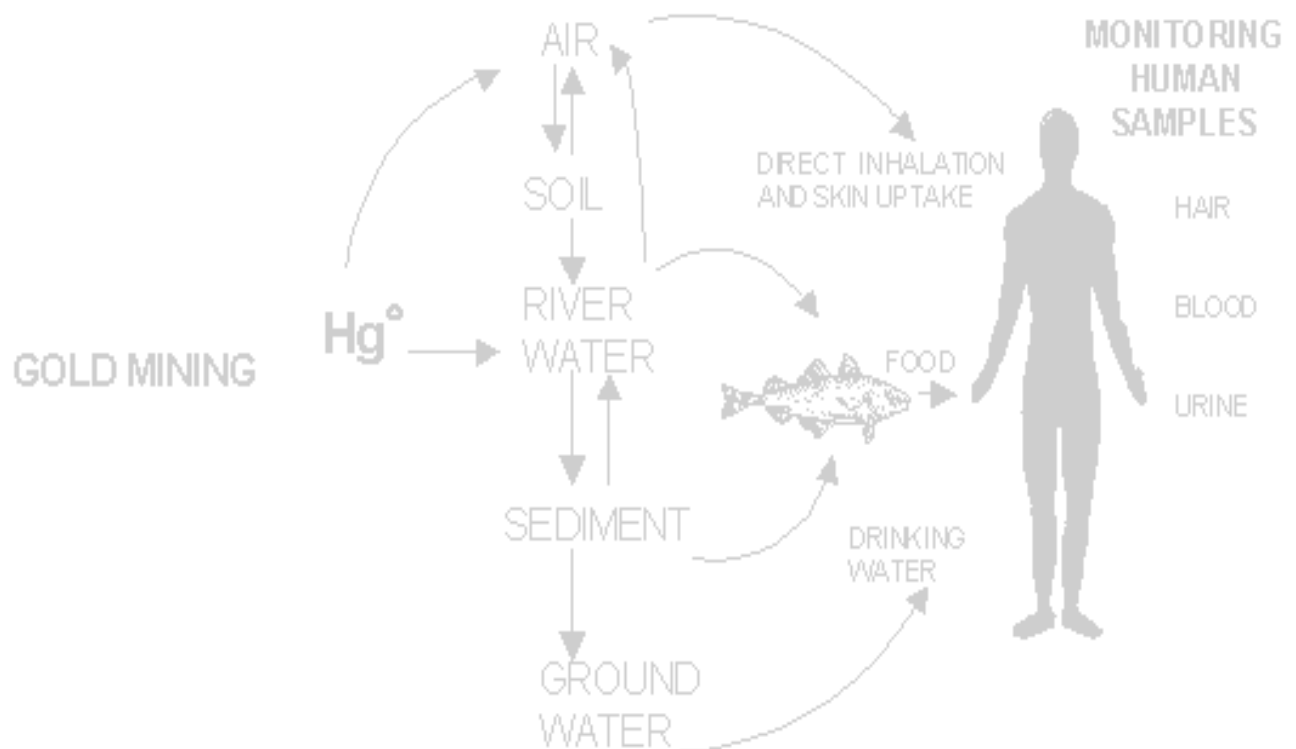


Mercury in the environment and the gold mining activity in the St Domingo district, Chontales-Nicaragua



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Resumen

Este documento presenta parte de la extensa información científica sobre el mercurio y fue preparado pensando en la necesidad existente en las áreas mineras de Nicaragua de contar con información básica sobre el destino ambiental del mercurio y del riesgo que este representa para la salud humana.

En la introducción, se resalta de manera general, el uso excesivo del mercurio en la extracción del oro y su consecuente liberación al medio ambiente. En el segundo capítulo, se describe la actividad minera en Santo Domingo-Chontales y se hace una comparación de la contaminación por mercurio con otras áreas mineras alrededor del mundo. El tercer capítulo presenta aquellos factores responsables de la retención y transporte del mercurio en el suelo y en el agua, específicamente en ríos. El cuarto capítulo, es una breve descripción de cómo el mercurio puede estar presente en el ambiente formando diferentes especies químicas. En el quinto capítulo se hace énfasis en las principales rutas de exposición, a través del cual el ser humano incorpora el mercurio a su organismo. Finalmente, en el capítulo seis y siete se consideran los efectos tóxicos del mercurio para organismos vivos incluyendo al ser humano, así como, se proponen algunas acciones para minimizar el impacto del uso del mercurio en el área de Santo Domingo.

Se espera que esta información sirva de soporte a aquellas entidades locales y nacionales en Nicaragua en la toma de decisiones para el buen manejo ambiental y de la salud humana, y para promover el cuidado ambiental en el área minera de Santo Domingo.

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1. Introduction

The contamination of the environment by anthropogenic activity is a world-wide problem of great concern. Therefore, scientific development is directed towards search for alternatives of remediation and environmental management that helps to mitigate this contamination, which affects not only parts of the biosphere but the entire planet.

Mercury is considered as one of the worst sources of anthropogenic impact on the global environment (Wilken and Horvat, 1997; Boening, 2000). Much research concerning the effects of mercury on terrestrial and aquatic biota has demonstrated the potential risk that it represents (WHO, 1989) because of its toxicity, accumulation and its tendency to biomagnify in terrestrial and aquatic ecosystem, and also because of its properties, mobility, transformation in the environment, and presence in humans.

In many developing countries in Central America, South America and Africa, the major use of mercury seems to be in gold mining for amalgamation with gold and other metals. In the Amazon region, mercury pollution occurs at rates of about 1 kg per kg of gold produced (Veiga and Meech, 1995). Since the end of the 1970s, more than one million artisanal gold miners (worker who extracts gold on manual basis) in Latin America have collected between 115 and 190 tons of gold, emitting more than 200 tons of mercury annually (Korte and Coulston, 1998). Although gold mining plays an important role in the economic development of these regions, negative effects from gold mining activities and gold mining explorations are evident (Salomons, 1995; Moreira, 1996).

Rural ecosystems in which mining activity has taken place have undergone dramatic deterioration (Salomons, 1995; Moreira, 1996), and surface waters used as recipients of wastes from mining activities are subject to increased sedimentation as a result of deforestation and runoff. Runoff transports scavenged soils from the watershed to the surface water and introduces toxic metals associated with soil particles (Roulet et al., 1998). Also metals suspended in aqueous wastes are discharged without treatment directly into the rivers and lakes. For instance, for more than one century the Sucio River located in the Chontales district of Nicaragua has received wastes from gold mining industry and artisanal activity. These wastes have reduced the biological diversity in the river by introducing mercury, lead, and cyanide (CIRA-UNAN, 1992). The levels of mercury found in water and sediments along the Sucio river (Silva, 1994; André et al., 1997) show that mercury can be transported by stream water and represents a threat to populations living in the mining areas. Once mercury enters into the river, it can be transformed to methylmercury, which is highly toxic and is easily taken up by fish. In mining regions, humans consume fish, which may be contaminated with mercury and other toxic metals (Peixoto and Cernichiari., 1998). In the human body, methylmercury is easily absorbed in the intestine and enters the blood from which it is distributed throughout the body (WHO, 1989), affecting the brain and the rest of the nervous system.

This paper is the result of a compilation and analysis of the information available in the international scientific literature on the environmental fate of mercury. This background information will hopefully support governmental and provincial agencies in Nicaragua in decisions to ensure that the best management of environment and health, is used to promote the development of a scientifically based environmental care to protect the management in the Santo Domingo gold mining area.

2. Gold Mining as a Source of Mercury Pollution of Rivers

2.1. A case study: Sucio River (Santo Domingo) in Nicaragua

Nicaragua is located in Central America (figure 2.1), with a total area of 129 494 km². About 7 % of its territory is covered by surface water (lakes and rivers). Its mineral resources, such as gold, silver, copper, lead, zinc, and other metals, have been exploited in different areas for several decades.

The gold mining activity is the main source of mercury pollution in Santo Domingo and La Libertad (figure 2.1). As in other mining areas, the quality and distribution of water is affected by deforestation, agriculture and fecal contamination of rivers (CIRA-UNAN, 1992; Silva, 1994; André et al., 1997).

In Santo Domingo, mercury has historically been used and is still being used to extract gold from crushed ores by forming pastry amalgam with gold particles. Native ores might contain other metals such as lead. The mercury is found in water and sediments from Sucio River at higher concentrations than background levels (table 2.1). Sucio River is the main water source used for gold extraction in Santo Domingo (figure 2.2). The water is used in the process and returned to the river as liquid mining wastes, containing high amounts of solid material from crushed ores. Previous studies have estimated that about 40 tons of mercury and 10 tons of lead have been released into the environment during the past 100 years of mining activity in Santo Domingo and La Libertad (Belt, 1874). It is presently estimated that 45 kg of mercury is used monthly in Santo Domingo, of which approximately 35 % vaporizes into the atmosphere and 47 % is lost to the Sucio River (André et al., 1997). Thus, only about 18 % of used mercury is amalgamated. This estimate agrees well with those found by Lacerda (1997) for other gold mining areas.

Mercury concentrations in Sucio River water are almost one order of magnitude higher than the permissible concentrations established for human consumption (WHO, 1989), and the sediments are contaminated as far as 50 km downstream from the La Estrella plant (figure 2.3 b) (André et al., 1997).

During the mining activity, metallic mercury is lost to the atmosphere through evaporation when gold particles in crushed ores are amalgamated with mercury, and when amalgam is burned on bonfires in rough and open field conditions (figure 2.4). The volatile mercury can be deposited on surface waters and soils with precipitation. For instance, André et al. (1997) found both the concentration of mercury in samples from a horizontal soil profile ($r^2 = -0.68$) and their soil organic content ($r^2 = 0.86$) correlated with the distance from the sources of mercury emission in the Santo Domingo area (figure 2.1 and 2.3). High concentration of mercury is found near of the main source of mercury (La Estrella Plant) (figure 2.3). Higher concentrations found in the opposite prevailing wind direction are probably due to other sources of mercury emission or may be due the local movement of air followed by dry or wet deposition of mercury.

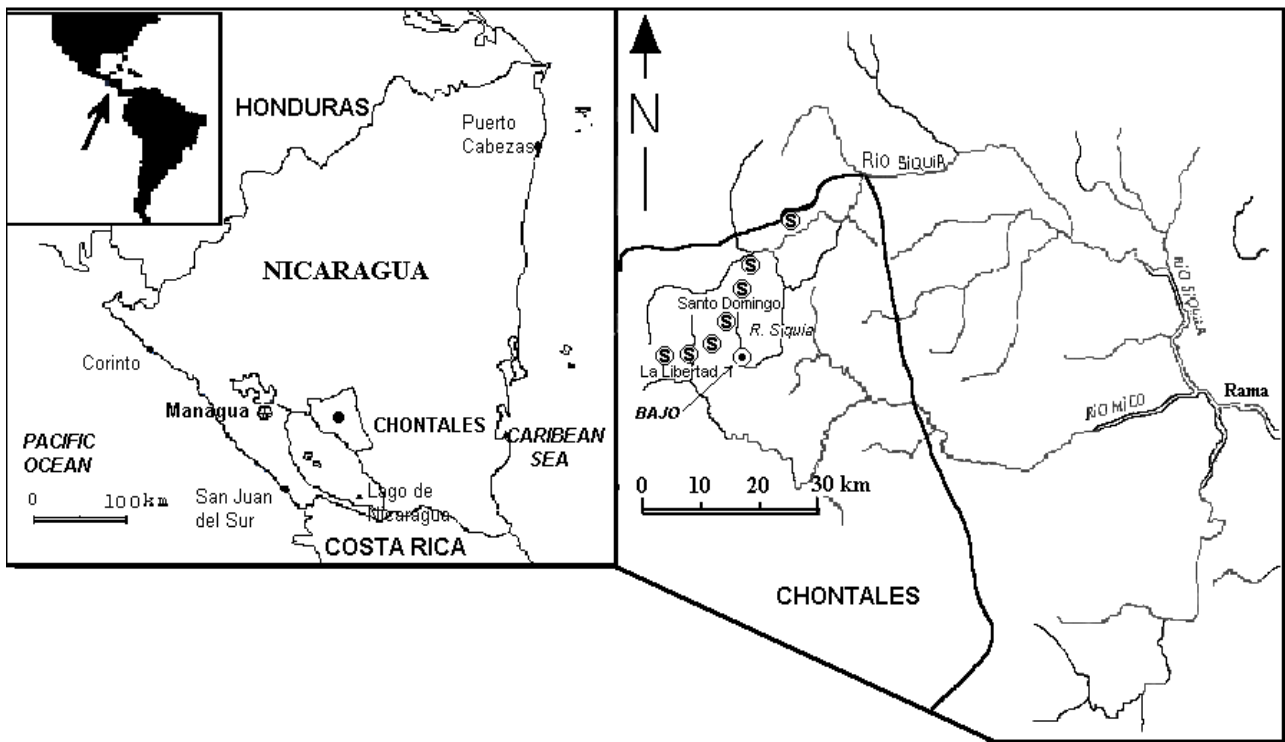


Figure 2.1 Map of American Continent (top insert), Nicaragua map (left) and Chontales mining district (right). Encircled S indicates sites where surface soil samples were taken for metal analysis. A vertical sediment profile was taken at Bajo and analyzed for metals.

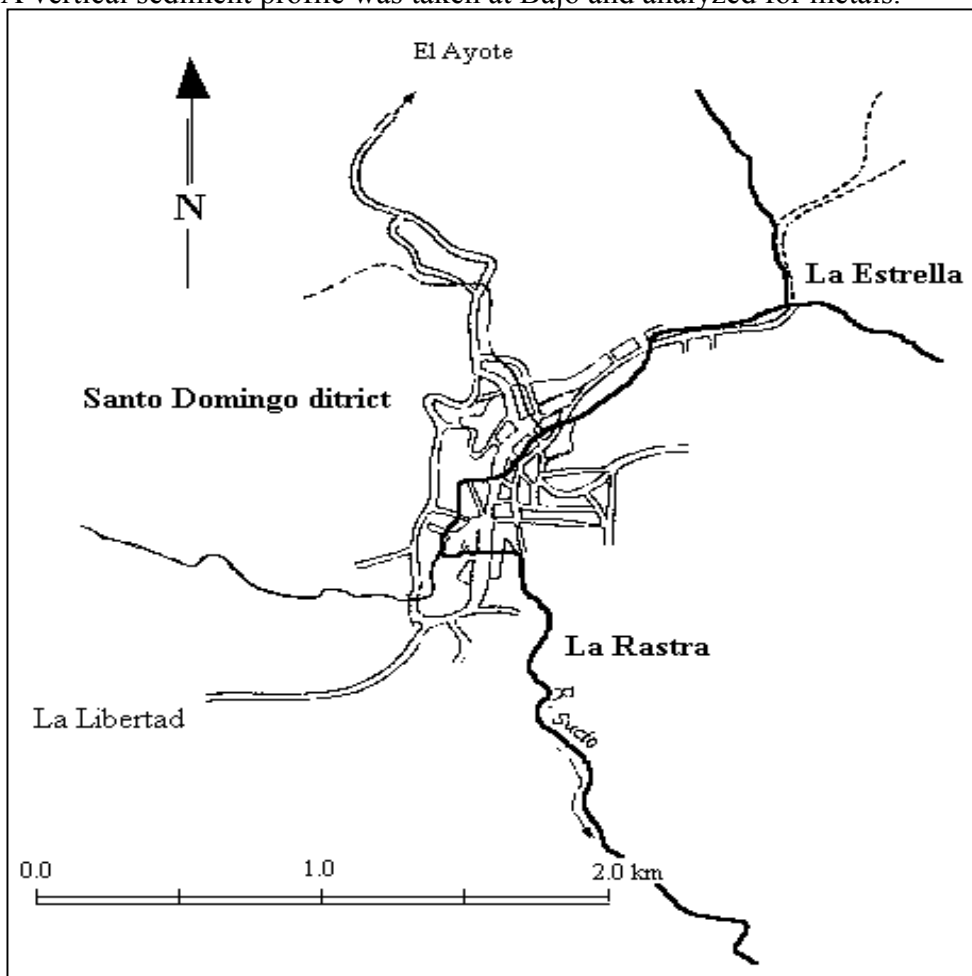


Figure 2.2 Sites of gold extraction (La Estrella, La Rastra), main sources of mercury in Santo Domingo (Chontales).

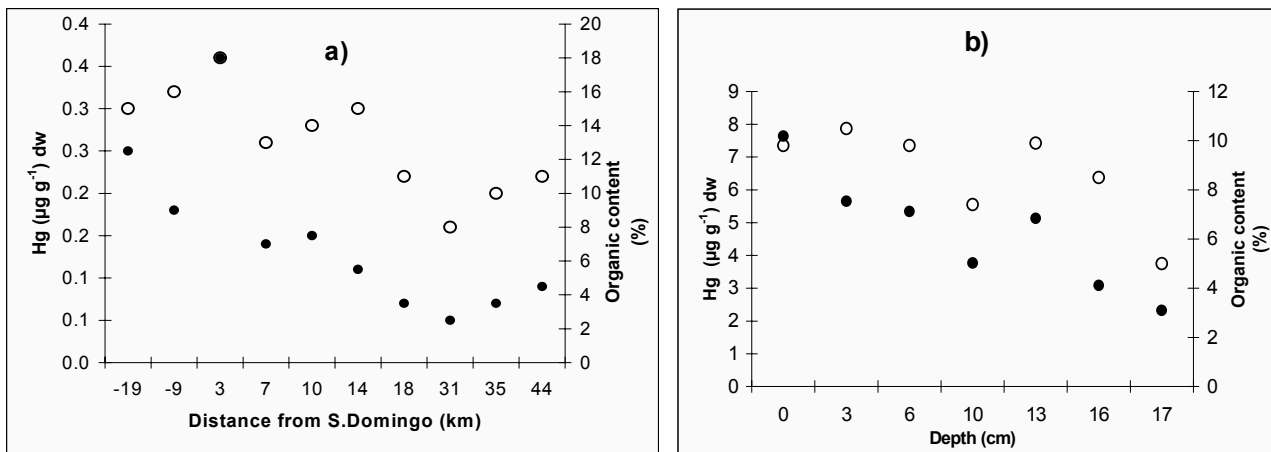


Figure 2.3. a) Horizontal profile NE-SW of mercury concentration (●) and organic content (o) in surface soil (figure 2.1), and b) mercury concentration (●) and organic content (o) in a vertical sediment profile (Bajo figure 2.1). André et al (1997).

Sources of mercury in Santo Domingo (process and small-scale mining)

Two main sources of the mercury and lead emission have been identified in Santo Domingo: one processing plant (La Estrella) and a small water driven stone-mill (La Rastra) (figure 2.2) (Silva, 1994; André et al., 1997).

Gold refining plant: During several years, the Estrella processing plant has released its waste more or less directly into Sucio River. Some sedimentation ponds were designed to trap solid material and to catch mercury remaining in solid material to be reused (figure 2.4a), nevertheless, this has not been efficient in preventing the direct deposition of the liquid waste into the river. Actually, the re-cycling of mercury during the gold extraction process is not efficient (Silva, 1994; André et al., 1997) and most of the mercury used to extract gold is present in liquid wastes containing large quantities of suspended material. For instance, in a vertical sediment profile taken 5 km from La Estrella plant downstream in Sucio River (figure 2.1 and 2.3b), André et al. (1997) found significantly higher concentrations of both mercury and lead than in ocean sediments ($0.02\text{-}0.10 \mu\text{g g}^{-1}$) (WHO, 1989). The mercury concentration decreases with depth, which may reflect an increased mercury concentration of the settling water. The heterogeneity found in the vertical mercury distribution may be due to resuspension of sediment-bound mercury during high river water flow.

