

# **TRANSPORT OF TOXIC CHEMICALS THROUGH SOILS: AN ENVIRONMENTAL CHALLENGE FOR THE MINING INDUSTRY**

**16**

*Ricardo Melamed*

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### TRANSPORT OF TOXIC CHEMICALS THROUGH SOILS:

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FOR THE MINING INDUSTRY

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MCT CNPq CETEM

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## PRESENTATION

**A**n ever increasing concern is being placed on the transport of toxic substances in the environment, soils not being the exemption.

*This monography, by Dr. Melamed, will be of great interest to the reader that is anxiously searching for studies that focuses on sorption mechanisms as results of interactions between mineral surfaces and toxic substances.*

*Rio de Janeiro, May, 1997.*

**Roberto C. Villas Bôas**  
**Director**

## CONTENTS

|  |    |
|--|----|
| ABSTRACT/RESUMO .....                        | 1  |
| 1. INTRODUCTION .....                        | 3  |
| 2. SPECIATION IN SOLUTION .....              | 4  |
| 3. THE ELECTRIFIED SURFACE OF MINERALS ..... | 6  |
| 4. ARSENIC SORPTION .....                    | 8  |
| 5. MERCURY CHEMISTRY .....                   | 16 |
| 6. NITRATE EXCLUSION .....                   | 22 |
| 7. CONCLUSION .....                          | 26 |
| REFERENCES .....                             | 27 |

## ABSTRACT

The quality of ground and surface waters should be of primary concern in a rational waste and tailings disposal technology. However, even after stabilization of toxic elements in the tailings, natural processes at the disposal site, may lead to dissolution and mobilization of toxic compounds, from the substrate to the soil underneath. In this case, the sorption phenomena in soils play a key role, which determines the transport of toxic compounds to receiving waters, and consequently their fate. This paper describes the importance of sorption mechanisms, as a result of the type of surface-chemical interaction, on the mobility of toxic chemicals. Specific oxyanion adsorption, metal adsorption and anion exclusion were highlighted. The effects of different physico-chemical parameters on the mobility of As, Hg and nitrate were emphasized.

**Key words:** specific adsorption, nucleation, speciation, anion exclusion, transport

## RESUMO

A tecnologia utilizada na disposição de rejeitos provenientes da indústria mineral metalúrgica é de fundamental importância para a qualidade das águas subterrâneas e superficiais. No entanto, mesmo após a estabilização de elementos tóxicos contidos nesses rejeitos, processos naturais no sítio de disposição podem acarretar na dissolução e mobilização de compostos tóxicos do substrato ao solo. Nesse caso, o fenômeno de sorção em solos determina o potencial de transporte de compostos tóxicos. Esse trabalho descreve a importância dos mecanismos de sorção, como resultado da interação de compostos químicos com a superfície dos minerais, na mobilidade de elementos tóxicos. Adsorção específica de ânions, adsorção de metais e exclusão de ânions foram abordadas. Os efeitos de diferentes parâmetros físico-químicos na mobilidade do As, Hg e nitrato foram enfatizadas.

**Palavras-Chaves:** adsorção específica, nucleação, especiação, exclusão de ânions, transporte

## 1. INTRODUCTION

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The exploration and processing of minerals generate wastes and tailings that require an appropriate management for the protection of the environment. This, in turn, requires an understanding of the processes involved within the substrate itself, as well as the interactions with the surroundings, recognizing the possible pathways of toxic elements from a mine or waste site to the atmosphere, to the soil, to water courses and to the groundwater. Because water is the major carrier of pollutants during leachate flow from disposal sites to water courses, the speciation of any toxic element, as a consequence of the water chemistry, affects the transport character of the chemical. Also, in considering the mobility of any compound through waste piles and soils, or seepage from tailing ponds, and ultimately the potential hazard to groundwater quality, the character of the surface with which toxic elements interact is important. In this regard, the sorption phenomena, as a result of the compound-mineral surface interaction, play a key role in the transport, reactions, bio-transformations and ultimately the fate of chemical constituents in aqueous systems. In addition, competition between chemical species for sorption sites on surfaces can be of major significance in the determination of the mobility of any potentially sorbing species.

This chapter is not intended to fully review retention mechanisms of chemicals, but rather to highlight some important reactions that may affect the mobility and fate of toxic elements, such as arsenic, mercury and nitrate generated at some point of the mining process.

## 2. SPECIATION IN SOLUTION

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The presence of ions in solution influence the structure of water. In the region nearest the ion, water molecules form a dense mass, namely the primary solvation shell. In the next outer region, water molecules, forming the secondary solvation shell, interact weakly with the ion. The properties of these shells vary with the concentration, valence and radius of the ion (Sposito, 1984).

In dilute solutions, major dissolved species can be seen as free ions. However, as the ionic strength increases, differences in ion activity become larger, due to short range interactions between adjacent ions forming complexes. In general, metal ions have vacant orbitals and can accept electrons, while ligands have at least one pair of electrons not shared in a covalent bond, and as such, can donate electrons. Metal ions may contain electrons in shared or unshared pair fashion. Similarly, ligands may be of low or high electronegativity.

