathbf{B}}_j, \quad (32)$$

where the  $\tilde{\mathbf{m}}_s$ 's are again linearly independent constant vectors chosen so that

$$\tilde{\mathbf{m}}_s \cdot \tilde{\mathbf{r}} = 0 \text{ for } s = 1, \dots, S \text{ and all } B.$$

Having removed the reaction terms in this fashion the model now reads

$$\frac{\partial Y_s}{\partial t} = d \frac{\partial^2 Y_s}{\partial z^2} \text{ for } 0 < z < \rho \text{ and } s = 1, \dots, S. \quad (33)$$

The boundary condition at the interface for equation (33) is

$$-d \frac{\partial Y_s}{\partial z} = k(\tilde{\mathbf{m}}_s \cdot \tilde{\mathbf{c}}^{eq}(\tilde{\mathbf{X}}) - Y_s) \text{ at } z = 0, \quad (34)$$

and the condition at  $z = \rho$  is the usual one of no flux

$$\frac{\partial Y_s}{\partial z} = 0. \quad (35)$$

Equilibrium is described by

$$B_j \equiv B_j^{eq}(\tilde{\mathbf{Y}}). \quad (36)$$

The behaviour in the water column is described by

$$\frac{\partial X_j}{\partial t} = D \frac{\partial^2 X_j}{\partial x^2} - v \frac{\partial X_j}{\partial x} - k(X_j - B_j^{eq}(\tilde{\mathbf{Y}}(t, x, 0))) \text{ for } j = 1, \dots, J, \quad (37)$$

with boundary condition

$$X_j = X_j^{dump} \text{ at } x = 0,$$

and reaction equilibrium equations

$$c_j = c_j^{eq}(\tilde{\mathbf{X}}).$$

We see that as far as the water in the river is concerned the only factor governing behaviour is chemical equilibrium and that the reaction rates do not appear, i.e. we have eliminated reaction terms from all of the diffusion equations.

### 3.3 Fast reaction and transport

In this subsection we discuss the limiting case where both reaction and transport are fast in the sediment.

The concentration of each of the species in the reduced sediment is now independent of depth, i.e.  $Y_s(t, x, z) = Y_s(t, x)$ , and we have

$$\frac{\partial Y_s}{\partial t} = \frac{k}{\rho} (\tilde{\mathbf{m}}_s \cdot \tilde{\mathbf{c}}^{eq}(\tilde{\mathbf{X}}) - Y_s) \text{ for } s = 1, \dots, S, \quad (38)$$

$$\frac{\partial X_j}{\partial t} = D \frac{\partial^2 X_j}{\partial x^2} - v \frac{\partial X_j}{\partial x} - k(X_j - B_j^{eq}(\tilde{\mathbf{Y}})) \text{ for } j = 1, \dots, J, \quad (39)$$

$$X_j = X_j^{dump} \text{ at } x = 0, \quad (40)$$

$$c_j \equiv c_j^{eq}(\tilde{\mathbf{X}}), \quad (41)$$

$$B_j \equiv B_j^{eq}(\tilde{\mathbf{Y}}). \quad (42)$$

Equation (38) describes the evolution of the reduced layer, equation (39) describes the behaviour in the water column and equations (41) and (42) gives the reaction equilibrium expressions.

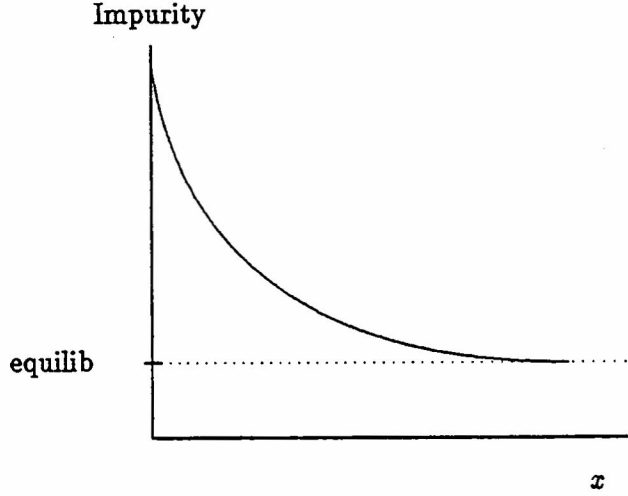


Figure 4: Long time behaviour of the IMPAQT model

### 3.4 IMPAQT model

The IMPAQT model takes the concentrations of  $\text{H}_2\text{S}$ ,  $\text{S}^{2-}$  and  $\text{HS}^-$  in the reduced layer to be constant. The equation describing the reduced layer would thus be of the form

$$B_j^{eq}(\tilde{Y}) = \text{constant} = B_j^{eq}.$$

The concentration of metal ions is described by

$$\frac{\partial X_j}{\partial t} = D \frac{\partial^2 X_j}{\partial x^2} - v \frac{\partial X_j}{\partial x} - k(X_j - B_j^{eq}(\tilde{Y})) \text{ for } j = 1, \dots, J, \quad (43)$$

$$X_j = X_j^{dump} \text{ at } x = 0, \quad (44)$$

$$c_j \equiv c_j^{eq}(\tilde{X}). \quad (45)$$

The steady state (large time) solution is obtained by discarding the time derivative in (43). The solution takes the form

$$X_j = B_j^{eq} + (X_j^{dump} - B_j^{eq}) \exp\left(-\frac{(\sqrt{v^2 + 4Dk} - v)x}{2D}\right). \quad (46)$$

Expanding the square root gives the leading order behaviour, namely exponential decay,

$$X_j = B_j^{eq} + (X_j^{dump} - B_j^{eq}) \exp\left(-\frac{kx}{v}\right). \quad (47)$$

### 3.5 Summary

In this section we have outlined a basic model describing the movement and adsorption of impurities in a simplified aquatic environment. We now review the strategy used in deriving and analysing the mathematical model.

Equations (11) and (12), which describe the relevant processes, contain linear diffusion/convection terms and reaction terms that describe the binding of heavy metal ions with sediment particles and the precipitation of heavy metal compounds. When formulating the model we assumed that the species had similar diffusivities. Making this assumption enables the coupled reaction-diffusion equations to be written instead as a lesser number of such equations together with a number of explicit reaction equilibrium expressions. These new equations are based on variables that are linear combinations of the original concentrations (so called pseudo species).

Three limiting cases of the parameters were considered. These basically dealt with how rapidly the reduced layer could remove impurity from the water column. The impurity is either removed by diffusion into the deep bulk of the reduced layer or by reaction with the  $\text{H}_2\text{S}$ ,  $\text{S}^{2-}$  and  $\text{HS}^-$  ions within the reduced layer. These cases were discussed in sections 3.1 and 3.2 respectively.

In section 3.4 we make the comment that the IMPAQT model takes the concentration of anions within the reduced layer to be very large compared with impurity concentrations thus leading to a further simplification in the equations describing the reduced layer. Making this assumption means that the reduced layer will effectively never lose its ability to adsorb heavy metal impurities as the anions cannot be depleted.

As an extension to the model, the authors suggest that spillages (whereby large amounts of contaminant are discharged over a short period of time) could also be accurately described with an appropriate change of boundary and initial conditions. The model would then consist of equations (11) and (12) together with an initial condition describing an initial impurity distribution (perhaps a delta function).