Small-scale gold mining (La Rastra): The miners extract gold from material that they obtain in the area and/or from material that has been processed by La Estrella plant. The ores are crushed by large stones in a circular tray, in which the stones are moved like milling stones, driven by a water wheel. The crushed material is carried by water and flows continuously over a concrete surface where mercury has been added (figure 2.4b). Fine solid particles and water get in contact with mercury, and the gold is amalgamated. Then the amalgamated gold is smelted on bonfire to remove the mercury through evaporation to the air. Fifty percent of the total mercury used by La Rastra is estimated to be lost to the air through evaporation, and the other 50% is discharged together with solid material and water directly into Sucio River (André et al., 1997).

Panhandlers: Artisanal miners use metallic mercury to extract gold from river sediments deposited into the Sucio River by La Estrella plant. Their number is about 50 in Santo Domingo, and about 15 400 in the whole gold mining area of Nicaragua (Silva, 1994). They are the major contributors of the diffuse mercury contamination along the river basin, since they work anywhere along the river. Their contribution to river pollution has been estimated to 4 kg of mercury per month (André et al., 1997).

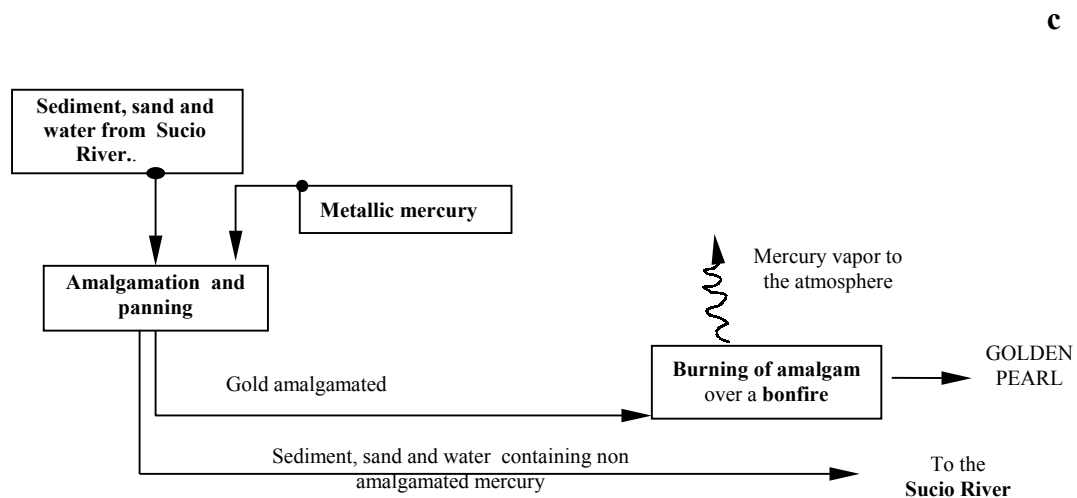
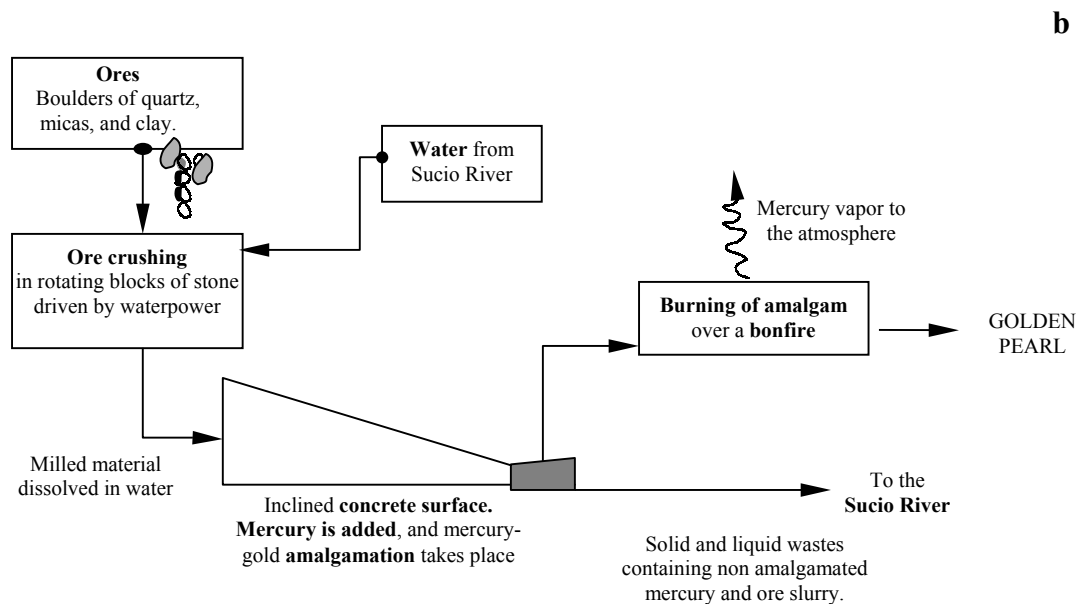
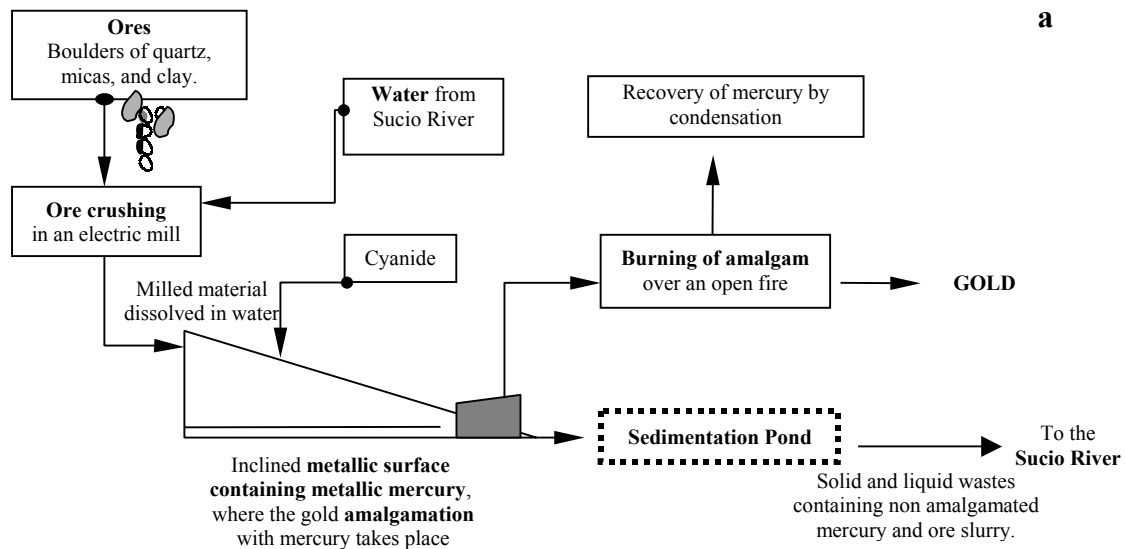


Figure 2.4. Gold extraction activity in Santo Domingo. a) La Estrella Plant, b) Small water driven stone-mill and c) panhandlers.

Artisanal miners release mercury into the atmosphere during the amalgamation activity and during firing of amalgams in the open air (figure 2.4c). They also spill metallic mercury into the river from gold pans during the mixing of the ore, leading to mercury accumulation in the bottom sediments. The artisanal miners choose to extract gold with mercury because it does not require sophisticated tools.

Table 2.1. Concentrations of total mercury in the environment in different gold mining areas

Gold mining areas.	Estimated Hg emission from gold mining		Mercury concentrations (sediment, soil and fish are in dry weight)				Human Population		Reference
	Period Tons	t yr ⁻¹	Water (µg l ⁻¹)	Sediment (µg g ⁻¹)	Soil (µg g ⁻¹)	Fish (µg g ⁻¹)	Urine (µg l ⁻¹)	Hair (µg g ⁻¹)	
Amazon, Brazil	1979/96 3000	180	9	19	-----	0.2 - 4	1200	0.7-176	Lacerda and Salomons (1991), L. D. Lacerda (1997), O. Malm (1998)
Victoria Fields, Tanzania	1991/95 24	6	0.01-7	0.02-136	0.05-28	0.03-0.05	-----	-----	L. D. Lacerda (1997), J. R. Ikingura et al (1997)
Dixing Region, China	1992/96 480	120	300	-----	1100	-----	3.6-539	-----	Y. Lin et al (1996), L. D. Lacerda (1997)
Sucio River Nicaragua.	-----	0.4	7	7	0.4	0.4	-----	56	Silva (1994), André et al (1997).
Total mercury concentration found in pristine environment			0.003	< 0.02	< 0.05	0.2	*4 - 5	*2.0	*WHO,1990 recommended level

2.2. Other case studies

Similar small-scale amalgamation activities are found in many developing countries, each with a significant contribution to global mercury emissions. The Amazon in Brazil, the Victoria fields in Tanzania (Ikingura et al., 1997), and the Dixing region in China (Lin et al., 1997), to mention some examples, have the same histories linked to gold mining activities as the Santo Domingo in Nicaragua. These mining areas face similar environmental problems. Techniques used for gold extraction are generally unsophisticated and employ considerable amount of mercury.

The total anthropogenic mercury emission from gold mining activities is estimated to correspond to approximately 50% of the total mercury input into the biosphere by natural weathering (Lacerda, 1997). The global mercury emission from gold mining is estimated to 460 tons per year, of which approximately 35% end up in soils and water (Lacerda, 1997). However the lack of data from other gold mining areas around the world suggest that the numbers may be underestimated. From small gold mines in China about 18 % of the mercury used to extract gold is lost to soils and waters (Lin et al., 1997), and in the Amazonian areas, between 15 and 50% of the mercury is lost directly to the rivers and between 65 and 83% into the atmosphere (Moreira, 1996).

The amounts of mercury annually released from different gold mining areas into the environment are not generally comparable with each other, as they may depend on many factors, such as the mining activity itself, the gold production, technique, and the amounts of mercury used. For instance, the annual mercury emission from Santo Domingo in table 2.1 is probably underestimated, as it assumes a working time of eight months per year and uses the monthly total mercury emission reported by André et al. (1997). Although the annual mercury emission in the Amazon is much higher than in Santo Domingo, mercury occurs at similar concentrations in the environment of both areas.

The mercury concentrations in soils given in the table 2.1 are from near the site of gold extraction, from where they often decrease to background levels within a distance of a few kilometers. Possibly, only a small part of the evaporated mercury is deposited close to the source.

The mercury concentrations in river water in the Amazon, Tanzania and the Santo Domingo are similar (table 2.1) and higher than the maximum permissible level of $1.0 \mu\text{g l}^{-1}$ in drinking water (WHO, 1989). This raises some concern about risks for aquatic life and people. Rivers from these gold mining areas should not be used for drinking water or for animals watering, since the levels of mercury in river water are above those recommended for drinking water (André et al., 1997).

Both water and sediment in rivers in gold mining areas are sources of mercury to fish, and fish has been considered the main source of mercury to humans in those areas. For instance, in the Amazon region and other mercury contaminated areas, mercury concentration in fish has been monitored as an indicator of river and lakes contamination (Bidone et al., 1997). Although mercury concentration found in fish from Sucio River are similar to concentrations found in fish from pristine surface waters (table 2.1), the values are not directly comparable due to absence of data on what species were analyzed, their age, and so on.

Mercury concentrations in human hair are due to the direct exposure, mainly from burning of the gold-mercury amalgam and are indicators of human mercury contamination (WHO, 1990). These concentrations could vary depending on exposure time, the kind of fish eaten, and the gold mining activity of the person. For instance, the mercury concentration in the hair of people eating fish from Santo Domingo was generally very low ($0.3 \mu\text{g g}^{-1}$) (André et al., 1997). Higher values were found in miners with more than eight years of exposure to mercury (table 2.1), but these values might include metallic mercury adhered directly on the hairs during the handling of metallic mercury (Silva, 1994). High hair mercury concentrations in the Amazon population are due to the direct mercury vapor exposure during the burning amalgam in open air.

Table 2.1 shows mercury concentration only in human hair in the Santo Domingo population, because of scarcity of data on the effect of mercury on humans living in that area. Some blood samples have been taken and analyzed for mercury, but no reports are available.

3. Transport and fate of mercury in soil, river and groundwater

3.1. Transport in soil

Mercury is deposited on soils and surface waters by dry and wet deposition, mainly in its oxidized forms (Hg(II)) and as elemental mercury (Hg⁰) (Porcella, 1994; Tsiros and Ambrose, 1999; Schlüter, 2000). Soils are the major sink for mercury, so when the concentration in the atmosphere increases, more mercury will be found in soils. In soils, mercury and other metals are associated with soil organic matter (SOM) (Boyd et al., 1981; Lodenius et al., 1987; Yin et al., 1996; Wallschläger et al., 1998), and with mineral surfaces (Tamura and Furuichi, 1997; Yin et al., 1997; Gissinger et al., 1999; Walcarius et al., 1999). It is also present in the soil solution. Deposited mercury can be retained, mobilized and volatilized by many processes in the soil (figure 3.1). The main processes responsible for retain mercury is the complexation by organic functional groups on particulate organic matter (POM), mostly thiol groups, and by binding with variable-charge minerals. Decomposition of organic matter and extraction of mercury by strong dissolved ligands, followed by diffusion and advection, are processes responsible for mercury mobilization in soil.

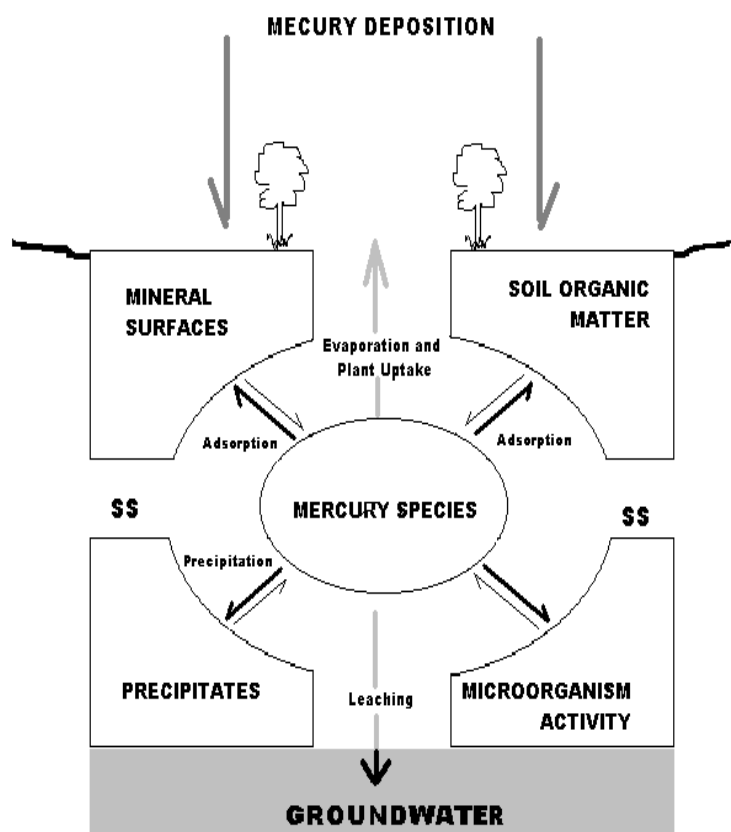


Figure 3.1 Mercury and soil component interaction (SS: Soil Solution)

3.1.1. Adsorption of mercury by Soil Organic Matter

SOM is a mixture of organic constituents, such as humic acids (ha), fulvic acids (fa), humins, polysaccharides, proteins, sugars, amino acids, and lipids. POM is responsible for retaining mercury in the soil by forming complexes via chemical bonds and to a much lesser extent by its adsorption on soil minerals due to electrostatic forces (Schlüter, 1997). Humic substances are the major component of SOM, and contains a large number of various functional groups mainly such as carboxylic and phenolic, but also a smaller number of strong metal complexing groups such as amine, carbonyl and sulfhydryl groups (Lodenius et al., 1987; Johansson and Iverfeldt, 1994; Matthiessen, 1996; Wang et al., 1997; Biester and Zimmer, 1998). Especially the S⁻² containing groups, such as R-SH compounds, form strong complexes with mercury (Nahar and Tajmir-Riaghi, 1996; Yin et al., 1997). Carboxylic acids are generally stronger acids than phenolics and are mainly responsible for the cation exchange capacity (CEC) of SOM. Although organic matter (OM) can reduce mercury toxicity to aquatic organisms by sequestering mercury (Richards et al., 2001), in soil it enhances the mercury bioavailability to microorganisms.

Deposited mercury is strongly sorbed in soils with high OM content (Hogg et al., 1978; Yin et al., 1996; Schlüter and Gäth, 1997; Yin et al., 1997). In soil, OM has been positively correlated with

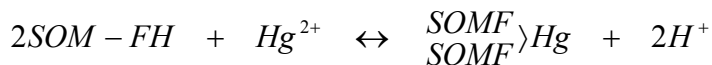
the concentrations of mercury (Yin et al., 1997), and the correlation is influenced by pH (Yin et al., 1996). Mercury adsorption is totally dominated by SOM under acid conditions (Yin et al., 1996), whereas adsorption on oxides and clay minerals becomes somewhat more important under less acid to neutral pH. For instance, when the soil pH increases, the solid phase OM tends to dissolve and can stay in solution with mercury associated to it as dissolved organic matter mercury (DOM-Hg) complexes (Yin et al., 1996; Schlüter, 1997; Schlüter and Gäth, 1997; Spark et al., 1997) such as other divalent metals (Lee et al., 1996; Spark et al., 1997). The presence of carboxylic and phenolic groups gives the net negative charge of DOM, which interacts with positive charge on mineral surfaces. Ligand exchange reactions between the functional groups of DOM and the hydroxyl groups on mineral particles can be the mechanism of this interaction (Kaiser and Zech, 1997; Spark et al., 1997; Kaiser and Zech, 1998). These negative charges are responsible to bind mercury, which can also be adsorbed directly on negatively charged mineral surfaces. This might mean that mercury and DOM simultaneously occupy all sorption sites on mineral particles and part of the mercury is binding by OM, which is dissolved by increasing pH. DOM-Hg complexes might be also sorbed as such on mineral surfaces, with DOM acting as a bridging ligand between Hg(II) and soil oxides (Schlüter, 1997; Spark et al., 1997).

Mercury may form ionic or strong covalent bonds with functional groups of the interior of the SOM molecules. This interaction can generally be illustrated as:



where F is the complexing functional group of SOM .

Hg(II) may bind to two functional groups simultaneously:



It is thought that the mechanism for mercury binding to functional groups of SOM is by chelation and cation exchange. The products of reactions between mercury ions and organic ligands can be bound in soil, sediments and organisms containing these ligands and compounds that bind them. This complexation greatly limits the mobility of mercury in soil. However, it can be eluted in runoff where dissolvable Hg-organic ligands can incorporate easily to it in the dissolved phase.

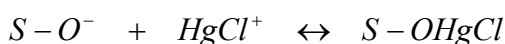
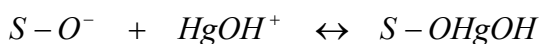
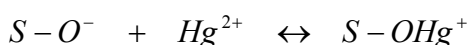
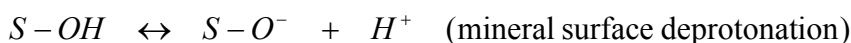
In most soils, ha and fa are the principal sorbents of mercury and most of other metals (Lodenius et al., 1987; Johansson and Iverfeldt, 1994; Matthiessen, 1996; Wang et al., 1997; Schlüter, 2000).