Two types of soluble complexes are formed between metals and ligands: outer-sphere or ion pairs and inner-sphere complexes. The attractive force involved in an ion pair is coulombic, i.e., a relatively weak electrostatic association exists between a hydrated cation and a ligand, with preservation of the hydration shell. Inner-sphere complexes are strong associations, in which a covalent bond exists between metals and ligands. No matter what type of complex is formed the associations between metals and ligands can produce complexes with neutral, positive or negative charge. Many elements hydrolyze in water to form hydroxo complexes. Mercury, for instance, may form hydroxo complexes in the absence of the  $\text{Cl}^-$  ligand. However, as  $\text{Cl}^-$  ligand concentration increases, a strong inorganic complex is formed. In general, metals that form hydroxo complexes are expected to form strong complexes with organic ligands. This is an important characteristic of speciation because dissolved ligands may compete with surface ligands for association with metals. If the

dissolved ligand succeed in complexing with all sites of the coordination shell of the metal, then specific adsorption is prevented.

### 3. THE ELECTRIFIED SURFACE OF MINERALS

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The surfaces of colloids are electrically charged, due to an excess or a deficit of electrons. The nature of this charge development is either from isomorphous substitution in minerals, or from the complexation of ions, in the pore water solution, with surface functional groups (Sposito, 1984). As isomorphous substitution occurs in the crystal lattice of clay minerals, due to replacement of cations of higher valence by cations with lower valence, the resulting negative charge imbalance is permanent and is not influenced by the composition of the soil solution. On the other hand, at the edges of clay minerals as well as metal oxides, the constituent metal ions are unable to complete their coordination pattern existing in the bulk of the crystal. The result is unsatisfied bonds. In this case, the metal ion coordinates with OH groups, producing an hydroxylated surface which may accept protons and become positive or donate protons and become negative, depending on the pH of the solution.

Ions of the opposite charge of the surface will accumulate in the liquid phase near the charged surface. However, due to the concentration gradient created, diffusion and thermal forces tend to draw back these ions into the liquid phase. By the same token, ions with charge of equal sign to the surface are repelled from the vicinity of the surface with the diffusion forces acting to equalize the concentration of co-ions in solution. The general distribution of ions results in a diffuse ionic atmosphere surrounding a charged particle, which is the basis for the diffuse double layer theory (Gouy, 1910; Chapman, 1913).

The Gouy/Chapman model does not take into account the actual size of counterions. Ions are treated as point charges. The Stern modification (Stern, 1924) attempts to correct null counter ion size of the diffuse double layer theory by allowing the ions to approach the surface within a certain minimum distance, producing a compact layer adjacent to the surface. Stern (1924) also introduced the possibility that ions might be adsorbed into the compact layer (the Stern layer) by forces

other than purely electrostatic. Grahame (1947) postulated that ions are specifically adsorbed (inner-sphere surface complex) into the Stern layer, when they lose some of their water of hydration, whereas the hydrated ions are only electrostatically attracted to the surface (outer-sphere surface complex).



#### 4. ARSENIC SORPTION

The processing of gold from refractory minerals, such as arsenopyrite ( $\text{FeAsS}$ ), requires that arsenic (As) is removed and stabilized before disposal in landfills, as tailings or dumps. The pyrometallurgical process involves the crushing of the ore, flotation of the sulphides, sulphide roasting, washing and leaching. The roasting step to oxidize arsenopyrite results in the transformation of As to As(III). In this process, arsenic is transformed into a finely divided powder of arsenious oxide, which is leached in the presence of cyanide. This later stage solubilizes most of the arsenic.

Further oxidation of the leached liquors to As(V) is usually carried out for the precipitation of As, as calcium or ferric arsenate compound, for disposal.

The stability of the metal arsenate is important for a safe disposal, with no pollution threat to the water and to the air. However, even when relatively protected, arsenical residues may be leached, eroded and volatilized, which were identified as the pathways for the arsenic spill from a zinc silicate ore disposal site in the Sepetiba Bay, Rio de Janeiro (Barcellos *et al.*, 1992). Metal arsenates with low solubility may have their stability altered depending on the physical-chemistry of the waste-site disposal system. Calcium arsenate has its solubility enhanced when in contact with atmospheric  $\text{CO}_2$ . In this reaction calcium arsenate is decomposed to  $\text{CaCO}_3$ , liberating contained arsenic (Robins and Tozawa, 1982). Solubility tests of various Fe-As compounds formed as products of high pressure leaching of arsenopyrite (Carageorgos, 1993) showed that the dissolution of Fe and As was incongruent, and that As dissolves preferentially over Fe in all solids studied. The products were identified as  $\text{Fe}(\text{OH})_3$ ,  $\text{H}_2\text{AsO}_4^-$ , and a concomitant drop in pH, during dissolution, was expressed as increased concentration of solution  $\text{H}^+$ . In general, all compounds formed as leached residues in the high pressure leaching process released As into solution which varied from about 1 to 130 mg As/l in 98 days

reaction time, depending on Fe/As ratio and temperature. The pH control is important in preserving the stability of arsenical wastes. At relatively high pH values, where the solubility of calcium arsenate is at its minimum, the decomposition of this compound to the hydroxyde may still occur, liberating the free arsenate oxyanion. At pH values of about 4, ferric arsenate decomposes to ferric hydroxyde (Carageorgos, 1993; Nishimura and Tozawa, 1981). During arsenopyrite processing, there is the possibility of oxidation of sulphides into sulphuric acid, with a resulting acid pH, and consequently, a delayed redissolution of metal arsenates. If redissolution of arseniferous wastes occur, and arsenic compounds are free to move downward into the soil matrix, the selection of the soil type, which will serve as disposal site is critical because the sorption process in soils may play a key role in preventing groundwater contamination. Figure 1 (Melamed *et al.*, 1995a) shows the breakthrough curves (BTCs) of arsenate on two very distinct soil systems. The mobility of As through the Panoche soil (fine-loamy, calcareous) was considerably greater than through the Oxisol soil (kaolinite, quartz, goethite). This large difference in retention capacities between the two soils is explained by their differences in mineralogy (Jacobs *et al.*, 1970; Fordham and Norrish, 1979), and by the differences in equilibrium pH between the two systems (Goldberg, 1986).