3.1.2. Adsorption of mercury on mineral surfaces

Mineral surfaces are represented by silica minerals, silicate clay minerals, iron, aluminium and manganese oxides, pyrite and quartz (Sarkar et al., 1999; Walcarius et al., 1999; Sarkar et al., 2000) and are major sorbents of metal ions in soils, such that partitioning coefficient has been positively correlated with the concentration of these oxides (Schlüter, 1997). As mercury has a high affinity for soil minerals (Kinniburgh and Jackson, 1978; Yin et al., 1996; Tamura and Furuichi, 1997) it could be expected to have low mobility in soils. However, the extent of mercury adsorption to soil mineral surfaces depends on soil pH, CEC, and the specific surface area of the soil particles (SSA) because protons, mercury ions and even organic matter can compete with each other for available mineral surface binding sites (Yin et al., 1996; Spark et al., 1997; Echeverría et al., 1998; Walcarius et al., 1999). Soils with a high CEC tend to adsorb more mercury than soils with a low CEC (Yin et al., 1996), because large quantity of cation on the mineral surface can be replaced by ionic mercury.

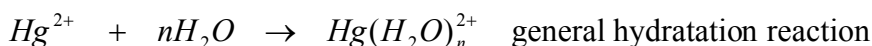
In addition to the sorption on minerals, mainly as DOM-Hg, mercury can be directly sorbed on mineral surfaces via chemical reaction between a surface hydroxyl group on the mineral surface and hydroxylated mercury species (Sarkar et al., 1999; Walcarius et al., 1999; Sarkar et al., 2000) or via cation exchange, resulting from electrostatic interaction (Yin et al., 1997; Kraepiel et al., 1999). The greatest Hg-Cl species (HgCl_2 , HgCl^+) adsorption occurs a low pH (pH <4), while adsorption of hydroxylated Hg (II) species (HgOH^+ , $\text{Hg}(\text{OH})_2$, HgOHCl) is favoured under less acid to neutral pH (Yin et al., 1996; Sarkar et al., 1999; Walcarius et al., 1999). This means that more of the divalent mercury in wet and dry deposition would be retained on the mineral phase in acid soil compared with an alkaline soil.

Adsorption of metals on mineral surfaces is well documented and explained by surface complexation models (SCMs) (Venema et al., 1996; Robertson and Leckie, 1997; Yin et al., 1997; Wen et al., 1998; Kraepiel et al., 1999; Walcarius et al., 1999). To explain the interaction between mercury species and the permanent negative charge on mineral surfaces, SCMs generally express the mineral surface (S) as S-OH, S-OH_2^+ , and S-O^- . Hydroxyl groups provide the negative surface charges. S-O^- is the predominant group at pH between 4 to 7, because of deprotonation of the mineral surfaces, whereas S-OH_2^+ is the most common group at high pH, because of protonation. Generally, the adsorption of mercury on mineral particles has been attributed to the presence of S-O^- groups (Wen et al., 1998; Walcarius et al., 1999), as pH of most natural soils is within 4 and 7. The adsorption mechanism involves the formation of strong bonds between mercury ionic species and unsatisfied-oxygen atoms of the surface groups (Tamura and Furuichi, 1997; Yin et al., 1997; Wen et al., 1998; Gissinger et al., 1999; Quémerais et al., 1999):

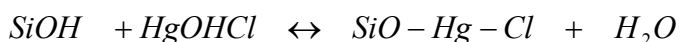
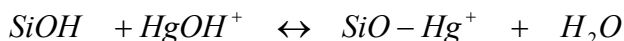
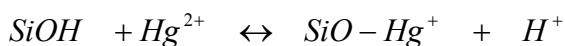


The surface complexation reactions take place at the interface between the soil solution and the solid mineral surface (Wen et al., 1998; Kraepiel et al., 1999), where the surface charge and the negative potential of the surface are pH dependent.

For instance, the mercury adsorption mechanism on a silica surface may be explained by hydration and hydrolysis of Hg(II) followed by a chemical reaction between hydroxylated mercury and the silica surface, since only hydroxylated mercury species are liable to bind to silica surfaces (Sarkar et al., 1999; Walcarius et al., 1999) and gibbsite (Sarkar et al., 1999). At pH lower than 7, the silica surface is mainly occupied by nonionized hydroxyl groups (Walcarius et al., 1999), such as the silanol group (SiOH). This group can attract metal ions electrostatically and form an inner-sphere type complex. The formation of inner-sphere surface complexes involves the formation of chemical bonds of ionic and hydroxylated mercury species with surface oxygen of deprotonated silanol groups of the silica (Yin et al., 1997; Schlegel et al., 1999; Walcarius et al., 1999):



$$\text{Hg}(\text{H}_2\text{O})_n^{2+} \leftrightarrow \text{Hg}(\text{OH})_n^{(2-n)} + n\text{H}^+ \quad \text{general hydrolysis reaction (the ionic potential is thought to be large enough to rupture O-H bonds in the water molecule)}$$



simultaneous silanol deprotonation and adsorption reaction.

The adsorption of mercury chloride species by this mechanism can be favoured at pH less than 4, as it has been tested (Yin et al., 1996; Walcarius et al., 1999), while the adsorption of the hydroxylated species can be favoured at pH above 4 (Walcarius et al., 1999).

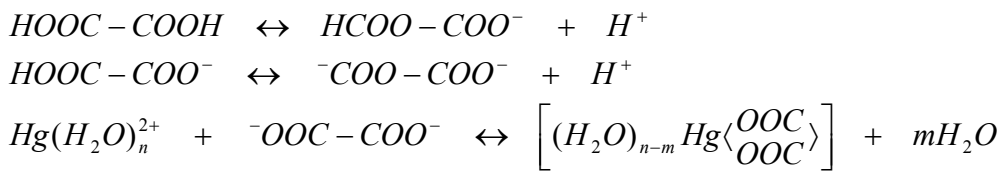
In soil CEC is mostly derived from clay minerals and organic matter. The sorption mechanism on clay minerals (e.g. kaolinite and montmorillonite) is mainly cation exchange inside the clay particles, as clay minerals have exchangeable Ca^{2+} , Mg^{2+} , Na^+ and K^+ (Altin et al., 1998; Kraepiel et al., 1999). In this way, ionic mercury can displace monovalent cations from the clay exchange sites. In oxides and hydroxides of Al, Fe, Mn, and Si, the permanent surface charge is small, but they have a CEC.

3.1.3. Desorption/Dissolution

Adsorption of mercury by soil components seems to be an irreversible process, since strong bonds are formed and large activation energy becomes necessary to break the ligand-mercury bond. However, diffusion of Hg(II) may take place in both intra-particle pores of minerals and intra-particle micropores of SOM adsorbed by mineral surfaces (Yin et al., 1997), and dissolution and desorption may take place, as mercury sorption is pH-dependent. In this sense, ionic mercury species and protons can compete with each other for available surface binding sites (Echeverría et al., 1998). It means that mercury can be desorbed from SOM and mineral surfaces, since mercury tends to form soluble complexes or colloids in the presence of soluble inorganic and organic ligands. Metals, such as copper, manganese and zinc, are removed from the reactive surface of sediment DOM. This also happens with mercury (Yin et al., 1996; Eimax et al., 1998) (Schlüter, 1997). In soils at pH above 6, dissolution of OM is greater than in acid soils and it form complexes with mercury (DOM-Hg) (Yin et al., 1996; Biester and Zimmer, 1998; Wallschläger et al., 1998).

As mercury may occur as soluble species (Hg^+ , Hg^{2+} , HgOH^+ , $\text{Hg}(\text{OH})_2$) in soil solutions (Yin et al., 1997; Schlüter, 2000), inorganic ligands can react with it, dependent on soil pH conditions. For instance, ionic and hydroxylated mercury species tend to complex with Cl^- ions to give HgCl^+ , HgCl_2 and $\text{Hg}(\text{OH})\text{Cl}$ (Yin et al., 1996; Gissinger et al., 1999). The effect of Cl^- on adsorption has been tested in adsorption experiments with different mineral surfaces and different concentrations of Cl^- (Yin et al., 1996; Gissinger et al., 1999; Walcarius et al., 1999). For example, without or in presence of very low Cl^- concentrations the greatest Hg(II) adsorption occurs at pH above 4, whereas in presence of higher concentration of Cl^- the Hg(II) adsorption occurs at pH below 4, because the formation of HgCl_2 increases, and the fraction of HgCl^+ , $\text{Hg}(\text{II})$, and $\text{Hg}(\text{OH})\text{Cl}$ decreases. Mercury in the form of HgCl_2 is poorly adsorbed by inorganic surfaces at pH above 4 (Yin et al., 1996; Gissinger et al., 1999). It is thought that DOM acts as bridging ligand between Hg(II) and soil oxides. This bridging is affected by the formation of mercury chloride (Schlüter, 1997). At pH above 4, chloride can be able to mobilise mercury by forming soluble inorganic mercury species.

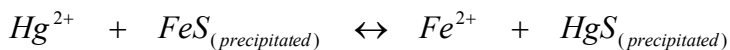
Ionic mercury (Hg^+ , Hg^{2+}) is a soft acid and forms stable complexes with organic ligands, such as CN^- , CO_3^{2-} , S^{2-} , and R-SH (sulfhydryl), in the soil solution. For instance, dicarboxylic acids (e.g. oxalic acid of biological origin) may dissociate and bind mercury:



In this way, the solubility of mercury increases. However, sulfhydryl groups (-SH), and inorganic sulphide from sulphate reduction can precipitate mercury as mercury sulphide (HgS) at high redox potentials. Since HgS is resistant to oxidation, mercury may remain precipitated in the soil also under oxidizing conditions (Barnett et al., 1997; Yin et al., 1997; Biester and Zimmer, 1998).

3.1.4. Precipitation

Although precipitation of metals in soils is less likely than adsorption due to the low metal concentrations, mercury may form insoluble precipitates (oxides, sulphites) depending of pH. Moreover, living organisms can also precipitate mercury as sulphides in anoxic environments (Allen, 1993; White et al., 1995). Ligands, such as hydroxides (OH⁻), carbonates (HCO₃⁻), silicates, phosphates, and sulphides (S²⁻), can precipitate with ionic mercury species. Sediments often contain a large amount of sulphite, largely present as iron monosulphite. Iron monosulphite can react with deposited mercury (Allen, 1993; Barnett et al., 1997):



It is thought that sulphides control the solubility of Hg²⁺ in reducing soils (Barnett et al., 1997; Biester and Zimmer, 1998).

3.1.5. Mercury uptake by plants

The levels of mercury in plants can be used as an indicator of the soil content of mercury (Rasmussen, 1994; Ellis and Eslick, 1997). Desorption or dissolution, diffusion and bulk flow toward the roots, adsorption by roots or foliar uptake (Rea et al., 2002), and translocation are the main processes involved in plant uptake of metals.

Positive correlations have been found between mercury levels in soils and those measured in roots, stems and leaf in plants (Ellis and Eslick, 1997). The uptake in plants depends on plant species (Godbold, 1994; Ellis and Eslick, 1997), soil properties (Wang et al., 1997) and mercury species (Godbold, 1994; Ellis and Eslick, 1997; Wang et al., 1997). For instance, inorganic mercury is more accumulated in vascular plants than methyl mercury as inorganic mercury is more water-soluble than the organic form and follows the same route within the plant as an essential element. (Godbold, 1994). Whereas mercury species can be translocated to various compartments of the plant and then emitted to the atmosphere through the stomata (Todd et al., 1998), its uptake seems to be mainly via the roots (Ellis and Eslick, 1997; Wang et al., 1997; Todd et al., 1998). However, if the mercury concentration in the soil solution is low, the diffusion becomes extremely slow. In this case, convective movement becomes more important for mercury uptake. This movement takes place when the plants transpire water and create water potential in the soil pores towards the roots. Roots may modify the soil solution chemistry of the root zone by exudation of protons and organic chelating agents, thereby increasing the solubility of mercury, because protons decrease the pH and the chelation agents bind mercury.

In soils, the primary variable controlling mercury uptake by plants may be the soil pH, because at low pH, the solubility of most metals increases and they become more available to plants. In alkaline soils, mercury is available as DOM-Hg complexes, whereas in acid soils, mercury may be

as free ionic mercury species available to plants or strongly bound to immobile OM and soil minerals, and inaccessible for plant. The availability of organic mercury to plants decreases when ha in soil increase, because mercury-ha complexes cannot be washed away by watering the plants (Wang et al., 1997; Gissinger et al., 1999). Furthermore, clay, iron, and manganese immobilize mercury, preventing the mercury absorption by roots. In soils with high concentration of bioavailable mercury, physiological effects, such as a reduction in photosynthesis, transpiration and root growth, can be expected (Godbold, 1994). This could be due to change in the membrane permeability and subsequent loss in roots of cytosolic and vascular elements such as K, Mg, and Mn (Godbold, 1994).

The transport of mercury from roots to other parts of the plant is a biological process that would seem to be unaffected by soil chemistry. Most of the metals in cationic form are accumulated preferentially in roots and not translocated (Hogg et al., 1978). For instance, mercury can be found in higher concentration in roots than in leaves. The translocation behaviour in plants is complex and not well understood for many of the elements. It is thought that soil chemical factors (alkalinity, phosphate level, cation concentration) (MacBride et al., 1981) and environmental factors (humidity, temperature) could influence the metal movement within plants.

3.1.6. Biological transformation

In soil, microorganisms can reduce both ionic mercury species and OM-mercury complexes to elemental mercury, which can escape to the atmosphere due to its high volatility (sec. 3.1.7) (White et al., 1995; Ghosh et al., 1996; Wang et al., 1997; Schlüter, 2000). Inorganic and organic mercury can eliminate some susceptible species in a bacterial community, and favour the proliferation of others, such as those that transform Hg(II) to Hg⁰ (White et al., 1995; Ghosh et al., 1996; Wang et al., 1997; Welp and Brümmer, 1997; Kungolos et al., 1999; Schlüter, 2000). Moreover, microorganisms decomposing SOM can release Hg(II) from humic matter and make it accessible for reduction to Hg⁰ (Lee et al., 1995). Some strains of bacteria break down monomethyl mercury (CH₃Hg⁺) to CH₄ and Hg⁰. CH₃Hg⁺ and dimethyl mercury ((CH₃)₂Hg) may transform to CH₄ and Hg(II) by an organomercurial lyase enzyme (Schlüter, 2000).

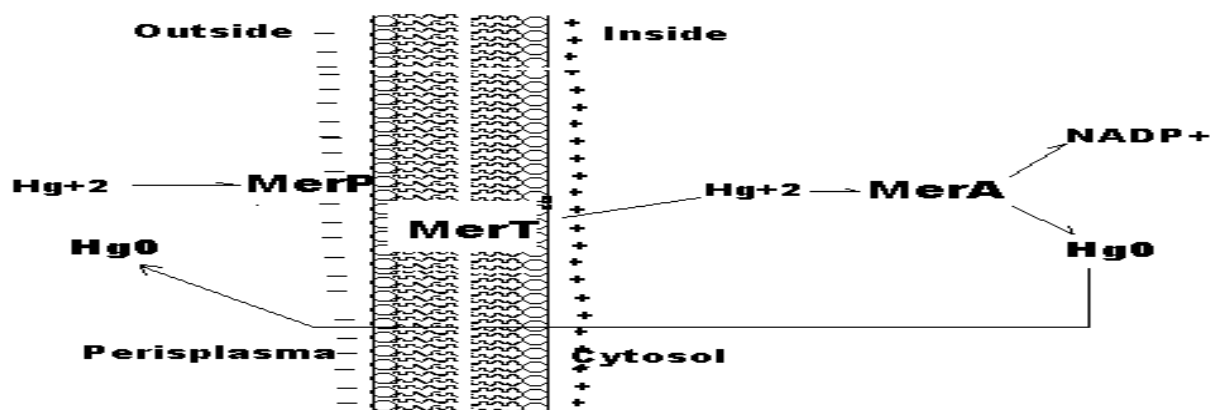


Figure 3.1.6.1 Mercury reduction in the bacteria cell (modified from B. P. Rosen, 1996)

Prokaryotic and eukaryotic organisms may become resistant to mercury. The most common resistance mechanism involves transport of ionic species, either into or out of the cell through transmembrane cation transporters. This is induced by the electrostatic forces between cationic mercury and the net negative charge of the cell surface of gram negative bacteria, which reduces mercury to a less toxic species (Hg⁰). In this process, a specialized carrier such as MercP and MerT transport proteins takes mercury into the cell. Hg(II) uptake occurs inside the cell by the

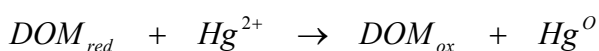
polypeptide MerP. It transfers Hg(II) into the MerT protein, which transports mercury into the cytosol. In the cytosol, mercury becomes available to a MerA protein, which catalyzes the two-electron transfer from the NADPH-dependent flavoprotein reductase to Hg(II). Elemental mercury produced in this way can diffuse passively out the cell (Rosen, 1996) and evaporate (figure 3.1.6.1). Chloride and pH affect this mechanism due the formation of charged HgCl^+ and HgCl_3^- complexes, which are relatively polar leading to an inhibition of the cellular uptake.

Whereas bacteria can volatilize mercury, other organism, such as fungi, can protect themselves by binding mercury to phenolic units, peptides, carbohydrates, aliphatic hydrocarbons and fatty acids (White et al., 1995). In biosorption, the Ca^{2+} , Mg^{2+} and K^+ ions present on the cell surface, are replaced by metals, indicating that ion exchange mechanisms take place.

3.1.7. Mercury volatilization

Volatilization is one of the pathways of the mercury flux in the environment and most mercury evaporates from soil in the form of elemental mercury, but it can also be evaporated in the form of dimethyl mercury and probably also as monomethyl mercury. (Schlüter, 2000).

In soils, the volatilization of Hg^0 is caused by both abiotic and biotic processes (sec. 3.1.6). The abiotic mercury reduction is influenced by redox conditions, pH and by ha and fa in the soil solution. Despite the fact that DOM is an efficient sorbent for mercury in the soil solution (Johansson and Iverfeldt, 1994; Schlüter, 2000), it can reduce Hg(II) followed by Hg^0 evaporation:



It is thought that mercury reduction followed by volatilization is mediated by microbial activity.

The most soluble and volatile mercury species, such as Hg^0 and $(\text{CH}_3)_2\text{Hg}$, can disappear from a soil when the soil temperature increases. Volatile mercury species also tend to migrate by gas diffusion in the soil pores toward the soil surface (Schlüter, 2000). Volatile mercury can be deposited again on the soil surface by high air humidity in the soil-atmosphere interface (Schlüter, 2000), as a result of condensation. On the other hand, although it has not been tested, it is suspected that volatile as well as non-volatile mercury species (CH_3HgCl , $\text{Hg}(\text{OH})_2$, CH_3HgOH , HgCl_2) can be evaporated by co-distillation with evaporating soil water (Schlüter, 2000).

3.1.8. Mercury removed from soils by runoff and leaching

Since mercury binds strongly to non-mobile OM and soil minerals (Hogg et al., 1978; Hempel et al., 1995; Kaiser and Zech, 1997; Wang et al., 1997; Kaiser and Zech, 1998), it cannot easily be leached through the vadose zone to groundwater and from terrestrial ecosystems to surface waters. But there are evidence that movement of water through contaminated permeable soils may remove both adsorbed mercury and soluble mercury species by mass-transport to groundwater and by heavy runoff to surface waters (Allan and Heyes, 1998), as runoff removes considerable amounts of minerals and organic matter from the soil (Lee et al., 1994; Tsiros and Ambrose, 1999). Minerals, organic matter and its associated mercury can be transported in suspension and in solution (Lee et al., 1995; Balogh et al., 1997; Babiarz et al., 1998). Methyl mercury and inorganic mercury has been found associated with suspended particulate matter (SPM), which has been transported from soil by runoff to the river and lakes (Mierle and Ingram, 1991; Balogh et al., 1997; Schlüter, 1997; Babiarz et al., 1998). The amount of mercury associated with SPM depends on size and nature of SPM molecules, and its mineral composition (Quémerais et al., 1999). Soluble mercury species can also migrate by diffusion in soil solutions and become absorbed by roots. Moreover, roots may absorb mercury by pulling water out of the soil pores (sec 3.1.5).

Two main processes of water movement can be responsible for the transport of mercury through the soil: a) runoff and b) infiltration (migration in porous media).

a) **Mercury transport by runoff:** Mercury in a soil solution and mercury adsorbed on soil particles may be removed by surface water runoff (Johansson and Iverfeldt, 1994; Lyon et al., 1997; Tsiros and Ambrose, 1999).

Here, I use the same approach as Ramireddygarri et al (1996). Assume that we have a land surface with a small slope (S_0) and the rainfall $R(x,t)$ varying in space and time (figure 3.1.8.1). Then the water balance for the area can be written as:

$$Q(x,t) = R(x,t) - I(x,t)$$

where, $Q(x,t)$ is the overland water flow; $R(x,t)$ is the precipitation; and $I(x,t)$ is the amount of water infiltration.

Due to both rainfall and infiltration variations, the depth of the water flowing on the land surface varies in time and the discharge (q) varies along the land surface. The overland water flow can be written as:

$$Q(x,t) = \frac{\partial y}{\partial t} + \frac{\partial q}{\partial x} \quad (1)$$

The overland water flow can be laminar or turbulent. For example, if the velocity of water is relatively low and the slope is small, the flow becomes laminar, but if the slope increases, the water velocity increases, and the flow becomes turbulent. The above equation (1) depends on several other parameters. For instance, the discharge (q) depends on the thickness (depth) of the water flowing on the land according to:

$$q = \alpha y^{m+1} \quad (2)$$

where, α and m are empirical coefficients that depend on the flow regimen and y is the depth of the water flow on the land.

For laminar flow, $m = 2$ and $\alpha = 8gS_0/K_r\mu$, where S_0 is the uniform soil surface slope, μ is the kinetic viscosity of water, K_r is a parameter related to the soil surface roughness, and g is the gravity constant. In a laminar flow, the water molecules move following smooth lines. This movement is generally slow and is dominated by viscous forces (Ramireddygarri et al., 1996).

For turbulent flow, $m = 0.5$ and $\alpha = C_z S_0^{1/2}$, where C_z is *Chezy's* coefficient. In a turbulent flow, which is characterized by high velocity, water molecules are moving in an erratic fashion, due to inertial forces, which are more influential than the viscous forces.

When the slope is not a constant, it is calculated as

$$S_0 = S_f + \frac{\partial y}{\partial x}, \quad \text{where, } S_f \text{ is the friction slope.}$$

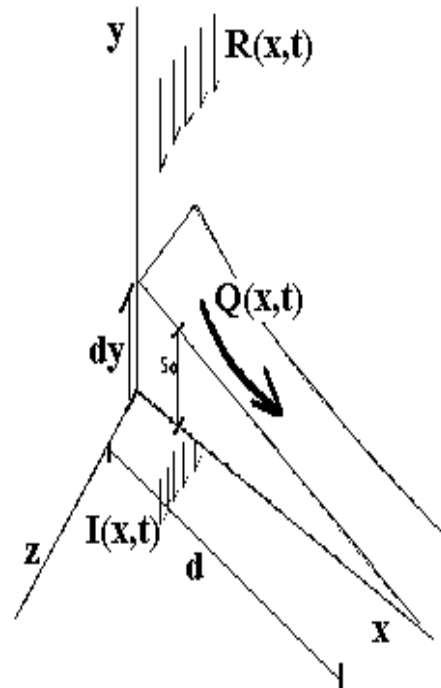


Figure 3.1.8.1 Rainfall, runoff and water infiltration in a land surface

Whether the flow is laminar or turbulent can be determined using the Reynolds number (**R**), which generally is written as follows:

$$R = \frac{\rho v d}{\mu},$$

where ρ is the water density, v is the discharge velocity, μ is the water viscosity and d is the hydraulic radius in the case of an open-channel. The transition from laminar to turbulent fluid flow occurs when the average velocity is such that the **R** number exceeds some value, which depends on field characteristics (e.g. stream flow, roughness of the stream bed, etc.). For instance, the transition between laminar and turbulent has been reported occur between Reynolds numbers from 500 to 4000 (Hart et al., 1999).

The combination of equation (1) and (2) gives an equation, which describes the movement of water on land surface:

$$Q(x, t) = \frac{\partial y}{\partial t} + \alpha(m+1)y^m \frac{\partial y}{\partial x} \quad (3)$$

A sediment transport model can describe the transport of the material eroded by the surface runoff water (Ramireddygar et al., 1996):

$$S(x, t) = \frac{\partial S_y}{\partial t} + \frac{\partial S_q}{\partial x} = \sigma \left[\frac{C_t (\rho_w y S_o - \tau_{cr})^p}{\rho_s} \right] + \frac{C_1 R^{c_2}}{\rho_s} \quad (4)$$

where $S(x, t)$ is the spatial and temporal variation of the total sediment concentration, $\partial S_y / \partial t$ is the temporal variation in the amount of the eroded sediment along the thickness of runoff (y), $\partial S_q / \partial x$ is the spatial variation of the amount of sediment dragged by runoff, ρ_s is the mass density of the particles, R is the rainfall rate, σ and C_t are coefficients for erodibility of the soil as a result of sheet erosion, ρ_w is the density of water, τ_{cr} is the critical shear stress, C_1 and C_2 are empirical constants, p is a constant within the range (1.0-2.5), $\rho_w y S_o$, is a measure of the force exerted by the surface flow on the soil particles on the bed.

The mercury transport depends of the equation (4) and can be described in a similar way (e.g. solute transport equation):

$$C(x, t) = \frac{\partial C_y}{\partial t} + \frac{\partial C_q}{\partial x} = \partial \frac{(D_x \partial C_y / \partial x)}{\partial x} + V(C_s - C) + P C_{sa} \quad (5)$$

(Advection-diffusion and adsorption equation)

where $C(x, t)$ is the spatial and temporal variation in the total mercury concentration in the runoff, $\partial C_y / \partial t$ is the temporal variation of the mercury concentration along the thickness of the runoff, $\partial C_q / \partial x$ is the spatial variation in the mercury concentration in the discharge, V is the convective mass transfer coefficient that relates mercury flux across the soil surface interface to the difference in mercury concentration between soil solution (C_s) and the runoff $C(x, t)$, D_x is the mercury diffusion coefficient, C_{sa} is the concentration of mercury adsorbed on to the soil, P is the amount of mercury bound by eroded sediment transported by the runoff.

$$P = \sigma \left[\frac{C_t (\rho_w y S_o - \tau_{cr})^p}{\rho_s} \right],$$

This is the first term in the right side of equation (4).

It is assumed that the mercury concentration in the soil is homogeneous along the slope and that mercury flux from the soil surface to the runoff is uniform.

Analytical solution of equations 3), 4) and 5) are presented in figure 3.1.8.2. The water discharge is the amount of water discharged on surface land, which varies with the time. At the beginning, rainfall increases gradually, increasing the amount of water discharged on surface land until it is expected to be constants. The amount of discharge decreases when the rainfall ceases. The same trend is expected to be valid for sediment discharged on a specific site (e.g. river system) at the land surface. The mercury concentration in the soil can be assumed to be constant. However the mercury concentration in the runoff increases with time, because large quantities are dissolved in runoff.

This can be a general description of the transport of mercury by runoff. Other parameters and variables may influence the behaviour. For instance, in a permeable soil the vertical movement of mercury infiltration becomes most important, whereas in soils with high clay and OM content, the runoff can control the transport of mercury.

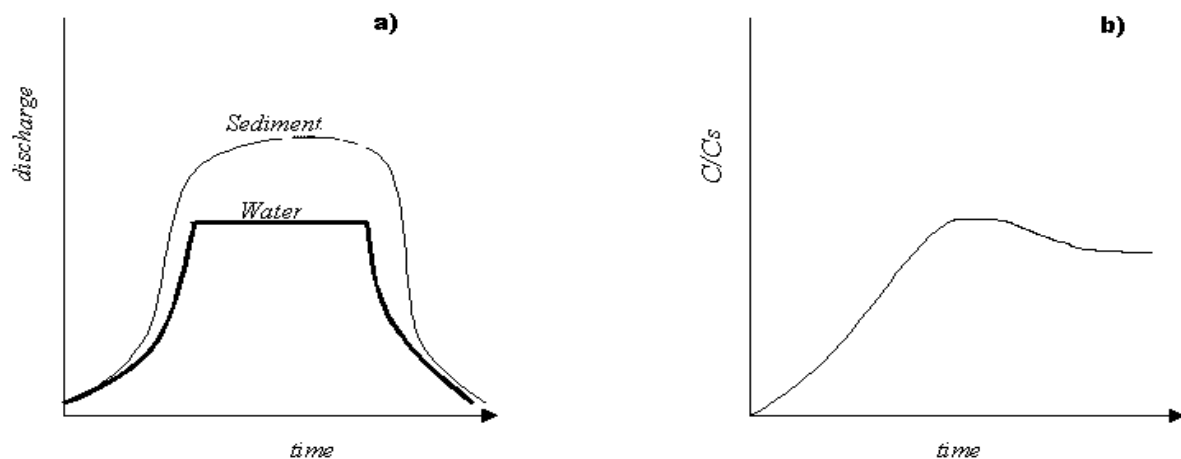


Figure 3.1.8.2 Analytical representation of a) (3), (4), and b) (5) equations. Boundary condition $t = 0$ ($x = 0$, $S = 0$, $C = 0$) and $t = t$ ($x = d$, $S = S$, $C = C$).

b) Mercury leaching by water infiltration

In section a), mercury was not considered in the infiltration. However, when all precipitation is infiltrated, water flowing in the unsaturated zone can leach mercury, as it has been demonstrated and modelled in lysimeter experiments with undisturbed soil columns (Hogg et al., 1978; Schlüter, 1997; Schlüter and Gäth, 1997). In contrast, environmental simulation models predict low mobility of mercury through organic soils at the upper soil profile (Tsiros and Ambrose, 1999) where the retention of mercury is reduced by its transformation to elemental mercury followed by volatilization.

The flow velocity of the water can easily describe transport of nonreactive solutes in the unsaturated zone. It is assumed that water mainly flows vertically and that solute travel with water. However, a reactive solute experiences a process called retardation, which can be due to adsorption processes and chemical transformation.

As with other metals, the one-dimensional advection, dispersion and adsorption equation can be used to describe the vertical transport of mercury in unsaturated soils at steady-state:

Adsorption = Dispersion - Advection

$$R_f \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial y^2} - V \frac{\partial C}{\partial y} \quad (6)$$

where C is the mercury concentration in the liquid phase, y is the depth along the direction of water flow, which percolates vertically downward along the maximal gradient of soil moisture potential, V is the water velocity, D is hydrodynamic dispersion expressed as $D = D' + \alpha$, where D' is the coefficient of molecular diffusion and α is the dynamic dispersivity. R_f is the retardation factor expressed by $R_f = 1 + K_d \rho_b / n$, where K_d is the water-soil distribution coefficient, ρ_b is the bulk density and n is soil moisture content (volumetric water content of the soil) (Genuchten and Alves., 1982; Chang et al., 2000). Here it is assumed that the mercury sorbed is directly proportional to the mercury in solution (linear retardation factor)(Chang et al., 2000). Distribution coefficients for cationic metals can be estimated when adsorption is via CEC (Appelo and Postma, 1999).

In most cases dispersion is negligible:

$$D \frac{\partial^2 C}{\partial y^2} \approx 0$$

and the equation (6) reduce to:

$$R_f \frac{\partial C}{\partial t} = V \frac{\partial C}{\partial y} ,$$

which can be solved for boundary condition $y=0$, $C=C_0$:

$$C(y,t) = C_0 \left[t - \frac{y}{V/R_f} \right]$$

Because the above equation is highly dependent on adsorption, water velocity, soil characteristics and precipitation rate (Schlüter, 1997; Schlüter and Gäth, 1997), it can have several analytical solutions for mercury leaching into the soil. For example, adsorption and precipitation might greatly limit movement of ionic mercury in a heterogeneous soil having high levels of organic matter or clays. It means that sorption will be stronger and retardation increases.

3.2. Transport in aquatic systems

Mercury can reach aquatic ecosystems by any of the following main routes:

Direct atmospheric deposition: mercury present on dust, particles and droplets may enter surface water by dry and wet precipitation or due to diffusion from air to water.

Leaching by runoff from contaminated soils: mercury in surface soils may be washed into surface water during rainfall (Sec 3.1.8).

Direct deposition of liquid and solid wastes: Solid and liquid wastes from gold mining activities may be a major source of mercury for aquatic environments.

In rivers, physical-chemical and biology processes, influence the fate and transport of the solutes. Thereby it is expected that the mercury concentration can vary both spatially and temporally within

the river. Predictive and descriptive models (solute transport equations) can be used to quantify this variation.

Prediction of the transport of mercury along of a river requires determination of the spatial and temporal variation of the mercury concentration and the processes controlling it (e.g. movement, adsorption, dissolution, oxidation-reduction, volatilization, etc.), as well as the quantification of the different mercury sources.

Within the water phase, mercury is present in both soluble and particulate forms. Soluble mercury species are free ionic mercury, inorganic and organic complexes (Wallschläger et al., 1998). To quantify the amount of mercury loading, it is necessary to measure the flow and mercury concentration associated with the effluent. A general equation can be used:

$$W = Q_{ef} C_{ef},$$

where W is the mass loading rate (mass/time), Q_{ef} is the volumetric flow rate of the mercury source, and C_{ef} is the mercury concentration in the effluent. The above equation can be incorporated into the mass balance equation.

Other, negligible mercury sources can be the runoff and acid deposition (sec 3.1.8).

Usually the river water is assumed to flow unidirectional (figure 3.2.1), and the biological processes are not considered. However the river ecosystem is still a complex ecosystem, in which a variety of processes can control the mercury transport.

When a pollutant is directly released into the river, it occupies primarily a volume with the bulk of solute concentration and immediately tends to move with the flowing water (advection movement). Simultaneously a small-scale process causes the bulk of concentration spreading out (dispersion movement), decreasing the solute concentration in the river by dissolution. Whereas the advection movement can control the transport of solute mass at the mean flow velocity, chaotic movement of the flow water can cause dispersion movement. However, since the velocity variation in the river (figure 3.2.1) becomes the dominant mixing mechanism, molecular diffusion process can be considered to be negligible.

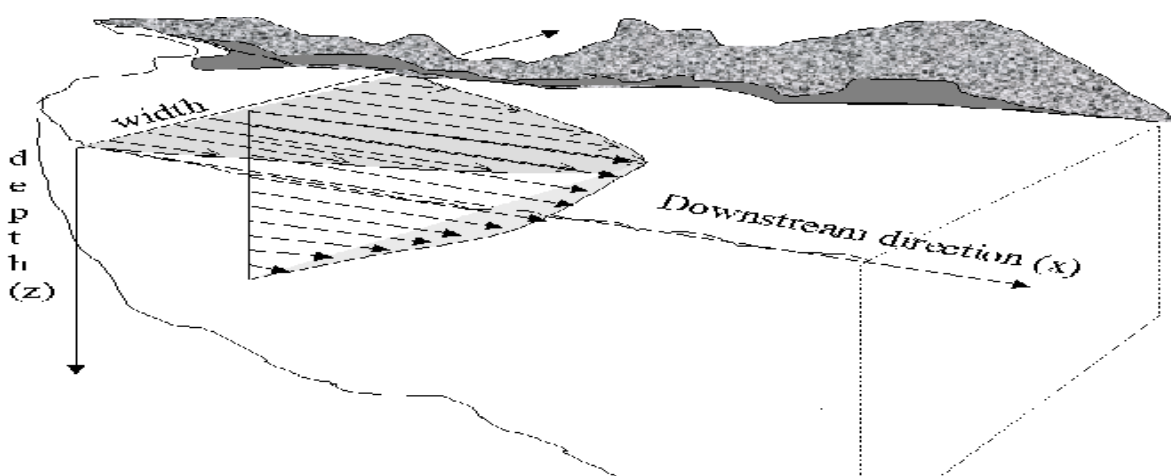


Figure 3.2.1 Vertical and horizontal variation in a river water velocity. Large arrows mean high water velocity.

Advection and dispersion movements are the major physical transport processes, which control the mercury transport. While advection affects the spatial variation more than dispersion, dispersion affects the dissolution of the bulk mercury concentration more than advection. Nevertheless, both process are varying with the time.

To explain the mercury movement in the river system, a solute mass balance can be developed. For this, consider the net mercury movement in a small spatially uniform volume of the river (control volume). It means that flow, cross sectional area, and mixing properties of the volume do not vary in space (figure 3.2.2):

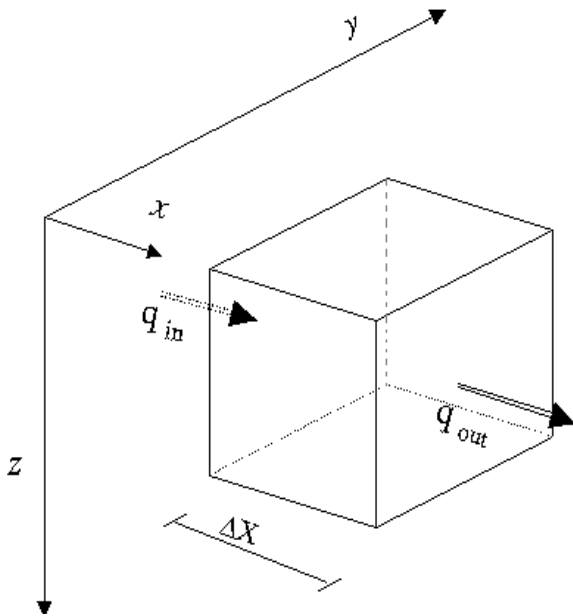


Figure 3.2.2 Solute fluxes across the control volume. Fluxes in the y and z direction are not considered.

Assuming that velocity in the control volume is constant with time (steady state), that all mercury is in movement in the volume, that the mercury concentration varies only in the downstream direction (figure 3.2.1), and that the mercury mass is uniformly distributed over the stream's cross sectional area, the mass conservation of mercury is given by the mass balance equation:

$$\text{Accumulation} = \text{Mass In} - \text{Mass Out}$$

where accumulation is given for the variation (Δ) in time of the amount of mercury in the control volume:

$$\text{Accumulation} = \frac{\Delta \text{ amount of mercury}}{\Delta \text{ time}} = \frac{\partial m}{\partial t}$$

The amount of mercury can be expressed by its concentration (C) and volume occupied (V) and replaced in the above equation:

$$\text{Accumulation} = V \frac{\partial C}{\partial t} \quad (1) \quad ,$$

and the instantaneous flux out (q_{out}) of the control volume, which is defined as the mass of mercury crossing a unit area per unit time, is equal to the flux into the control volume (q_{in}) plus the change in the flux inside of the control volume:

$$q_{out} = q_{in} + \left(\frac{\partial q}{\partial x} \right) \Delta x \quad (2)$$

Both mercury fluxes can be due to advection and dispersion movements.