The capacity of the Oxisol soil to retain As (Figure 1) is outstanding. About 30 pore volumes of As solution were displaced through the Oxisol before As was detected in the effluent, and 160 pore volumes were displaced before the highest effluent As concentration was reached. With 160 pore volumes displaced, effluent As concentration approached but did not reach the input concentration. The tailing and reduced maximum of the BTC suggest that surface nucleation of As with oxides was the major sorption mechanism involved at the latest stage of the As-BTC (Willet *et al.*, 1988; van Riemsdijk and Lyklema, 1980). In contrast, As-BTC on the Panoche soil shows that As was detected in the effluent at about 5 pore volumes and did reach the input concentration at 15 pore volumes. These results reflect the importance to follow a criteria for the selection of the soil used as a waste disposal site.

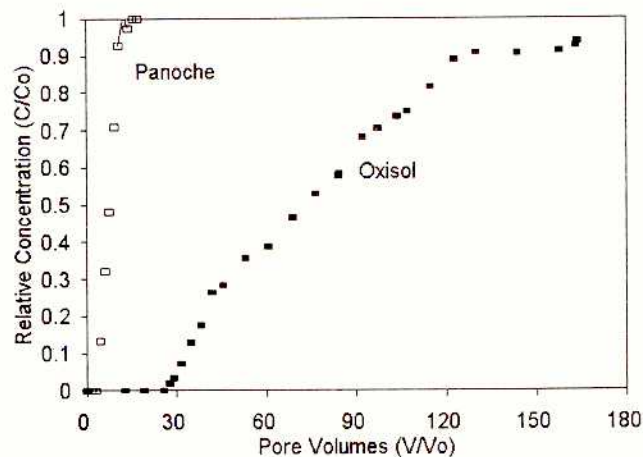


Figure 1 - As-BTCs on Panoche and Oxisol Soils

Fordham and Norrish (1979) studied arsenate uptake by the components of several acidic soils by means of statistical analysis of the data. In all the soils in which they were present, micron-size iron oxide-hydroxide pellets were outstanding in their ability to take up arsenate. Goethite and hematite pellets appeared to react equally well with arsenate. In one of the soils, where many particles were in fact microaggregates containing fine-grained units of gibbsite, hematite and kaolin, the arsenate uptake was dependent mostly on the proportion of hematite present. Titanium dioxide pellets, with surface deposits containing finely divided iron oxide, were able to take up more arsenate than expected from their ferric oxide contents. Both rutile and anatase were identified by X-ray diffraction, but no differences could be discerned between the two mineral forms in their ability to take up arsenate. Gibbsite, even though present in fine state, had little influence on arsenate uptake. Quartz was found to have no reactivity with arsenate.

Figure 2 (Melamed *et al.*, 1995a) shows changes in effluent pH during As displacement through the Oxisol soil column. The initial effluent pH was 5.45, which was the pH of the background

electrolyte solution. This pH is below the  $pK_2$  (pH 6.7) of the arsenic acid. Thus, the monovalent anion ( $H_2AsO_4^-$ ) was the predominant species in solution. The initial effluent pH value was also below the point of zero charge (PZC) (pH 6.0) of the soil which indicated that the density of surface functional aquo-groups ( $OH_2^+$ ) was high, resulting in a positive surface potential that favored the adsorption of As.

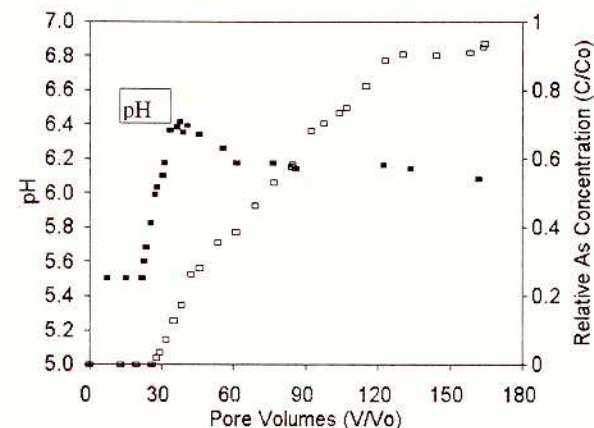
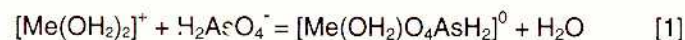


Figure 2 - Effluent pH during arsenate movement through the Oxisol soil

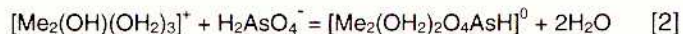
Arsenic appeared in the effluent at  $V/V_o=20$ . The constant value (5.45) of the effluent pH indicated that the primary ligand exchange mechanism, during phase 1 of the As-BTC, involved the substitution of As for labile  $OH_2^+$  groups (Rajan, 1976). This ligand exchange reaction is represented by:



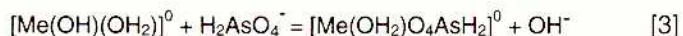
where Me is the coordinating metal atom at the oxide surface.