Now, we can multiply the advective water velocity (U) by the concentration of mercury to give us the advective fluxes, which are defined as the mercury mass per a unit volume and per unit time.

The advective flux into the control volume ($q_{i,adv}$) will be:

$$q_{i,adv} = UC_i \quad (3)$$

Using the same deduction of equation (2), the advective flux out of the control volume ($q_{o,adv}$) will be:

$$q_{o,adv} = UC_o = UC_i + \left(\frac{\partial C}{\partial x} \right) \Delta x \quad (4)$$

To obtain the dispersive mass fluxes, we can use the *Fick's Law of Diffusion*, in which the mass flux due to molecular diffusion is proportional to the concentration gradient ($\partial C/\partial x$). Then the dispersive mass flux into the control volume ($q_{i,disp}$) becomes:

$$q_{i,disp} = -D_x \frac{\partial C}{\partial x} \Big|_i \quad (5)$$

and by analogy with (2) and (4) equations the dispersive flux out of the control volume ($q_{o,disp}$) will be:

$$q_{o,disp} = -D_x \frac{\partial C}{\partial x} \Big|_o = - \left[D_x \frac{\partial C}{\partial x} \Big|_i + D_x \left(\frac{\partial^2 C}{\partial x^2} \right) \Delta x \right] \quad (6)$$

where, subscript "i" and "o" means input and output of the control volume, and D_x is the longitudinal dispersion coefficient given in area per unit time.

Now, the total mercury fluxes to the control volume are obtained by adding equation (3) to (5), and equation (4) to (6):

$$q_{in} = UC_i - D_x \frac{\partial C}{\partial x} \Big|_i \quad (7)$$

$$q_{out} = UC_i + U \left(\frac{\partial C}{\partial x} \right) \Delta x - D_x \frac{\partial C}{\partial x} \Big|_i - D_x \left(\frac{\partial^2 C}{\partial x^2} \right) \Delta x \quad (8)$$

The substitution of the (1), (7), and (8) equations in the mass balance equation gives:

$$V \frac{\partial C}{\partial t} = UC_i - D_x \frac{\partial C}{\partial x} \Big|_i - UC_i - U \left(\frac{\partial C}{\partial x} \right) \Delta x + D_x \frac{\partial C}{\partial x} \Big|_i + D_x \left(\frac{\partial^2 C}{\partial x^2} \right) \Delta x \quad ,$$

or:

$$\frac{V}{\Delta x} \frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} \quad (9)$$

where ($V/\Delta x$) is the cross-sectional area and the volume of the control volume is given by $V = A\Delta x$. Since the fluxes are defined as the mass of mercury crossing a unit area per unit time, the equation (9) is reduced to:

$$\frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} \quad (10)$$

This is the Advection-Dispersion Equation, where U and D_x are constants in space and time. This model could describe the spatial and temporal variation of mercury concentration along river. However, it was deduced by assuming a spatially uniform, that is, the river has not lateral water inflow, and it was also assumed a constant cross-sectional area .

Other physical processes, such as lateral inflow (e.g water added to the river due to the ground water inflow, overland flow, springs, etc.) become important as they can increase the volumetric flow rate of the river flow Q (volume of water/time) (Bencala and Walter, 1983). Likewise, lateral inflow can be a source of water to the river and dilute the concentration of mercury in the river. It can also be source of mercury or other contaminants to the river, and significantly increase the mercury concentration downstream.

Another physical process that can influence the transport of mercury is the transient storage (Bencala and Walter, 1983). In the transient storage, mercury can be temporally retained in stagnant zones of the water in the river. The movement of soluble mercury in these zones becomes slow relative to the movement in the main water body.

A derivation similar to advection-dispersion equation was presented by Robert et al, (1995), where the restriction of spatially and temporally constant parameters was eliminated and the effect of lateral inflow and transient storage was included:

$$\frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial x} + \frac{1}{A} \partial (AD_x \partial^2 C / \partial x^2) / \partial x + q_l \frac{(C_l - C)}{A} + \alpha (C_m - C) \quad (11)$$

where, q_l is the lateral inflow rate per unit length of river (volume of water/time.length), α is a first order mass-transfer coefficient controlling the rate of exchange between the main water flow and the transient storage zone given in an inverse unit of time (1/T), C_m is the average mercury concentration in the storage zone.

As water in the storage zone can be immobile relative to water in the main stream, the equation describing C_m is given by (Bencala and Walter, 1983):

$$\frac{\partial C_m}{\partial t} = \alpha A \frac{(C_m - C)}{A_s} \quad (12),$$

where, A_s is the cross-sectional area of the storage zone.

Likewise, chemical processes such as precipitation/dissolution (sec 3.1.4), sorption/desorption are also important. In the **sorption** process, dissolved chemical species (sorbate) become associated with a solid surface (sorbent). Both the formation of chemical complexes and electrostatic attraction between sorbate and sorbent interaction take place during the sorption process (sec 3.1.1, 3.1.2).

In natural water, both inorganic (hydrous oxides of aluminium, iron and manganese, alumina-silicates) and organic sorbents (particulated suspended matter, dissolved organic mater) are present and can interact with ionic mercury species. In a river, sorption can take place in both liquid (water

stream) and solid (streambed) phases, such that in the water, dissolved mercury can interact with suspended particles, and sediments can remove dissolved mercury from water column.

Sorption processes are described by sorption isotherms, which relate the mass of sorbed solute to the mass of dissolved for a chemical system at equilibrium. An example is the Freundlich isotherm given as:

$$C_s = K_f C_l^n ,$$

where, C_s is the amount of solute sorbed per mass of sorbent, C_l is the amount of dissolved solute concentration per volume of solvent, K_f is the Freundlich isotherm constant, and n is a dimensional constant. K_f and n is a measure of the sorption capacity and sorption intensity, respectively.

When $n = 1$, the Freundlich isotherm become as:

$$C_s = K_d C_l \quad (13) ,$$

where, K_d is known as the distribution coefficient, which is a ratio of the amount of sorbed solute to the amount of solute in the dissolved phase at equilibrium.

Both physical and chemical processes controlling the fate and transport of mercury can be considered by adding new terms to the general advection-dispersion equation. This equation could have different forms for the different processes and the specific reactions under study. For example, if only sorption of mercury on to the bed of the river is considered , and the sorption can be described by the above equation, the advection-dispersion and sorption equation can be written as:

$$\frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - \rho K_d \frac{\partial C}{\partial t} \quad (14) ,$$

where, ρ is the mass of sorbent per volume of stream water.

If sorption takes place the concentration in the river water will decrease. In contrast, desorption will increase the mercury concentration in the water phase.

The last equation is useful when the rate sorption/desorption is high relative to the flow velocity of the river. In many cases, instantaneous equilibrium cannot be assumed, due high water flow velocities and the fact that not all of the mercury in the liquid phase has access to the sorbent surfaces. A kinetic approach is required as given by the following advection-dispersion and sorption equation:

$$\frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - \rho \lambda (K_d C - S) \quad (15) ,$$

where, λ is a first order rate constant for sorption, which is expressed in an inverse unit of time (1/T), $K_d C$ is the mass of mercury sorbed at equilibrium, S is the mass of mercury present in the sediment (mass of mercury sorbed/mass of sediment).

3.3. Transport in groundwater

Mathematical models have been developed to predict the transport and fate of reactive solutes moving in both saturated and unsaturated zones. Adsorption, dilution, exchange reactions and precipitation seem to be the major physicochemical processes that can alter the metal concentrations during the transport in an aquifer.

In the unsaturated zone, mercury is transported by leached flow rate interacting with soil matrix, for instance by sorption processes and the buffer capacity of the soil affects the mercury mobility. Charge and grain size from surface soils and aquifers influence the adsorption capacity for many metals, because smaller particles have large surface area and coarser grains are coated with OM and with oxide and hydroxides of iron, which could enhance the adsorption of mercury. Solute transport processes involve the groundwater flow description and the solute-aquifer interaction. It means an equilibrium reaction, adsorption and precipitation kinetic understanding. A mass balance for the reactive solute can describe the transport. This balance can result in a simple differential equation for a steady state or in a differential equation for more complex problem.

In a saturated anisotropic porous media, the governing water flow equation can be written as (Freeze and Cherry, 1979):

$$S_s \frac{\partial h}{\partial t} = \frac{\partial}{\partial x_i} \left(K_{ij} \frac{\partial h}{\partial x_j} \right) \quad (1)$$

And for unsaturated anisotropic as:

$$C(\Psi) \frac{\partial \Psi}{\partial t} = \frac{\partial}{\partial x_i} \left(K_{ij}(\Psi) \frac{\partial \Psi}{\partial x_j} \right) + \frac{\partial}{\partial t} (K_{i3}(\Psi)) \quad (2)$$

$$\therefore C(\Psi) = \frac{\partial \theta}{\partial \Psi}$$

where S_s is the coefficient of specific storativity (1/L), h is the hydraulic head (L), t is time (T), x_i are Cartesian coordinates (L), K_{ij} is the hydraulic conductivity tensor (L/T), Ψ is the pressure head (L), $C(\Psi)$ is the specific moisture capacity and θ is the moisture content.

The water flow equation is coupled with the solute transport equation through Darcy's equation; flow velocity in the advective term and the dependence of dispersion on flow velocity in the dispersive term.

General description of solute transport is given by the following equation (Bear, 1979):

$$\frac{\partial}{\partial t} (\theta C) - \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial C}{\partial x_j} \right) + \frac{\partial}{\partial x_i} (\theta v_i C) = \theta R \quad (3)$$

where D_{ij} is the hydrodynamic dispersion tensor (L²/T), v_i is average pore water flow velocity (L/T) and R is the chemical source (desorption) /sink (adsorption) term (MT/L³) representing the changes

in aqueous solute concentrations. The hydrodynamic dispersion is the sum of mechanical dispersion and molecular diffusion:

$$D_{ij} = \alpha_i v_i$$

where α_i is the dispersivity in the i direction (L) and

$$v_i = \frac{q_i}{\theta} = \frac{-K_{ij}}{\theta} \frac{\partial h}{\partial x_i}$$

where q_i is Darcy velocity (L/T). The above equation is known as Darcy's law.

Numerical techniques such as the finite difference method, the integral finite method and the finite element method have to be used to solve the above water flow and solute transport equations. In the case of one-dimensional and steady state system, the velocity profile can be calculated from Darcy's law.

During its transport in groundwater, the fate of reactive solutes (for instance mercury) depends on chemical interactions with solid aquifer material. The interaction changes the solute concentration in groundwater at a specific location, until equilibrium has been attained. The solute concentration can be controlled by equilibrium or is determined by reaction kinetics in combination with flow velocity or residence time. Two different approaches, the kinetic and equilibrium based, are used to model the solute distribution. For that, free energy values and equilibrium constants are needed and then tedious calculations with time consumption are necessary. The adsorbed concentration can be related to the concentration in water with the Henry's law:

$$\frac{C_a}{C_w} = K_d$$

where K_d is the distribution coefficient which relates the adsorbed solute concentration C_a to the its concentration in water, C_w .

R from the equation (3) is related with the distribution coefficient in terms of changes in the solute concentration:

$$R = K_d \left(\frac{\partial C}{\partial t} \right)_x$$

the changes in solute concentration in groundwater at location x can be caused by displacement of a concentration gradient, after correction for amounts, which are absorbed or desorbed given by the expression:

$$\left(\frac{\partial C}{\partial t} \right)_x = -v \left(\frac{\partial C}{\partial x} \right)_t - R$$

The R expression substitution in the last equation becomes:

$$(1 + K_d) \left(\frac{\partial C}{\partial t} \right)_x = -v \left(\frac{\partial C}{\partial x} \right)_t$$

where the term $(1 + K_d)$ is known as retardation factor (R_f). Assuming a linear distribution coefficient, the retardation factor becomes:

$$R_f = 1 + \frac{\rho K_d}{\varepsilon}$$

where, ρ is the soil bulk density (typically from 1.5 to 1.9 g cm⁻³) and ε is the effective soil porosity (typically 0.35 to 0.55).

Metals transport in groundwater has been studied and it seems to be complicated.

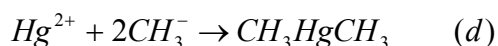
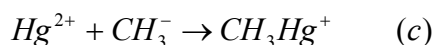
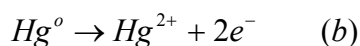
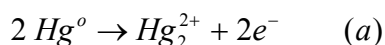
4. Mercury speciation

Speciation involves separation and analytic techniques to identify mercury in its different chemical forms. Speciation is important in predicting the transport and fate of mercury in the environment and its impact on biota and human. Wet deposition can be the primary mechanism by which mercury is transported to land and surface waters, then translocated from terrestrial ecosystem to aquatic system. In the environment, mercury undergoes biotic and abiotic chemical transformation resulting in different mercury species with different toxicity (Allen, 1993; Hughes et al., 1995; Witters, 1998). Table 4.1 shows some properties of the most relevant toxic species.

4.1. Inorganic mercury:

In the environment, mercury is found physically as gas and liquid or associated with solid particulates. Chemically, it exists in three oxidation states. In its zero oxidation state (Hg°), elemental mercury is liquid at room temperature with little tendency to dissolve in water (Table 4.1). However, it can stay in water due to its high density. Hg° has high vapor pressure and can stay in the atmosphere more than one year. When it loses one electron, it is converted to mercurous ion or monovalent mercury (Hg_2^{2+}) (eqn. (a)), which contains two atoms of mercury. If it loses two electrons, it is converted to mercuric ion or divalent mercury (Hg(II)) (eqn. (b)), the most reactive mercury species in the environment.

Mercuric ion forms a large number of organic compounds such as monomethyl mercury (CH_3Hg^+) (often called methyl mercury (MeHg)) and dimethyl mercury (eqn. (c) and (d)), in which mercury is covalently bound to carbon atoms.



4.2. Organic mercury

Mercury leaves the earth's surface as vapor (Hg°) and returns dissolved in rainwater as Hg(II) and as MeHg due to slow oxidation of Hg° and the decomposition of CH_3HgCH_3 . Oxidation is mostly carried out in fog and cloud droplets by O_3 , HClO , HSO_3^{-} (Morel et al., 1998). Dimethyl mercury comes from degassed ocean and fresh water surfaces.

In aquatic environments dimethyl mercury is generally not persistent due to its high volatility and it can dissociate to MeHg at neutral or acid pH. MeHg has high toxicity, is stable and bioaccumulates (Bloom, 1992).

Dimethyl mercury and MeHg are formed enzymatically by anaerobic sulfur reducing bacteria (SRB) in both sediment and water through the methylation of mercuric ions (Compeau and Bartha, 1985; Gilmour and Henry, 1991). The availability of mercury for methylation is controlled by sulfide by the formation of Hg(HS)_2 , HgS(HS)^{-} , and HgS_2^{2-} complexes. Methylation is the main step in the mercury cycle that influences the ecological fate of mercury and depends on the

availability of mercuric ions, growth of the methylating microorganism, pH, and temperature. For instance, organic matter can stimulate growth of microbial populations reducing oxygen levels, by which the formation of methyl mercury seems to be enhanced. The rate of methylation can vary with seasonal changes of nutrient concentration, oxygen, pH, DOC, redox condition, and the presence of sulfide in sediment (Guimaraes et al., 1995; Regnell et al., 1996). During summer, methylation can increase due the high biological productivity, but other factors such as photodegradation can demethylate mercury (Nriagu, 1994; Sellers et al., 1996).

In aquatic systems, photoreduction seems to be more important than microbial mercury reduction. In oxic water, bacteria can also methylate mercury (Fischer et al., 1995; Watras et al., 1995a; Regnell et al., 1996) and mercury can be present as CH_3HgCl and CH_3HgOH . Humic and fulvic material may abiotically methylate mercury as well (Lee et al., 1985; Weber, 1993).

Elemental mercury is not available for methylation because it does not bind organic or inorganic ligands. Mercurous ions bind only with organic ligands and cannot be methylated. Mercuric ions interact with both organic and inorganic ligands, such as Cl^- , to form HgCl_2 , HgCl^+ , HgClOH , HgCl_3^- . The formation of these depends on the chloride concentration and pH.

Inorganic species are primarily bound to particulate and organic substances and may not be available for direct uptake by aquatic organisms.

Table 4.1. Some chemical and physical properties of mercury species.

Specie	Molecular formula	Molecular weight	Solubility (g l^{-1})	Density (g cm^{-3})	Oxidation state
Elemental mercury	Hg⁰	200	5.6×10^{-5} at 25 °C	13.5 at 25 °C	+1, +2
Mercurous Chloride	Hg₂Cl₂	472	2.0×10^{-3} at 25 °C	7.1 at 19 °C	+1
Mercuric Chloride	HgCl₂	271	69 at 20 °C	5.4 at 25 °C	+2
Methylmercury chloride	CH₃HgCl	251	0.1 at 21 °C	4.0 at 20 °C	+2
Dimethylmercury	C₂H₆Hg	230	1.0 at 21 °C	3.1 at 20 °C	+2

5. Main mercury exposure routes in humans during gold mining

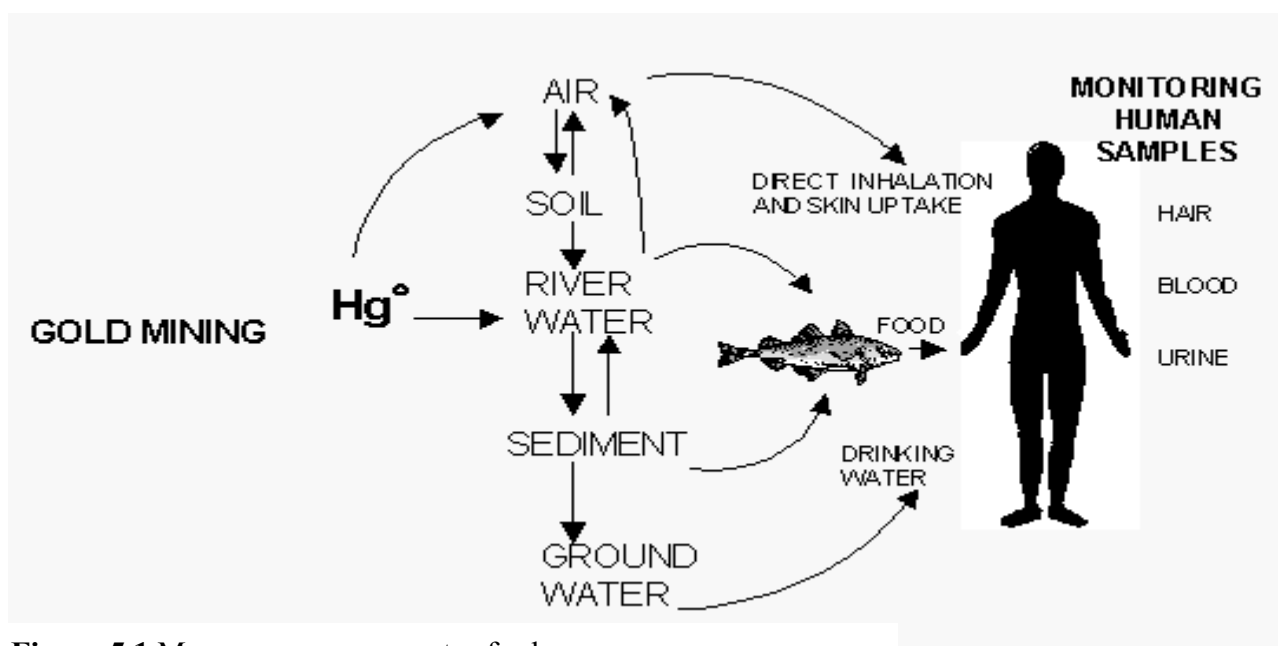


Figure 5.1 Mercury exposure routes for humans.

People from gold mining areas are repeatedly exposed to inorganic mercury and methyl mercury. Mercury enters into the human body through mercury-contaminated fish, direct inhalation, mercury-contaminated drinking water, and skin uptake (Fig. 6.1). In the body, mercury undergoes the following processes: absorption, distribution, metabolism, and excretion.

Burning of gold-mercury amalgam releases metallic mercury vapor (Hg^0) into the air, which can be absorbed through the respiratory tract, the gastrointestinal tract, and the skin (Lipfert, 1997). Levels of mercury in blood, hair and urine samples is an indicator of metallic mercury exposure (Akagi et al., 1995) with urine samples as more reliable indicator of long term of exposure

Mercury also contaminates surface water as metallic liquid (Hg^0), which is trapped in sediments as inorganic mercury. In anaerobic conditions, it can be biotransformed to organic mercury compounds (e.g., MeHg and monovalent MeHg) by sulfate reducing bacteria (Compeau and Bartha, 1985; Gilmour and Henry, 1991). Organic mercury can be taken up from sediments by phytoplankton, which are eaten by invertebrates and small fish, which are eaten by large predatory fish. In this way, mercury is transported through aquatic food chains from sediment to humans. Runoff water from soils containing mercury is also an important source of mercury to fish (Lindqvist, 1984).

Methyl mercury in blood and in scalp hair can also be used as indicator of human methyl mercury exposure (Lindqvist, 1984; Akagi et al., 1995; Palheta and Taylor, 1995; Dolbec et al., 2002). Once the gastrointestinal tract has absorbed methylmercury, mercury is transported through the body in the bloodstream before its accumulation in different target organ in the body. Most of the total mercury in hair and blood from people exposed through fish consumption and living in gold mining seems to be methyl mercury (Akagi et al., 1995; Palheta and Taylor, 1995; Dolbec et al., 2002) such that, the ratio between total mercury and methyl mercury is almost 1. In the scalp hair, methyl mercury is incorporated in the hair follicle. A strong correlation has been found between the concentrations of total mercury in hair and blood (WHO, 1990; Akagi et al., 1995) indicating that in hair the concentration of mercury can be as indicator of methyl mercury contamination in fishing

population and those exposed to methyl mercury through consumption of contaminated fish (WHO, 1990).

5.1. Inhalation and skin uptake

Mercury is mainly inhaled as metallic mercury vapor and readily absorbed by red blood cells in the lungs. In the blood, the adsorption is facilitated and enhanced by the lipid solubility of Hg° and its high vapor pressure, which allows it to cross the lipid-containing cell membranes and dissolve in blood lipids. The distribution of absorbed metallic mercury is limited by slow oxidation. Inside the red blood cells, it is oxidized to divalent mercury (Hg(II)) by hydrogen peroxide and catalase enzymes (Clarkson, 1994). Catalase is found in almost all tissues, so oxidation can occur throughout the body. Enzymatic oxidation of Hg° seems to be a defensive mechanism. Divalent mercury is soluble in water and can be easily excreted from the body via urine as sulfhydryl conjugates (Clarkson, 1994), but in plasma and erythrocytes, protein sulfhydryl groups can bind divalent mercury (Hall et al., 1994).

Both metallic and ionic mercury species can reach the brain cells (Clarkson, 1994; Pamphlett and Waley, 1996; Pamphlett and Waley, 1998). The latter crosses the blood-brain barrier more slowly than metallic mercury (Hursh et al., 1988; Clarkson, 1994). If the oxidation of metallic mercury takes place in the brain, ionic mercury can be retained in it and cause tremor, insomnia, depression, irritability, etc.

Mercury can be exhaled. In the liver, divalent mercury is reduced to Hg° (Dunn et al., 1981) and transported to the lungs and then exhaled. Alternatively, Hg(II) can react with reduced glutathione (G) in the liver forming a mercury-glutathione complex (GS-Hg-SG) due to its strong tendency to bind to sulfur-containing functional groups. GS-Hg-SG is released into the bile and then carried to the intestines and excreted with the feces (Ballaton and Clarkson, 1984; Ishihara, 2000). Elimination of mercury from the body after exposure to metallic mercury is mostly via feces. Metallic mercury vapor can also occur in sweat but in very small amounts.

The skin poorly absorbs metallic mercury. When 1 cm^2 of skin is exposed to 1.0 mg of mercury in 1 m^3 of surrounding air, it can absorb about 0.02 ng of mercury (Hursh et al., 1989). Mercury is mostly absorbed through the sebaceous gland cells or through follicular walls, because they are more permeable than the epidermal cell layers. Moist skin is a symptom for mercury dermal exposure. Metallic mercury penetrates the skin more readily than ionic species.

5.2. Fish consumption

Human exposure to mercury through consumption of mercury-contaminated fish has been widely documented and its accumulation in the human body has been associated with irreversible alterations of the nervous system. In fish, mercury enters mainly via their food and through the gills. Once mercury has crossed the gills, it is transported by blood to various tissues, mainly accumulating in the liver (Clarkson, 1994; CTEM et al., 2000). Although most of the environmental mercury to which fish is exposed is inorganic, methyl mercury is commonly found in fish, because inorganic mercury is relatively unavailable for fish assimilation (Lawson and Mason, 1998; Morel et al., 1998). Mercury can be retained as inorganic mercury but mostly as methyl mercury (Bidone et al., 1997), which is slowly eliminated bound to sulphhydryl groups. In fish, the exposure to methyl mercury is enhanced by oxygen depletion and low pH in the water, for which mercury methylation is favored. Mercury bound to large organic matter molecules is thought to be too polar and it could not cross biological membranes.

In humans, the gastrointestinal tract could absorb about 95% of methylmercury in ingested fish (Aberg et al., 1969). Methyl mercury is found mainly in red blood cells in a ratio to plasma methyl mercury of about 20:1. In blood, its half-life seems to be about 40 days (Smith et al., 1994). In the body, the transport of methyl mercury into the tissues is mediated by the formation of a methyl mercury cysteine complex (Aschner and Aschner, 1990). The complex is transported into the cells via neutral amino acid carrier proteins (Kerper et al., 1992).

Bioaccumulation of methyl mercury can be due to its stability in the body and due to reabsorption of methyl mercury secreted into the bile. There is no evidence for methylation in the body. In contrast, demethylation in the body is slow and involves hydroxyl radicals produced by cytochrome P-450 reductase (Suda and Hirayama, 1992). In the body, methyl mercury is converted to ionic mercury by microorganisms living in the intestines. About 90% of the absorbed dose of methyl mercury can be excreted as ionic mercury.

In humans, mercury is mostly found in blood and hair in its methylated form and has been associated to fish diet (Lindqvist, 1984; Akagi et al., 1995). For example, mercury responsible for the Minamata disease came from consumption of seafood containing methyl mercury, and mercury in hair (0.02 to 84 mg g⁻¹) in woman at the upper Madera River in Brazil reveal contamination by consumption of contaminated fish (Hursh et al., 1989). Mercury concentration of 1.4 mg g⁻¹ and 11.6 mg g⁻¹ in hair samples after daily and monthly respectively consumption of mercury of contaminated fish are suggested by WHO (1976) as safe levels to human health. Levels above the established guidelines are of great concern, and preventive actions must be considered in order to preserve the population health.

Efforts have been made to prevent consumption of fish contaminated with mercury. Simple models have been proposed to predict possible hazardous exposure to mercury by fish consumption. There is a quantitative relationship between the personal daily intake of mercury (PDI) and fish consumption (Fig. 5.2). However, this relationship is affected by the fish species eaten, size of meal, and number of daily meals. Fish mercury concentrations have been estimated with reference to age and weight of fish, and species of fish (Renzoni et al., 1998), and the concentrations are positively correlated with the first two factors (Renzoni et al., 1998).

With a constant mercury intake during several months, the adult blood concentration (µg/l) can be approximately 0.8 times the daily mercury intake (µg) (Sherlock et al., 1984). From the levels of mercury in fish and the daily fish consumption, the PDI can be estimated (Paradis et al., 1997).

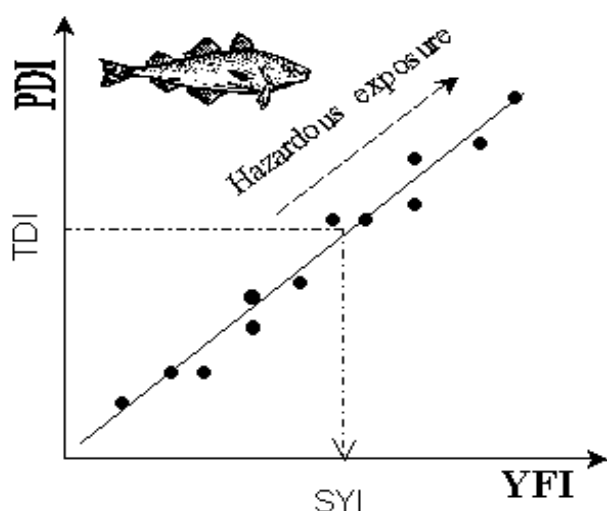


Figure 5.2. Personal mercury intake and fish consumption.

The tolerable daily intake of mercury (TDI) for a person is 0.47 µg of Hg per kg body weight (WHO, 1990). If PDI > TDI, the personal consumption of contaminated fish is considered to be hazardous. The maximum safe yearly intake of fish (SYI) can be determined from TDI (Fig. 5.2). This and other findings are good approaches to assess the risk associated with consumption of mercury-contaminated fish. However, they are based on several assumptions, such as steady-state condition, which can result in

underestimated values, they do not include other mercury sources, and they still need to be improved in order to be more predictable.

5.3. Drinking water

Inorganic and organic mercury can be ingested from contaminated drinking water. Metallic mercury is unlikely to be ingested in this way, but if it is, sulfide in the body prevents its absorption by coating it. The gastrointestinal tract efficiently absorbs both inorganic and organic mercury. Inorganic mercury may be absorbed by electrostatic attraction of mercury by the brush border membrane followed by diffusion through it. (Endo et al., 1990; Foulkes and Bergman, 1993). More than 95% of the methyl mercury content in drinking water is taken up (Aberg et al., 1969).

6. Toxicity

6.1. Toxicity to humans

Depending on its speciation and the dose received, mercury can be toxic to humans, animals and plants. Exposure to mercury affects the gastrointestinal tract, respiratory tract and kidney. At least 95% of ingested methyl mercury is taken up in the gastrointestinal tract (Inskip and Piotrowski, 1985), which is the main path of entry in humans. In the human body, methyl mercury seems to have a half-life between 70 and 80 days (CTEM et al., 2000). The kidney is the target organ for inorganic species, but in extreme cases of mercury exposure, the brain may also be a target organ for elemental mercury. About 80% of the inhaled metallic mercury is readily absorbed into the body, where it can stay for one or two months (CTEM et al., 2000). An increase in urinary excretion of some proteins such as N-acetyl- β -glucosaminidase, β_2 -microglobulin and retinol-binding protein, may indicate kidney damage (Divine et al., 1999). During prolonged exposure to mercury vapor, humans suffer from irritability, tremor and erethism, memory disturbance (hallucinations and delirium), fatigue and confusion (Piikivi & Hanninen, 1989). No chronic effects on humans are expected after continuous inhalation of air with less than $0.3 \mu\text{g m}^{-3}$ metallic mercury (WHO, 1990). Inorganic mercury could be considered as a neurotoxin that causes sporadic motor neuron disease (Arvidson, 1992; Pamphlett and Waley, 1996). It has been found in large amounts in cortical motor neurons and smaller amounts in some brain stem and cerebellar neurons (Pamphlett and Waley, 1996; Pamphlett and Waley, 1998). It is suspected that in the inorganic form, mercury can bypass the blood-brain barrier (Aschner and Aschner, 1990; Arvidson, 1992) and damage neurons.

In the case of methylmercury exposure, the critical organ seems to be the brain, but the developing nervous system is more sensitive. Adult and fetal brains are susceptible to methylmercury, as shown by neurotoxic to methylmercury exposure (WHO, 1990; Myers et al., 2000). Chronic exposure has resulted in neurological damage, paresthesia (a sensation of pricking, tingling, or creeping on the skin), ataxia (an inability to coordinate voluntary muscular movements that is symptomatic of some nervous disorders), sensory disturbance, tremors, impairment of hearing, blurred vision (Cavalleri and Gobba, 1995), speech difficulties, blindness, deafness and death (Harada, 1995; Myers et al., 2000). Some of these effects have been endpoints of neurotoxicity in children and women who have consumed large amounts of mercury-contaminated fish during pregnancy (Altmann et al., 1998; Cox et al., 1995; Grandjean et al., 1997; Myers et al., 2000; WHO, 1990).

Historical mercury poisonings serve to highlight the reasons why environmental managers should be concerned about mercury toxicology. In the 50's many people were poisoned by consumption of organic mercury contaminated fish in Minamata bay (Japan). The concentrations ranged from 6 to 36 mg of methylmercury per kg of fish (Tamashiro et al., 1986), and in 1971-72 hundreds of Iraqis died after ingesting bread containing a mean concentration of 9 mg kg^{-1} of organic mercury (Bakir et al., 1973; Marsh et al., 1987). No chronic effects on humans are expected after of daily consumption of food with less than $0.3 \mu\text{g kg}^{-1}$ methylmercury (WHO, 1990). Methylmercury penetrates the placental barrier and affects the developing fetuses (CTEM et al., 2000). It moves through the placenta as a methylmercury-cysteine conjugate by the same transport system as methionine and phenylalanine (Kajiwara et al., 1996). Children with prenatal exposure to low levels of methylmercury experience mental retardation, cerebral palsy, blindness, deafness, increased blood pressure and decrease heart rate (Salonen et al., 1995; Sorensen et al., 1999). Heart disease has also been detected in adults. For instance, a studied fishermen population with a daily consumption of 0.03 kg of fish containing $95 \mu\text{g}$ of mercury had a risk of acute myocardial infarction (Salonen et al., 1995).

The end points used in human toxicity assessment are mainly developmental neurotoxicity, overt neurological symptoms in adults, and impaired neurological development and delayed sequelae in children (Grandjean et al., 1997; Davidson et al., 1998). They have been evaluated for human populations that are heavily dependent on consumption of fish and marine-mammals. In the Seychelles islands, no prenatal effects were observed in populations with a mean mercury concentration of $6.8 \mu\text{g g}^{-1}$ in maternal hair collected at birth (Davidson et al., 1998; Myers et al., 2000). Nevertheless, in a Faroe Island study, where children were exposed to similar levels as in the Seychelles population, memory, attention and language abnormalities were related with prenatal exposure (Grandjean et al., 1997).

Maternal hair and adult blood are biomarkers of methylmercury exposure. About 90% of mercury in the hair appears as methylmercury. The half-life in blood and hair is between 48 and 53 days (Sherlock et al., 1984; Cox et al., 1989). In a study on humans, a mean concentration of mercury of $0.2 \mu\text{g g}^{-1}$ in adult blood was associated with $300 \mu\text{g}$ of mercury intake per day for which a critical dose of $4.3 \mu\text{g kg}^{-1}$ per day corresponds to a lowest-observed-adverse-effect level (LOAEL) (Friberg and Group, 1971). It means that a person of 70 kg body weight and a daily intake of more than $300 \mu\text{g}$ of mercury would exceed the LOAEL ($300/70 = 4.3$). However, susceptibility depends on factors such as age and health status, and an uncertainty factor of 10 has been proposed to be added to the critical dose. Uncertainty factors are mathematical adjustments for reasons of safety when knowledge is incomplete and these are used to account for variations in people's sensitivity. The uncertainty is illustrated by observations on prenatal exposure, in which maternal hair concentrations of organic mercury varied between 4 and $15 \mu\text{g g}^{-1}$, corresponding to a daily intake of 0.3 to $1.3 \mu\text{g kg}^{-1}$. The high value agreed with the no-observed-adverse-effect level (NOAEL), and the uncertainty factor varied from 3 to 10 (Grandjean et al., 1997; Davidson et al., 1998). Mercury has also been found in umbilical cord tissue. A mean of 0.24 ng g^{-1} d.w. was reported from 176 children born in Minamata between 1950 and 1975 (Akagi et al., 1998). Children with congenital Minamata disease had higher methylmercury concentrations in the cord than other children from the same area (Abreu et al., 1998; Harada et al., 1999).

In gold mining areas a significant exposure source of mercury is freshwater fish, which bioaccumulates methylmercury from polluted water (Friberg and Group, 1971; Bidone et al., 1997; Davidson et al., 1998). For instance, in some mining regions, fish have reached levels of total mercury from $130 \mu\text{g kg}^{-1}$ in detritivore species to more than $500 \mu\text{g kg}^{-1}$ in piscivore fish (Moreira, 1996). The level of daily exposure through consumption of contaminated fish for adult population in these mining areas is $1.6 \mu\text{g kg}^{-1}$, which is more than five times greater than the reference dose of $0.3 \mu\text{g kg}^{-1} \text{ day}^{-1}$ (Bidone et al., 1997). Humans from gold mining areas, with less than $50 \mu\text{g g}^{-1}$ of total mercury in the hair, show reduced psychomotor performance (Lebel et al., 1996; Lebel et al., 1998; Dolbec et al., 2002). Another significant route of exposure in gold mining sites is the inhalation of mercury-contaminated air. Atmospheric mercury concentrations in gold mining areas in Brazil are up to 0.2 mg m^{-3} (Moreira, 1996), which can cause reduction of coordination ability and increase in tremor intensity (Netterstrom et al., 1996).

6.2. Toxicity to microorganisms, aquatic and terrestrial organisms

Ecological effects include diversity decline, death and low growth and photosynthesis rates. Chronic toxic effects may include shortened life span, reproductive problems, and low fertility.

Organic mercury is more toxic to microorganisms than inorganic mercury species (WHO, 1989) and adverse effects appear at exposure concentration of $1 \mu\text{g}$ of methyl mercury per liter (WHO, 1989). Effects on survival and growth are notorious when microorganisms are exposed to mercury. Single species cultures (such as unicellular green algae) suffer from reduced photosynthesis when inorganic mercury concentration exceed $20 \mu\text{g l}^{-1}$ (WHO, 1989) but the reduction as well as

inhibition of growth is dependant on pH, cell density, light intensity, temperature, and exposure time (WHO, 1989). Diversity may decline, as some mercury susceptible genera disappear from the community, while mercury-resistant genera persist (WHO, 1989).

Ionic inorganic mercury and methyl mercury have high acute toxicity to aquatic organisms. For instance, 1 mg l⁻¹ and more of inorganic mercury decrease the chlorophyll content in some plants and reduce photosynthesis by 50% in others (WHO, 1989; Boening, 2000). Organic mercury is toxic to aquatic plants at concentrations that are several times lower than these.

For aquatic invertebrates, the toxicity data vary greatly depending on their different susceptibilities to different mercury species, developmental stage, the development of tolerance, and the chemical and physical properties of the medium where they live (Table 6.2.1). Concentrations from 1 to 10 µg l⁻¹ generally result in acute toxicity for the most sensitive developmental stage of many species of aquatic invertebrates (Boening, 2000). Organic species are 10-100 more toxic than inorganic species.