The initial reaction of As with the oxide component of the soil can also be explained by the formation of a binuclear complex,

involving the coordination of two oxygen atoms of the As molecule with two metal atoms at the oxide surface, as follows:



In reactions 1 and 2, the pH is constant during ligand exchange. Simultaneously with the appearance of As at  $V/V_0=20$ , the effluent pH increased sharply to a maximum of 6.4, at  $V/V_0=40$ . The increase in pH suggests that the primary ligand exchange mechanism, during phase 2, was between  $\text{H}_2\text{AsO}_4^-$  and surface OH groups. The exchange with OH groups is favored by the depletion of surface  $\text{OH}_2^+$ , and by the decrease in PZC of the soil associated with the inner-sphere complexation of As (Anderson and Malotky, 1979; Hingston *et al.*, 1972). The exchange mechanism in phase 2 was written (Melamed *et al.*, 1995a):



As the pH increased to 6.4, the  $\text{pK}_2$  of the arsenic acid (pH 6.7) was approached, which increased the proportion of soluble divalent  $\text{HAsO}_4^{2-}$  species in solution. The increase in divalent As species, combined with the decrease in surface potential resulting from As complexation, increased the mobility of As (Barrow, 1985). The presence of complexed As can also be regarded as a self competitive mechanism in the movement of As (Barrow, 1974, Camargo *et al.*, 1979; Logan and McLean, 1973).

The four plane model (Bowden *et al.*, 1977) was discussed by Barrow (1985, 1987). In this model ions that replace hydroxyls or water molecules occupy a plane close to the surface and ions that form outer-sphere surface complexes are allocated to a different plane. The position of the planes on which adsorption occurs are not fixed. Ions differ not only in their affinity to the surface but also in their mean position in the DDL when they are adsorbed. Surface speciation is avoided. Instead it is assumed in the model that the surface activity of an ion is proportional to the ratio of occupied sites to vacant sites. The expression derived by Bowden *et al.* (1977) has the form of a competitive Langmuir equation:

$$A_i = [N_t k_i a_i \exp(-z \Psi_a F/RT)] / [1 + k_i a_i \exp(-z \Psi_a F/RT)] \quad [4]$$

where

$A_i$  is adsorption of ion  $i$ ,  $N_t$  the maximum adsorption,  $k_i$  a binding constant,  $a_i$  the activity in solution,  $z$  is the ion valence,  $\Psi_a$  the surface electrostatic potential,  $F$  is the Faraday constant,  $R$  the gas constant and  $T$  the temperature.

In the case of arsenate sorption,  $z$  is negative and because the electrostatic potential decreases as pH increases, the value of the exponential term decreases. This effect tends to decrease adsorption. It is opposed by increased dissociation of the acid. If, for instance, the dissociated species to be adsorbed has a  $z$  value of -1, then at pH values below the  $\text{pK}$ , the concentration of this anion, though low, increases ten-fold for each unit increase in pH. For monovalent anions, this increase suffices to more than counterbalance the decrease in potential, and adsorption increases. Once the  $\text{pK}$  is reached, however, there is little further scope for increases in the concentration of the monovalent anion, so the effect of the electrostatic potential predominates and adsorption decreases. The effect is slightly different when a divalent species adsorbs because the  $z$  term has a value of -2, and hence the exponential term has a greater effect, i.e., the effect of changing the electrostatic potential is greater. The result is that adsorption decreases with increasing pH, with a slight increase in slope near the  $\text{pK}_2$  of the acid. Hence, the model involves a choice between known species in solution rather than proposing surface species.

Phase 3 (Figure 1) started at  $V/V_0 = 40$ . The tailing and reduced maximum As concentration displayed by the As-BTC of the control column, coupled with the decrease in effluent pH to a constant pH = 6.1, appeared to involve the following mechanisms: i) a decrease in ligand exchange involving As and surface OH groups, and sorption dominated by surface nucleation of As (Willett *et al.* 1988; Van Riemsdijk and Lyklema, 1980); ii) sorption of protons due to the increase in negative charge associated with the inner-sphere surface complexation of As, with a tendency to buffer the system to the

PZC, which is the point of minimum solubility (Parks and de Bruin, 1962). The four plane model also accounts for the slow process that follows adsorption. Barrow (1985) defends the mechanism of solid state diffusion in which the anion penetrates the particles after a period of time elapsed. The immediate source of the diffusive process is the surface concentration of adsorbate, not the solution concentration. The slow step observed in titration data was attributed to diffusion of protons into, or out of, the surface. If an adsorbed anion diffuses into the interior of the adsorbing material, a surface site will be vacated. However, the electrostatic potential of the surface will be less favorable for adsorption than it was originally (Barrow, 1985). A solid state diffusion mechanism was also used by Van Riemsdijk *et al.* (1984) to describe the effects of time on the reaction of phosphate with soils.

For further stabilization of arsenical wastes, Laguitton (1976) suggested the use of phosphate in combination with lime, to take advantage on the stability of a combination of calcium phosphate and calcium arsenate, which are known to form solid solution. The suggestion that phosphate in the lime system would further stabilize arsenic was found correct in terms of thermodynamic stability. However, if redissolution occurs, the presence of phosphate may contribute to an increase in arsenic mobility in soils through competition for adsorption sites (Roy *et al.*, 1986), thus preventing arsenate from forming inner-sphere surface complexes with oxides (Barrow, 1989; Goldberg, 1986). The leftward shifts of the As-BTCs (Figure 3) indicate that As mobility through the Oxisol soil increased with P levels. At the highest P level, As appeared in the effluent after 10 pore volumes of solution were displaced (20 pore volumes less than in the control), and the greatest concentration of As in the effluent occurred when 60 pore volumes of solution moved through the column (60 pore volumes less than in the control). These data confirm the competitive effectiveness of P with As for sorption on the oxide surface (Miller *et al.*, 1989; Roy *et al.*, 1986; Goldberg, 1986; Hingston, 1981, Barrow, 1974).

Frost and Griffin (1977) demonstrated a much lower retention capacity on clay minerals (montmorillonite and kaolinite) of arsenite as compared to arsenate. In addition of

being more toxic, As(III) is more mobile. Because the pK of arsenious acid ( $H_3AsO_3$ ) is about 9.2, adsorption is low at the acidic range and weakly basic solutions, and increases slightly as pH 9.2 is approached.

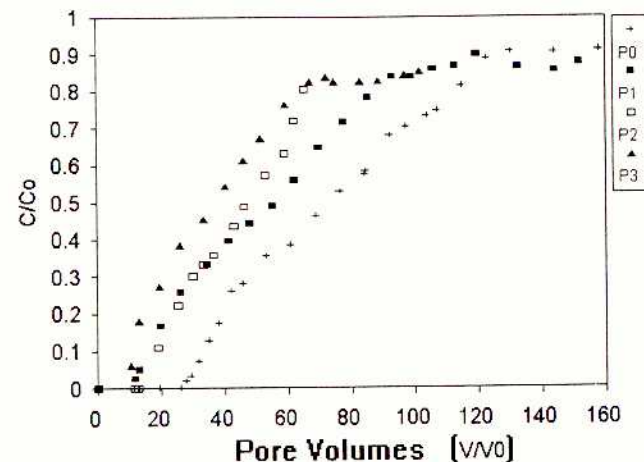
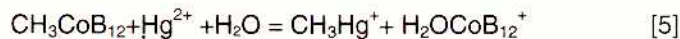


Figure 3 - Effect of phosphate on arsenate movement through Oxisol soil

## 5. MERCURY CHEMISTRY

The use of metallic mercury ( $\text{Hg}^0$ ) for gold recovery is of concern because it has been shown that, after discharge to the environment, specially by burning the Au-Hg amalgam, volatilized  $\text{Hg}^0$  can be transformed by ozone to ionic mercury ( $\text{Hg}(\text{II})$ ) (Iverfeldt and Lindqvist, 1986; Munthe and McElroy, 1992), which, in turn, may be transferred to rivers and soils through wet deposition (Padberg and Stoepler, 1991). Once in the ionic form, mercury can be transformed to methyl mercury ( $\text{CH}_3\text{Hg}^+$ ), the most toxic form of the metal. Methyl mercury accumulates and biomagnifies in the food chain (Huckabee *et al.*, 1979), causing damage to the central nervous system of humans (Wood *et al.*, 1978). The biotic transformation of mercury to methyl mercury was considered to be a detoxification mechanism, in which micro-organisms transfer a methyl carbanion ( $\text{CH}_3^-$ ) from methylcobalamin to a  $\text{Hg}(\text{II})$  species in either aquated, ionic, or complexed form (Craig and Moreton, 1985):



In addition of being very toxic, methylation of ionic mercury was also shown (Melamed *et al.*, 1995b) to enhance the mobility of Hg through the aquatic environment. Figure 4 shows  $\text{Hg}(\text{II})$  adsorption kinetics and the effect of the addition of methylcobalamin ( $\text{CH}_3\text{CoB}_{12}$ ), a methylating agent, at 90 minutes reaction time.

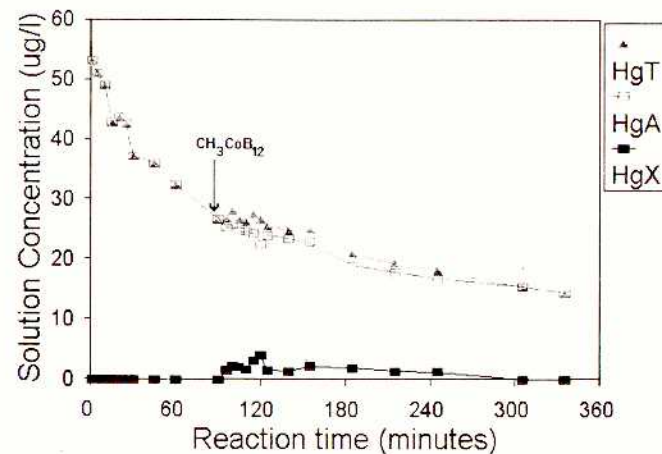


Figure 4 - Adsorption kinetics of Hg on river sediments. Arrow indicates addition of methylcobalamin.  $\text{Hg}^T$ : Total mercury;  $\text{Hg}^A$ : ionic mercury;  $\text{Hg}^X$ : methyl mercury

Initially, the rate of adsorption was relatively fast, and about 50% of  $\text{Hg}(\text{II})$  in solution was taken up by the river sediments. Then, upon addition of the methylating agent, a temporary decrease in adsorption rate was observed, reflected by a relative stabilization of  $\text{Hg}^T$  and  $\text{Hg}^A$  solution concentrations, as well as a concomitant increase in  $\text{Hg}^X$ . This decrease in Hg adsorption rate after the addition of  $\text{CH}_3\text{CoB}_{12}$  is attributed to the relative lower affinity of  $\text{Hg}^X$  (methyl mercury) for sorption at the sediment/solution interface as compared to  $\text{HgCl}_2\text{O}$ . This change in affinity upon methylation arises primarily from the fact that methyl groups have neither empty orbitals nor non-bonding electrons available for intermolecular interactions (Thayer, 1989).