Concentrations of mercury in fish tissue generally increase with increasing age of the fish, and males seem to have more mercury than females of equal age (WHO, 1989). Fish accumulate mercury via their food and via passive uptake from water through the gills (Ribeiro et al., 1996). The toxicity is influenced by salinity, water hardness, and temperature (table 6.2.1) (WHO, 1989). The 96-h LC₅₀ vary from 0.03 to 0.40 mg l⁻¹ for freshwater species and are higher for marine fish (WHO, 1989; Boening, 2000). Physiological and biochemical effects (respiratory rate reduction, lack of movement, reduction of food consumption, reduction in blood hemoglobin content, reduced body weight and protein content, etc.) have been reported in fish exposed to mercury. Toxicity data for other aquatic organisms, such as marine mammals and amphibians, vary with exposure time and mercury species (WHO, 1989).

Table 6.2.1 Toxicity of inorganic and organic mercury to aquatic organisms at adult stage.

Organism	pH	Exposure time	LC ₅₀ HgCl (mg l ⁻¹)
Marine organisms (the temperature and salinity were 20 °C and 20 g l ⁻¹ , respectively)			
Sandworm (<i>Neris virens</i>)	7.8	24 h	3.10
	7.8	96 h	0.07
Hermit crab (<i>pagurus longicarpus</i>)	7.8	24 h	2.20
	7.8	96 h	0.05
Softshell clam (<i>Mya arenaria</i>)	7.8	24 h	5.20
	7.8	96 h	0.40
Starfish (<i>Asterias forbesi</i>)	7.8	24 h	1.80
	7.8	96 h	0.06
Fresh water organisms (the range of temperature was 10-32 °C and the range of alkalinity 0.5-10 mg CaCO ₃ l ⁻¹)			
Waterfly (<i>Daphia hyalina</i>)	7.2	48 h	0.005
Copepod (<i>Cyclops abyssorum</i>)	7.2	48 h	2.2
Crab (<i>Oziotelphusa senex senex</i>)	7.0-7.3	48 h	0.591
Fish (range of temperature was 10-32 °C, alkalinity 7.7-11.7 CaCO ₃ l ⁻¹ for tilapia and catfish and 70 mg CaCO ₃ l ⁻¹ for rainbow trout)			
Tilapia (<i>Tilapia mossambica</i>)	7.0-7.3	24 h	1.256

Catfish (<i>Sarotherodon mossambicus</i>)	7.0-7.3	24 h	1.7
Rainbow trout (<i>Oncorhynchus mykiss</i>)	8.5	24 h	0.9

Fish (range of temperature was 10-32 °C, alkalinity 7.7-11.7 CaCO₃ l⁻¹ for tilapia and catfish and 70 mg CaCO₃ l⁻¹ for rainbow trout)

	pH	LC ₅₀	H ₃ HgCl (mg l ⁻¹)
Rainbow trout (<i>fingerling</i>)	8.5	24 h	0.084
Rainbow trout (<i>Oncorhynchus mykiss</i>)	8.5	24 h	0.125

Mercury reduces food intake, cardiovascular and kidney function, and embryo survival in birds. Most of the mercury accumulates in liver and kidneys (Rand, 1995; WHO, 1989). Gallinaceous (seed eating) birds have been used in toxicity test, and reported LD₅₀ from a single oral dose vary from 14 to 4558 mg of mercury per kg body weight depending on the species (WHO, 1989).

Laboratory studies have demonstrated that mercury is toxic to terrestrial organism over a broad range of concentrations (WHO, 1989). In animals, mercury detoxification begins with biotransformation of methyl mercury in the liver. Once mercury is excreted into the bile and enters the small intestine, it can be either reabsorbed in the gut or eliminated in feces (WHO, 1989).

As opposed to terrestrial organisms, marine organisms accumulate mercury in the tissues. Mercury stays long in fish tissues, which is of great concern for human consumption. For instance, Methyl mercury could has a half-life of 2 years in large older fish, particularly predatory species, which accumulate more mercury than small younger fish.

7. Perspectives

In gold mining areas such as St Domingo, the excessive use of mercury for gold extraction has resulted in local contamination of the environment (Veiga and Meech, 1995; André et al., 1997) and probably in mercury accumulation in humans. A monitoring of mercury concentration in hair, blood, and urine in human samples will be helpful to determine whether the contamination has reached the same levels as in other gold mining regions (Palheta and Taylor, 1995; Dolbec et al., 2002). In fact, mining workers are directly exposed to mercury by inhalation of metallic mercury vapor during amalgamation and heating processes (Veiga and Meech, 1995; André et al., 1997). Moreover, the local population can be indirectly exposed through drinking water and contaminated food as in others gold mining areas (Palheta and Taylor, 1995; Veiga and Meech, 1995).

While the negative effects of mercury on humans in gold mining areas are associated with both consumption of contaminated freshwater fish and occupational exposure, the major effects of gold mining activity in nature are mostly found in surface water. For instance, the major effects include increased sedimentation and water acidification, increase in both soluble and particulate mercury concentrations, temporal accumulation of mercury in sediment, death of sensitive species, and bioaccumulation within food chains.

Contaminated soil and sediments can be treated in different ways to remove mercury (Veiga and Meech, 1995). Promising alternatives are electrokinetics, phytoremediation (Heaton et al., 1998; Bizily et al., 1999; Lasat, 2000), soil flushing, solidification/stabilization, liming + selenium addition, and covering deposits with hard crust of laterites (a residual product of rock decay that is red in color and has a high content of iron oxides and aluminum hydroxide) (EPA, 1997, Veiga and Meech, 1995) (table 7.1). Nevertheless, most of the remedial procedures are costly, and those which involve the use of chemicals must be employed with great care (Veiga and Meech, 1995).

Table 7.1. Alternatives to treat metal contaminated sites

Method	Description	Limiting factors
Phytoremediation	It relies on the uptake of metals from the soil and their translocation into aboveground plant tissue. Phytoremediation also reduces the metal mobility by controlling the soil erosion and reducing the leaching through an increased evapotranspiration.	Long term for soil remediation. Surface contamination
	It has been applied in Europe and U.S.	
Electrokinetics	Contaminants in form of charged species or ions are transported to electrodes, where they are removed and treated above ground.	Electrode spacing and duration of remediation is site specific. Its application requires adequate soil moisture.
	It has been full-scale applied in Europe and in U.S.	

Mercury, which has been released into surface water, can either stay close to the source for long time or be widely dispersed in local sediments and air. Optimizing the use of mercury in the process of gold extraction can reduce the mercury dose released to surface water. For that the following actions must be considered:

- 1) The miners and their families should become conscious about the effects of mercury on natural sources and human health. They have limited knowledge about the technology for gold extraction and ecotoxicology effects of mercury.
- 2) The quantities of mercury used in gold extraction, recovered and released into the environment should be estimated.
- 3) Once the loss of mercury is reduced, a monitoring twice a year at least of mining effluent must be considered.

The establishment of an environmental mercury budget requires data on the size of the mercury sources, the location and extension of highly contaminated sites, and the distribution and accumulation of the mercury in the river basin.

Regardless of the technical feasibility of remediation processes, the cost will limit their application in St Domingo, since mining workers lack economic resources. It will be a better strategy to develop a program for education and training of mining workers on adequate use of mercury in gold extraction and on effects of mercury on environmental resources and humans. In addition, environmental laws must be specified to limit to mercury emissions to the environment. Fortunately, exposure levels of mercury in some gold mining areas are below those associated with acute severe effects. However, long-term exposure to mercury in the local environment could result in adverse effects on susceptible individuals such as children.

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9. References

- Aberg, B., L. Ekman, et al. (1969). "Metabolism of Methyl Mercury(²⁰³Hg) Compounds in Man." *Arch. Environ. Health* **19**: 478-484.
- Abreu, S. N., M. E. Pereira, et al. (1998). "The Use of a Mathematical Model to Evaluate Mercury Accumulation in Sediments and Recovery Time in a Coastal Lagoon (Ria de Aveiro, Portugal)." *Wat. Sci. Tech.* **37**(6/7): 33-38.
- Akagi, H., P. Grandjean, et al. (1998). "Methylmercury Dose Estimation from Umbilical Cord Concentrations in Patients with Minamata Disease." *Environmental Research* **77**(Sec. A): 98-103.
- Akagi, H., O. Malm, et al. (1995). "Human Exposure to Mercury Due to Gold Mining in the Tapajos River Basin, Amazon, Brazil: Speciation of Mercury in Human Hair, Blood and Urine." *Water, Air, and Soil Pollution* **80**: 85-94.
- Altin, O., H. Ö. Özbek, et al. (1998). "Use of General Purpose Adsorption Isotherms for Heavy Metals-Clay Mineral Interactions." *Journal of Colloid and Interface Science* **198**: 130-140.
- Allan, C. J. and A. Heyes (1998). "A Preliminary Assessment of Wet Deposition and Episodic Transport of Total and Methyl Mercury from Loworder Blue Ridgewatersheds, S.E. U.S.A." *Water, Air, and Soil pollution* **105**(3-4): 573-592.
- Allen, H. E. (1993). *The Significance of Trace Metal Speciation for Water, Sediment and Soil Quality Criteria and Standards. The Science of the Total Environment.* Amsterdam, Elsevier Science Publishers B.V: 23-45.
- André, L., k. Rosén, et al. (1997). "Minor Field Study of Mercury and Lead from Gold Refining in Central Nicaragua." *Luleå tekniska universitet.*
- Appelo, C. A. J. and D. Postma, Eds. (1999). *Geochemistry, Groundwater and Pollution*, A. A. Balkema.
- Arvidson, B. (1992). "Inorganic mercury is transported from muscular nerve terminals to spinal and brainstem motoneurons." *Muscle Nerve* **15**: 1080-1094.
- Aschner, M. and J. L. Aschner (1990). "Mercury Neurotoxicity: Mechanisms of Blood-brain Barrier Transport." *Neurosci. Biobehav. Rev* **14**(2): 169-176.
- Babiarz, C. L., J. P. Hurley, et al. (1998). "Seasonal Influence on Partitioning and Transport of Total Mercury in Rivers from Contrasting Watersheds." *Biochemistry* **41**: 237-257.
- Bakir, F., S. F. Damluji, et al. (1973). "Methylmercury poisoning in Iraq." *Science* **181**(96): 230-241.
- Balogh, S. J., M. L. Mayer, et al. (1997). "Mercury and Suspended Sediment Loadings in the Lower Minnesota River." *Environmental Science and Technology* **31**: 198-202.
- Ballaton, N. and T. W. Clarkson (1984). "Inorganic Mercury Secretion into Bile as a Low Molecular Weight Complex." *Biochem. Pharmacology* **33**(7): 1087-.
- Barnett, M. O., L. A. Harris, et al. (1997). "Formation of Mercury Sulfide in Soil." *Environmental Science & Technology* **31**(11): 3037-3043.
- Bear, J. (1979). *Hydraulics of Groundwater*, McGraw-Hill Pub Co.
- Belt, T. (1874). *The Naturalist in Nicaragua; A Narrative of Residence at the Gold Mines of Chontales; Journeys in the Savannahs and Forest.* London, J. S. Dent and Sons.
- Bencala, K. E. and R. A. Walter (1983). "Simulation of Solute Transport in a Mountain Pool-and-Riffle Stream: A Transient Storage Model." *Water Resources Research* **19**(3): 718-724.
- Bidone, E. D., Z. C. Castilhos, et al. (1997). "Fish Contamination and Human Exposure to Mercury in Tartarugalzinho River, Amapa State, Northern Amazon, Brazil. A Screening Approach." *Water, Air and Soil Pollution* **97**: 9-15.
- Biester, H. and H. Zimmer (1998). "Solubility and Changes of Mercury Binding Forms in Contaminated Soils After Immobilization Treatment." *Environmental Science and Technology* **32**: 2755-2762.

- Bizily, P. S., C. L. Rugh, et al. (1999). "Phytoremediation of methylmercury pollution: merB expression in *Arabidopsis thaliana* confers resistance to organomercurials." Proceedings of the National Academy of Science of the USA **96**: 6808–6813.
- Bloom, N. S. (1992). "On the Chemical Form of Mercury in Edible Fish and Marine Invertebrate Tissue." Can J. Fish Aquat Sci **49**: 1010-1017.
- Boening, D. W. (2000). "Ecological Effects, Transport, and Fate of Mercury: A General Review." Chemosphere **40**: 1335-1351.
- Boyd, S. A., L. E. Sommers, et al. (1981). "The Mechanism of Copper(II) Binding by Humic Acid: An Electron Spin Resonance Study of a Copper(II)-Humic Acid Complex and Some Adducts with Nitrogen Donors." Soil Science Society of America Journal **45**: 745-749.
- Cavalleri, A. and F. Gobba (1995). "Reversible Color Vision Loss in Occupational Exposure to Metallic Mercury." The Science of the Total Environment **168**: 63-69.
- CIRA-UNAN (1992). "Mercury Concentrations in Water and Sediment Samples from Sucio River. Santo Domingo-Chontales." Unpublished document at CIRA-UNAN Document Center.
- Clarkson, T. W. (1994). The Toxicology of Mercury and Its Compounds. Mercury Pollution-Integration and Synthesis. C. J. Watras and J. W. Huckabee, Lewis. chp VIII.1: 631-641.
- Compeau, G. C. and R. Bartha (1985). "Sulfate Reducing Bacteria: Principal Methylator of Mercury in Anoxic Estuarine Sediments." Appl. Environ. Microbiol **50**: 498-502.
- Cox, C., T. W. Clarkson, et al. (1989). "Dose-response analysis of infants prenatally exposed to methyl mercury: An application of a single compartment model to single-strand hair analysis." Environmental Research **49**(2): 318-332.
- CTEM, BEST, et al. (2000). Toxicological Effects of Methylmercury. Washington, D.C.
- Chang, C. M., M. K. Wang, et al. (2000). "Transport Modelling of Copper and Cadmium with Linear and Nonlinear Retardation Factor." Chemosphere **43**: 1133-1139.
- Davidson, P. W., G. J. Myers, et al. (1998). "Effects of Prenatal and Postnatal Methylmercury Exposure from Fish Consumption on Neurodevelopment: Outcomes at 66 Months of Age in the Seychelles Child Development Study." Journal of the American Medical Association **280**(8): 701-707.
- Divine, K., F. Ayala-Fierro, et al. (1999). "Glutathione, Albumin, Cysteine, and Cys-Gly Effects on Toxicity and Accumulation of Mercury Chloride in LLC-PK1 Cells." Journal of Toxicology and Environmental Health Part A **57**(7): 489-505.
- Dolbec, J., D. Mergier, et al. (2002). "Methylmercury exposure affects motor performance of a riverine population of the Tapajós river, Brazilian Amazon." Int Arch Occup Environ Health **73**: 195-203.
- Dunn, J. D., T. W. Clarkson, et al. (1981). "Ethanol Reveals Novel Mercury Detoxification Step in Tissues." Science **213**: 1123-.
- Echeverría, J. C., M. T. Morera, et al. (1998). "Competitive Sorption of Heavy Metal by Soils. Isotherms and Fractional Factorial Experiments." Environmental Pollution **101**: 275-284.
- Eimax, J. W., O. Kampe, et al. (1998). "Assessing the Deposition and Remobilisation Behaviour of Metals Between River Water and River Sediment Using Partial Least Squares Regression." Fresenius J. Anal. Chem **361**: 149-154.
- Ellis, R. W. and L. Eslick (1997). "Variation and Range of Mercury Uptake into Plants at a Mercury-Contaminated Abandoned Mine Site." Bull. Environ. Contam. Toxicol **59**: 763-769.
- Endo, T., S. Nakaya, et al. (1990). "Mechanisms of absorption of inorganic mercury from rat small intestine: III. Comparative absorption studies of inorganic mercuric compounds in vitro." Pharmacol. Toxicol **66**(5): 347-353.
- Fischer, R. G., S. Rapsomanikis, et al. (1995). "Bioaccumulation of Methylmercury and Transformation of Inorganic Mercury by Macrofungi." Environmental Science and Technology **29**: 993-999.

- Foulkes, E. C. and D. Bergman (1993). "Inorganic Mercury Absorption in Mature and Immature Ratjejunum: Transcellular and Intercellular Pathways in Vivo and in Everted Sacs." *Toxicol. Appl. Pharmacol* **120**: 89-95.
- Freeze, R. A. and J. A. Cherry (1979). *Groundwater*. Englewood Cliffs, NJ, 604 pp., Prentice-Hall.
- Friberg, L. and S. E. Group (1971). "Methylmercury in fish: A toxicological-epidemiologic evaluation of risks report from an expert group." *Nord. Hyg. Tidskr* **4**(Suppl): 19-364.
- Genuchten, M. T. V. and W. J. Alves. (1982). *Analytical Solutions of the One-Dimensional Convective-Dispersive Solute Transport Equation*. U. S, Dept Agriculture.
- Ghosh, S., P. C. Sadhukhan, et al. (1996). "Volatilization of Mercury by Resting Mercury-Resistant Bacterial Cells." *Bull. Environ. Contam. Toxicol* **56**: 259-264.
- Gilmour, C. C. and E. A. Henry (1991). "Mercury Methylation in Aquatic System Affected by Acid Deposition." *Environmental Pollution* **71**: 131-169.
- Gissing, P. B.-., M. Alnot, et al. (1999). "Modeling the Adsorption of Mercury(II) on (Hydr)oxides II: α -FeOOH (Goethite) and Amorphous Silica." *Journal of Colloid and Interface Science* **215**: 313-322.
- Godbold, D. L. (1994). *Mercury in Forest Ecosystem: Risk and Research Needs*. Mercury Pollution- Integration and Synthesis. C. J. Watras and J. W. Huckabee, Lewis. Chp. 3: 295-303.
- Grandjean, P., P. Weihe, et al. (1997). "Cognitive Deficit in 7-Year-Old Children with Prenatal Exposure to Methylmercury." *Neurotoxicology and Teratology* **19**(6): 417-428.
- Guimaraes, J. R., O. Malm, et al. (1995). "A Simplified Radiochemical Technique for Measurement of Net Mercury Methylation Rates in Aquatic Systems Near Goldmining Areas, Amazon, Brazil." *Science of the Total Environment* **175**(2): 151-162.
- Hall, L. L., P. V. Allen, et al. (1994). *The Kinetics of Intravenously-Administered Inorganic Mercury in Humans. Kinetic Models of Trace Elements and Mineral Metabolism During Development*. K. M. S. Subramanian and M. E. Wastney. Boca Raton, FL, CRC Press: 1-21.
- Harada, M. (1995). "Minamata Disease: Methylmercury poisoning in Japan caused by environmental pollution." *Critical Reviews in Toxicology* **25**(1): 1-24.
- Harada, M., H. A. H, et al. (1999). "Methylmercury level in umbilical cords from patients with congenital Minamata disease." *The Science of the Total Environment* **234**(1-3): 59-62.
- Hart, D. R., P. J. Mulholland, et al. (1999). "Relationships Between Hydraulic Parameters in a Small Stream Under Varying Flow and Seasonal Conditions." *Hydrological Processes* **13**: 1497-1510.
- Heaton, A. C. P., C. L. Rugh, et al. (1998). "Phytoremediation of Mercury- and Methylmercury-Polluted Soils Using Genetically Engineered." *Journal of Soil Contamination* **7**(4): 497-509.
- Hempel, M., R. D. Wilken, et al. (1995). "Mercury Contaminated Sites-Behaviour of Mercury and Its Species in Lysimeter Experiments." *Air and Soil Pollution*: 1089-1098.
- Hogg, T. J., J. R. Bettany, et al. (1978). "The Uptake of ^{203}Hg -Labeled Mercury Compounds by Bromegrass from Irrigated Undisturbed Soil Columns." *Journal of Environmental Quality* **7**(3): 445-450.
- Hogg, T. J., J. W. B. Stewart, et al. (1978). "Influence of the Chemical Form of Mercury on its Adsorption and Ability to Leach Trough Soils." *Journal of Environmental Quality* **7**(3): 440-445.
- Hughes, K., M. E. Meek, et al. (1995). "Speciation in Health Risk Assessments of Metals: Evaluation of Effects Associated with Forms Present in the Environment." *Regulatory Toxicology and Pharmacology* **22**: 213-220.
- Hursh, J. B., T. W. Clarkson, et al. (1989). "Percutaneous Absorption of Mercury Vapor by Man." *Arch. Environ. Health* **44**: 120-127.
- Hursh, J. B., S. P. Sichak, et al. (1988). "In Vitro Oxidation of Mercury by the Blood." *Pharmacology Toxicology* **63**: 266-273.