In alluvium type gold mining, in which placer ores are dredged and processed on river barges,  $\text{Hg}^0$  is introduced directly into the rivers, and the metal can be frequently observed at the bottom of the water column. Although  $\text{Hg}^0$  is relatively immobile in the aquatic environment, and its solubility is low

(25 $\mu\text{g/L}$ ) in water (Hem, 1970), Hg contamination in people living upstream and downstream from gold recovery operations has been reported (Cleary *et al.*, 1994). The relevance of dissolved organic acids in enhancing the solubility of metallic mercury was demonstrated by Veiga (1993) and Melamed *et al.* (1995b). Although the role of complexation with dissolved organic ligands in the Hg biogeochemical cycle is not clear (Verta *et al.*, 1986; Driscoll *et al.*, 1994), the complex formed is more mobile, with a relative lower affinity for adsorption at the surface of sediments (Melamed *et al.*, 1995b). Melamed *et al.* (1996a) also showed that a decrease in pH decreases the degree of complexation, which was attributed to the competitive behaviour of  $\text{H}^+$  with Hg(II) for complexation at the humic acid chain (Langford and Cook, 1995; Fletcher and Beckett, 1987). Fletcher and Beckett (1987) found that ion exchange with protons is a principal component in metal binding by soluble organic matter, which displays two distinguishable groups of exchange sites.

In gold mining activities where the ore is explored in quartz veins,  $\text{Hg}^0$  can reach levels of 200 mg/kg in the tailings (Farid *et al.*, 1991), which are left exposed over the soil surface, susceptible to oxidation and leaching. The leaching of Hg from the tailings to the soil underneath and the transport through the soil profile is strongly dependent on pH of the soil solution. Figure 5 (Melamed *et al.*, 1996b) shows the effect of pH and ionic strength on the retention of Hg(II) onto an Oxisol. The "adsorption edge" indicates a relative low adsorption of Hg(II) below pH 3. Adsorption increases in the range of pH 3 to 5 and stabilizes. Hg(II) adsorption follows the same pattern of specific adsorption of other hydrolyzable cations (MacNaughton and James, 1974) such as Pb, Cu and Zn, reflecting the effective competitive behaviour of protons with Hg(II) for adsorption at the mineral surface of this soil, and the presence of  $\text{Hg}(\text{OH})_2^0$  as the predominant species interacting at the surface as pH increases (Bolan and Barrow, 1984). Although there was practically no effect of ionic strength on Hg adsorption, the data in Figure 5 indicate a slight tendency towards increased Hg adsorption as the ionic strength increases, in the range of pH values from 3.5 to 4.7. This pH range is below the point of zero charge (PZC) of the Oxisol (pH 4.7), where the surface is net

positively charged. An increase in electrolyte concentration may enhance the adsorption of Hg(II) due to the favorable surface potential, promoted by increased concentration in electrolyte anions near the surface (Bolan and Barrow, 1984).

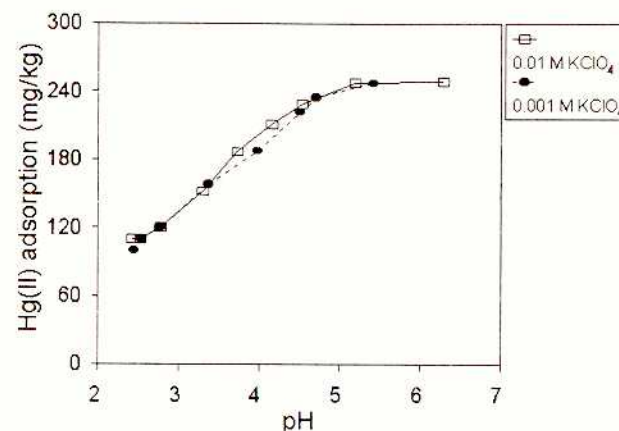


Figure 5 - The "adsorption edge" of Hg(II) on Oxisol at 0.01 M and 0.001 M  $\text{KClO}_4$  background electrolyte concentrations.

The complexity of Hg chemistry in the environment reflects the various possible Hg species and complexes with different physical-chemical properties (Luoma, 1983). These complexes depend upon the types and concentration of the ligands involved in the system. Thus, mercury speciation and complexation, as well as physico-chemical parameters, determine the partition of the metal between solid and liquid phases and control Hg mobility and availability. The effect of nature of the electrolyte on Hg adsorption and transport is demonstrated in Figures 6 and 7 (Melamed *et al.*, 1996b). A much higher adsorption of Hg resulted in the  $\text{KClO}_4$  system as compared to the KCl system (Figure 6). These results are in agreement with other studies of Hg(II) interaction with pure  $\text{SiO}_2$  (MacNaughton and James, 1974). The formation of mercury chloride complex in solution promotes a much lower interaction of Hg at the soil solution interface, due to an outer-sphere surface complex interaction. The presence of phosphate (P) has practically no effect on

Hg(II) adsorption in the KCl system. However, P enhances the adsorption of Hg(II) in the  $\text{KClO}_4$  system considerably, due to the favorable surface potential and negative charge created.

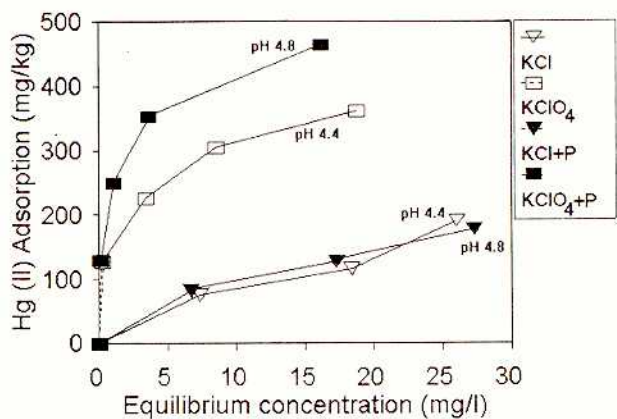


Figure 6 - Effect of P on Hg(II) adsorption isotherms on Oxisol under different electrolytes systems

As a result, as demonstrated in Figure 7 (Melamed *et al.*, 1996b), the retention of Hg(II) in the upper half of the soil column is much higher in the  $\text{KClO}_4$  system than in the KCl system. Mercury moves deeper in the soil column when chloride is present, due to the formation of the mercury chloride complex. The mobility of Hg(II) in presence of P is decreased more effectively in the  $\text{KClO}_4$  system.

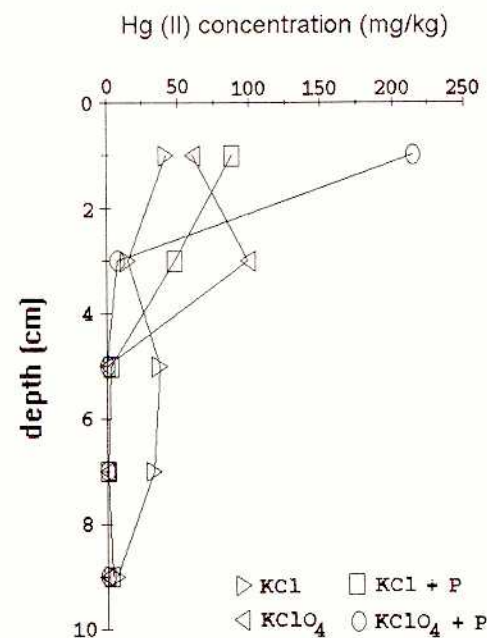


Figure 7 - Hg(II) transport through Oxisol soil column in KCl and  $\text{KClO}_4$  systems in the presence of phosphate (P)

## 6. NITRATE EXCLUSION

Nitrate contamination to surface and groundwaters, due to the use of explosives in mining operations, is of concern in many parts of the world. To predict the transport and fate of nitrate in natural systems, the understanding of anion interaction with mineral surfaces is of fundamental importance.

Although anions were generally assumed to be non-reactive during miscible displacement, negatively charged ions are actually repelled from a region near negatively charged surfaces (Wagenet, 1983). The phenomena give rise to a local deficit of anions in the vicinity of negatively charged particles and an excess of anions in the bulk solution (De Haan and Bolt, 1963). Many studies have shown that negative adsorption of anions at a negatively charged surface result in anion exclusion during solute transport (Smith, 1972; Kissel *et al.*, 1973). The importance of anion exclusion is that the anions are removed from the relatively immobile water associated with the DDL and positioned in the faster moving pore water. The result is that the average rate of transport of the anion in the soil is greater than the average pore water velocity. Thus, for a given duration of displacement, anions will move further in a porous material in the presence of anion exclusion than in its absence because the volume of water immediately adjacent to the clay surfaces does not hold anions, and as such, does not participate in the leaching reaction. So, the larger the anion exclusion volume, the greater the mobility of salt at a given soil water content and water application (Thomas and Swoboda, 1970).

The lack of complete mixing with increasing non-equilibrium for solute transfer by diffusion between inter and intra-soil aggregates at high pore water velocities was studied by many investigators (Van Genuchten and Wierenga, 1976; Gaudet *et al.*, 1977, Nkedi-Kizza *et al.*, 1982, 1984). Van Genuchten and Wierenga (1976) described a model in which the liquid phase is partitioned into mobile (macroporosity-convection controlled) and immobile (microporosity-diffusion controlled) regions. They

suggested that only a certain fraction of sorption sites, i.e., those located around the larger pores participated actively in the adsorption process. This would have the same effect as a reduction in adsorption, leading to a relatively faster movement of the chemical and earlier breakthrough curves (BTC). At the same time, a considerable portion of the chemical must diffuse to remaining sites located inside aggregates. The slow diffusion process would continuously remove material from the larger saturated pores resulting in extensive tailing. James and Rubin (1986), on the other hand, demonstrated that at sufficiently low flow rates the diffusive mixing between mobile and immobile water is sufficiently fast, and that the anion exclusion function developed by Bresler (1973) would improve predictions of the convection-dispersion equation. Smith (1972) suggested that when the flow rate is fast, spatial variations become important and the anion simply may not have enough time to associate with all the soil water before passing through the soil. However, when the flow rate is slow, even though the anion has time to associate with all the soil water, electrical repulsion can prevent its association both with water near negatively charged soil surfaces and with water in any expanded clay interlayers.