- Ikingura, J. R., M. K. D. Mutakyahwa, et al. (1997). "Mercury and Mining in Africa with Special Reference to Tanzania." *Water, Air and Soil Pollution* **97**: 223-232.
- Inskip, M. J. and J. K. Piotrowski (1985). "Review of the Health Effects of Methylmercury." *Journal of Applied Toxicology* **5**: 113-133.
- Ishihara, N. (2000). "Excretion of Methyl Mercury in Human Feces." *Archives of Environmental Health* **55**(1): 44-48.
- Johansson, K. and Å. Iverfeldt (1994). The Relation Between Mercury Content in Soil and the Transport of Mercury from Small Catchments in Sweden. *Mercury Pollution- Integration and Synthesis*. C. J. Watras and J. W. Huckabee, Lewis. chp. III: 323-1328.
- Kaiser, K. and W. Zech (1997). "Natural Organic Matter Sorption on Different Mineral Surfaces Studied by DRIFT spectroscopy." *Sciences of Soils* **2**.
- Kaiser, K. and W. Zech (1998). "Soil Dissolved Organic Matter Sorption as Influenced by Organic and Sesquioxide Coatings and Sorbed Sulfate." *Soil Sci. Soc. Am. J* **62**: 129-136.
- Kajiwarra, Y., A. Yasutake, et al. (1996). "Methylmercury transport across the placenta via neutral amino acid carrier." *Archives of Toxicology* **70**: 310-314.
- Kerper, L. E., N. Ballatori, et al. (1992). "Methyl Mercury Transport Across the Blood-Brain Barrier by an Amino Acid Carrier." *Am. J. Physiol* **262**(5): R761-R765.
- Kinniburgh, D. K. and M. L. Jackson (1978). "Adsorption of Mercury(II) by Iron Hydrous Oxide Gel." *Soil Science Society of America Journal* **42**: 45-47.
- Korte, F. and F. Coulston (1998). "Some Considerations on the Impact on the Ecological Chemical Principles in Practice with Emphasis on Gold Mining and Cyanide." *Ecotoxicology and Environmental Safety* **41**: 119-129.
- Kraepiel, A. M. L., K. Keller, et al. (1999). "A Model for Metal Adsorption on Montmorillonite." *Journal of Colloid and Interface Science* **210**: 43-54.
- Kungolos, A., I. Aoyama, et al. (1999). "Toxicity of Organic and Inorganic Mercury to *Saccharomyces cerevisiae*." *Ecotoxicology and Environmental Safety* **43**: 149-155.
- Lacerda, L. D. (1997). "Global Mercury Emission from Gold and Silver Mining." *Water, Air and Soil Pollution* **97**: 209-221.
- Lasat, M. M. (2000). "Phytoextraction of metals from contaminated soil: a review of plant/soil/metal interaction and assessment of pertinent agronomic issues." *Journal of Hazardous Substance Research* **2**: 5-25.
- Lawson, N. M. and R. P. Mason (1998). "Accumulation of Mercury in Estuarine Food Chains." *Biogeochemistry* **40**: 235-247.
- Lebel, J., D. Mergler, et al. (1998). "Neurotoxic Effects of Low-Level Methylmercury Contamination in the Amazonian Basin." *Environmental Research* **79**: 20-32.
- Lebel, J., D. Mergler, et al. (1996). "Evidence of early nervous system dysfunction in Amazonian population exposed to low-levels of methylmercury." *Neurotoxicology* **17**(1): 157-168.
- Lee, S.-Z., H. E. Allen, et al. (1996). "Predicting Soil-Water Partition Coefficients for Cadmium." *Environmental Science and Technology* **30**: 3418-3424.
- Lee, Y. H., K. Bishoop, et al. (1995). "Output of Methylmercury from a Catchment in Northern Sweden." *Water, Air and Soil Pollution* **80**: 477-481.
- Lee, Y.-H., G. C. Borg, et al. (1994). Fluxes and Turnover of Methylmercury: Mercury Pool in Forest Soils. *Mercury Pollution- Integration and Synthesis*. C. J. Watras and J. W. Huckabee, Lewis. chp. III: 329-342.
- Lee, Y. H., H. Hultberg, et al. (1985). "Catalytic Effect of Various Metal Ions on the Methylation of Mercury in the Presence of Humic Substances." *Water, Air and Soil Pollution* **25**: 391-400.
- Lin, Y., M. Guo, et al. (1997). "Mercury Pollution from Small Gold Mining in China." *Water, Air and Soil Pollution* **97**: 233-239.
- Lindqvist, O. (1984). "Mercury in the Swedish Environment. Global and Local Sources." National Swedish Environmental Protection Board. Report.

- Lipfert, F. W. (1997). "Estimating Exposure to Methylmercury: Effects of Uncertainties." *Water, Air and Soil Pollution* **97**: 119-145.
- Lodenius, M., et al. (1987). "Sorption of Mercury in Soils with Different Humus Content." *Bull. Environ. Contam. Toxicol* **39**: 593-600.
- Lyon, B. F., R. Ambrose, et al. (1997). "Calculation of Soil-Water and Benthic Sediment Partition Coefficients for Mercury." *Chemosphere* **35**(4): 791-808.
- MacBride, M. B., L. D. Tyler, et al. (1981). "Cadmium Adsorption by Soil and Uptake by Plants as Affected by Soil Chemical Properties." *Soil Science Society of America Journal* **45**: 739-744.
- Marsh, D. O., T. W. Clarkson, et al. (1987). "Fetal methylmercury poisoning: Relationship between concentration in a single strands of maternal hair and child effects." *Arch. Neurol.* **44**(10): 1017-1022.
- Matthiessen, A. (1996). "Kinetic Aspects of the Reduction of Mercury Ions by Humic Substances. I. Experimental Design." *Fresenius J. Anal Chem* **354**: 747-749.
- Mierle, G. and R. Ingram (1991). "The Role of Humic Substances in the Mobilization of Mercury from Watersheds." *Water, Air, and Soil Pollution* **56**: 349-357.
- Moreira, J. C. (1996). "Threats by Heavy Metals: Human and Environmental Contamination in Brazil." *The Science of the Total Environment*. **188** Suppl.(1): S61-S71.
- Morel, F. M. M., A. M. L. Kraepiel, et al. (1998). "The Chemical Cycle and Bioaccumulation of Mercury." *Annual Review of Ecology Systematics* **29**: 543-566.
- Myers, G. J., P. W. Davidson, et al. (2000). "Twenty-Seven Years Studying the Human Neurotoxicity of Methylmercury Exposure." *Environmental Research* **83**: 275-285.
- Nahar, S. and H. A. Tajmir-Riaghi (1996). "Complexation of Heavy Metal Cations Hg, Cd, and Pb with Proteins of PSII: Evidence for Metal-Sulfur Binding and Protein Conformational Transition by FTIR Spectroscopy." *Journal of Colloid and Interface Science* **178**: 648-656.
- Netterstrom, B., B. Guldager, et al. (1996). "Acute Mercury Intoxication Examined With Coordination Ability and Tremor." *Neurotoxicology and Teratology* **18**(4): 505-509.
- Nriagu, J. O. (1994). "Mechanistic Steps in the Photoreduction of Mercury in Natural Waters." *The Science of the Total Environment* **154**: 1-8.
- Palheta, D. and A. Taylor (1995). "Mercury in environmental and biological samples from a gold mining area in the Amazon region of Brazil. *The Science of the Total Environment*." *The Science of the Total Environment* **168**: 63-69.
- Pamphlett, R. and P. Waley (1996). "Motor neuron uptake of low dose inorganic mercury." *J. Neuro Sci* **135**: 63-67.
- Pamphlett, R. and P. Waley (1996). "Uptake of inorganic mercury by the human brain." *Acta Neuropathology* **92**: 525-527.
- Pamphlett, R. and P. Waley (1998). "Mercury in human spinal motor neurons." *Acta Neuropathology* **96**: 515-519.
- Paradis, S., B. Wheatley, et al. (1997). "Mercury Contamination Through Fish Consumption: A Model for Predicting and Preventing Hazardous Behaviour on a Community Level." *Water, Air, and Soil Pollution* **97**: 147-158.
- Peixoto, B. A. A. and E. Cernichiari. (1998). "Longitudinal Hair Mercury Concentration in Riverside Mothers along the Upper Madeira River-Brazil." *Environment Research*. **77**(n2).
- Porcella, D. B. (1994). *Mercury in the Environment: Biogeochemistry. Mercury Pollution-Integration and Synthesis*. C. J. Watras and J. W. Huckabee, Lewis. chp. 1: 3-19.
- Quémerais, B., D. Cossa, et al. (1999). "Sources and Fluxes of Mercury in the St. Lawrence River." *Environ. Sci. Technol* **33**: 840-849.
- Ramireddygar, S. R., R. S. Govindaraju, et al. (1996). *Modeling of Heavy Metal Transport and Soil Erosion in Surface Runoff*. Joint Conference on the Environment, Albuquerque, New Mexico, Great Plains/Rocky Mountain Hazardous Substance Research.
- Rasmussen, P. E. (1994). *Mercury in Vegetation of the Precambrian Shield. Mercury Pollution-Integration and Synthesis*. C. J. Watras and J. W. Huckabee, Lewis. chp. IV: 417-425.

- Rea, A. W., S. E. Lindberg, et al. (2002). "Mercury Accumulation in Foliage Over Time in Two Northern Mixed-Hardwood Forests." *Water, Air, and Soil Pollution* **133**: 49–67.
- Regnell, O., A. Tunlid, et al. (1996). *Canadian Journal of Fisheries and Aquatic Sciences*. **53**: 1535-.
- Renzoni, A., F. Zino, et al. (1998). "Mercury Levels Along the Food Chain and Risk for Exposed Populations." *Environmental Research* **77**: 68-72.
- Ribeiro, C. A. O., J. R. D. Guimaraes, et al. (1996). "Accumulation and Distribution of Inorganic Mercury in a Tropical Fish (*Trichomycterus zonatus*)." *Ecotoxicology and Environmental Safety* **34**: 190-195.
- Richards, J. F., P. J. Curtis, et al. (2001). "Effects of Natural Organic Matter Source on Reducing Metal Toxicity to Rainbow Trout (*Oncorhynchus Mykiss*) and on Metal Binding to Their Gills." *Environmental Toxicology and Chemistry* **20**: 1159-1166.
- Robertson, A. P. and J. O. Leckie (1997). "Cation Binding Predictions of Surface Complexation Models: Effects of pH, Ionic Strength, Cation Loading, Surface Complex, and Model Fit." *Journal of Colloid and Interface Science* **188**: 444-472.
- Rosen, B. P. (1996). "Bacterial Resistance to Heavy Metals and Metalloids." *JBIC* **1**: 273-277.
- Roulet, M., M. Lucotte, et al. (1998). "Distribution and partition of total mercury in waters of the Tapajós river basin, Brazilian Amazon." *Science of Total Environment* **213**: 203-211.
- Salomons, W. (1995). "Environmental Impact of Metals Derived from Mining Activities: Processes, Predictions, Prevention." *Journal of Geochemical Exploration* **52**: 5-23.
- Salonen, J. T., K. Seppänen, et al. (1995). "Intake of Mercury From Fish, Lipid Peroxidation, and the Risk of Myocardial Infarction and Coronary, Cardiovascular, and Any Death in Eastern Finnish Men." *Circulation* **91**(3): 645-655.
- Sarkar, D., M. E. Essington, et al. (1999). "Adsorption of Mercury(II) by Variable Charge Surfaces of Quartz and Gibbsite." *Soil Science Society of America Journal* **63**: 1626-1636.
- Sarkar, D., M. E. Essington, et al. (2000). "Adsorption of Mercury(II) by Kaoline." *Soil Science Society America Journal* **64**: 1968-1975.
- Schlegel, M. L., A. manceau, et al. (1999). "Sorption of Metal Ions on Clay Minerals. I. Polarized EXAFS Evidence for the Adsorption of Co on the Edges of Hectorite Particles." *Journal of Colloid and Interface Science* **215**: 140-158.
- Schlüter, K. (1997). "Sorption of Inorganic Mercury and Monomethyl Mercury in an Iron-Humus Podzol Soil of Southern Norway Studied by Batch Experiments." *Environmental Geology* **30**(3/4): 266-279.
- Schlüter, K. (2000). "Review: Evaporation of Mercury from Soils. An Integration and Synthesis of Current Knowledge." *Environmental Geology* **39**(3-4): 249-271.
- Schlüter, K. and S. Gäth (1997). "Modelling Leaching of Inorganic Hg(II) in a Scandinavian Iron-Humus Podzool - Validation and Long-Term Leaching Under Various Deposition Rates." *Water, Air, and Soil Pollution* **96**: 301-320.
- Sellers, P., C. A. Kelly, et al. (1996). "Photodegradation of Methylmercury in Lakes." *Nature* **380**: 694-697.
- Sherlock, J., J. Hislop, et al. (1984). "Elevation of mercury in human blood from controlled chronic ingestion of methylmercury in fish." *Human Toxicology* **3**: 117-131.
- Silva, G. (1994). "Diagnóstico de la Contaminación Ambiental Generada por la Actividad Minera Sobre los Ríos Sucio, Mico y Sinecapa Nicaragua." Universidad Federal de Pará /Centro de Geociencias.
- Smith, J., P. Allen, et al. (1994). "The Kinetics of Intravenously Administered Methyl Mercury in Man." *Toxicol. Appl. Pharmacol* **128**: 251-256.
- Sorensen, N., K. Murata, et al. (1999). "Prenatal methylmercury exposure as a cardiovascular risk factor at seven years of age." *Epidemiology* **10**(4): 370-375.
- Spark, K. M., , et al. (1997). "Sorption of Heavy Metals by Mineral-Humic Acid Substrates." *Aust. J. Soil Res* **35**: 113-122.

- Suda, I. and K. Hirayama (1992). "Degradation of Methyl- and Ethylmercury into Inorganic Mercury by Hydroxyl Radical Produced From Rat Liver Microsomes." *Arch. Toxicol* **66**(6): 398-402.
- Tamashiro, H., M. Arakaki, et al. (1986). "Methylmercury exposure and mortality in southern Japan: A close look at causes of death." *Jornal of Epidemiology Community Health* **40**(2): 181-185.
- Tamura, H. and R. Furuichi (1997). "Adsorption Affinity of Divalent Heavy Metal Ions for Metal Oxides Evaluated by Modeling with Frumkin Isotherm." *Journal of Colloidal and Interface Science* **195**: 241-249.
- Todd, L. L., G. E. T. Jr, et al. (1998). "Mercury and Plants in Contaminated Soils: 1. Uptake, Partitioning, and Emission to the Atmosphere." *Environmental Toxicology and Chemistry* **17**(10): 2063-2071.
- Tsiros, L. X. and R. B. Ambrose (1999). "An Environmental Simulation Model for Transport and Fate of Mercury in Small Rural Catchments." *Chemosphere* **39**(3): 477-492.
- Veiga, M. M. and J. A. Meech (1995). "Gold Mining Activities in the Amazon: Clean-up Techniques and Remedial Procedures for Mercury Pollution." *Pollution Ambio* **24**(6): 371-375.
- Venema, P., T. Hiemstra, et al. (1996). "Comparison of Different Site Binding Models for Cation Sorption: Description of pH Dependency, Salt Dependency, and Cation-Proton Exchange." *Journal of Colloid and Interface Science* **181**: 45-59.
- Walcarius, A., J. Devoy, et al. (1999). "Electrochemical Recognition of Selective Mercury Adsorption on Minerals." *Environmental Science and Technology* **33**: 4278-4284.
- Wallschläger, D., M. V. M. Desai, et al. (1998). "How Humic Substances Dominate Mercury Geochemistry in Contaminated Floodplain Soils and Sediments." *Journal of Environmental Quality* **27**(5): 1044-1054.
- Wang, D. Y., C. L. Qing, et al. (1997). "Effects of Humic Acid on Transport and Transformation of Mercury in Soil-Plant Systems." *Water, Air, and Soil Pollution* **95**: 35-43.
- Wang, F., J. Chen, et al. (1997). "Modeling Sorption of Trace Metals on Natural Sediments by Surface Complexation Model." *Environmental Science and Technology* **31**: 448-453.
- Watras, C. J., N. S. Bloom, et al. (1995a). "Methyl mercury production in the anoxic hypolimnion of a dimictic seepage lake." *Water, Air and Soil Pollution* **80**: 735-745.
- Weber, J. H. (1993). "Review of Possible Paths for Abiotic Methylation of Mercury(II) in the Aquatic Environment." *Chemosphere* **26**: 2063-.
- Welp, G. and G. W. Brümmer (1997). "Microbial Toxicity of Cd and Hg in Different Soils Related to Total and Water-Soluble Contents." *Ecotoxicology and Environmental Safety* **38**: 200-204.
- Wen, X., Q. Du, et al. (1998). "Surface Complexation Model for Heavy Metal Adsorption on Natural Sediment." *Environ. Sci. Technol* **32**: 870-875.
- White, C., S. C. Wilkinson, et al. (1995). "The Role of Microorganisms in Biosorption of Toxic Metals and Radionuclides." *International Biodeterioration & Biodegradation*: 17-40.
- WHO (1989). *Mercury Environment Aspect, Geneva- Environmental Health criteria* 86.
- WHO (1990). *Methyl mercury, International Program on Chemical Safety, Geneva: Environmental Health Criteria* 101.
- Wilken, R. D. and M. Horvat (1997). ""Mercury as a Global Pollutant" - International Conference." *Fresenius J. Anal. Chem.* **358**: 361-362.
- Witters, H. E. (1998). "Chemical Speciation Dynamics and Toxicity Assessment in Aquatic Systems." *Ecotoxicology and Environmental Safety* **41**: 90-95.
- Yin, Y., H. E. Allen, et al. (1997). "Kinetics of Mercury (II) Adsorption and Desorption on Soil." *Environ. Sci. Technol.* **31**: 496-503.
- Yin, Y., H. E. Allen, et al. (1997). "Adsorption/Desorption Isotherms of Hg(II) by Soil." *Soil Science* **162**(1): 35-45.

- Yin, Y., H. E. Allen, et al. (1997). "Effects of pH, Chloride and Calcium(II) on Adsorption of Monomethylmercury by Soils." *Environmental Toxicology and Chemistry* **16**(12): 2457-2462.
- Yin, Y., H. E. Allen, et al. (1996). "Adsorption of Mercury (II) by Soil: Effects of pH, Chloride, and Organic Matter." *Journal of Environmental Quality* **25**: 837-844.

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