Because anion exclusion and immobile water effects work in the same direction it becomes difficult to separate the extent that each of them contributes to the movement of anions ahead of the average pore water velocity. Krupp *et al.* (1972) and Melamed *et al.* (1994) demonstrated the interaction between electrostatic effects and flow velocity on anion movement. In the latter study, the Br<sup>-</sup> anion was used as a tracer for NO<sub>3</sub><sup>-</sup> due to its similar interaction with the soil surface, similar ionic radii, and because Br<sup>-</sup> is not subjected to biological transformations or oxidation-reduction reactions, as is the nitrate ion (Smith and Davis, 1974; Onken *et al.*, 1977). The increase in negative surface charge of the Oxisol soil used, induced a faster movement of Br<sup>-</sup> through their columns (Figure 8), as reflected by the shifts in breakthrough curves to the left. The extent of the effect of increasing the net negative surface charge of the soil on the mobility of the anion, resulted in retardation factors less than 1, implying anion exclusion.



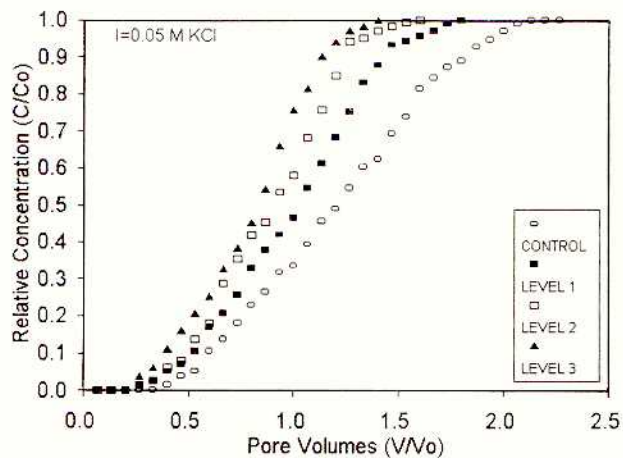


Figure 8 - Transport of Br through Oxisol at four levels of increasing net negative charge

When the flow velocity was varied,  $\text{Br}^-$  movement was enhanced under the slowest flow velocity (Figure 9a), and as the flow velocity progressively increased (Figures 9b, 9c), the effect of surface charge on  $\text{Br}^-$  movement diminished, reflecting in progressively reduced separation areas of the BTCs (Figures 9a,b,c).

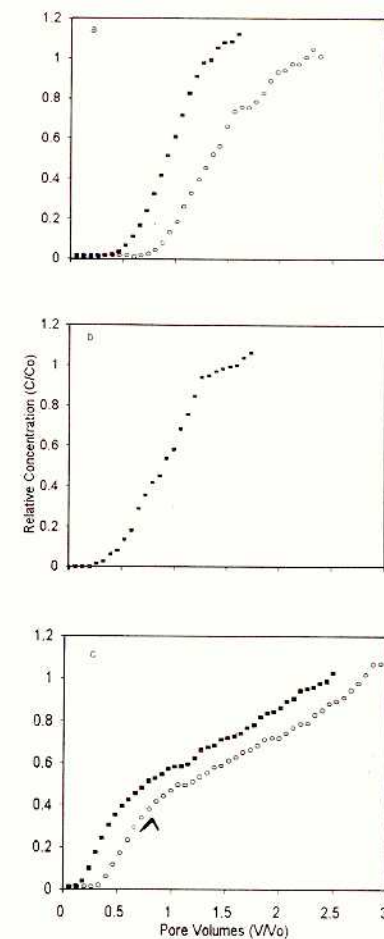


Figure 9 - Transport of Br through Oxisol at 2 levels of net negative charge (o - low negative charge; ■ - high negative charge) and 3 pore water velocities: a) 2.9 cm/h; b) 8.7 cm/h; c) 48.1 cm/h

## 7. CONCLUSIONS

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In this chapter, some important reaction mechanisms, affecting the transport of arsenic, mercury, and nitrate were highlighted. The effect of the character of the surface, the particular interaction of the compound with the surface, as well as solution speciation on the transport of chemicals through soils were emphasized.

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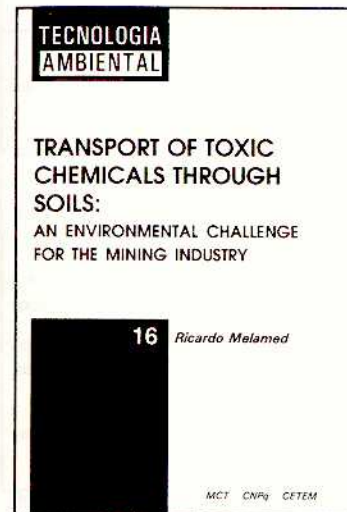
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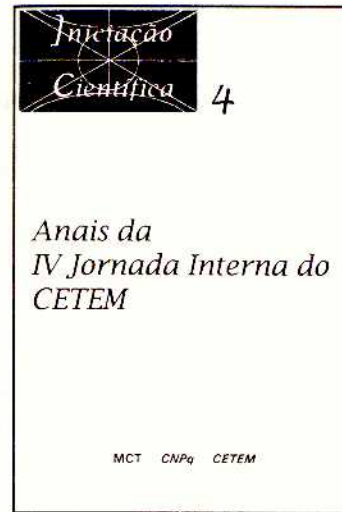
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