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*Chapter 1*

# MERCURY BEHAVIOUR IN THE WATER COLUMN OF AN IMPACTED COASTAL LAGOON: RIA DE AVEIRO (PORTUGAL) AS A CASE STUDY

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## Abstract

As mercury presents high toxicity and is of great concern when dealing with protection of human health, mercury pollution related issues are the main subject of this work. At first, two general themes are discussed, namely: *I)* Mercury: highlights of physicochemical and biogeochemical properties of interest and of the main natural and anthropogenic metal sources; and *II)* Biogeochemical cycling of mercury in the water column of natural waters. Secondly, a case study performed in Ria de Aveiro (Portugal) during the last 10 years will be presented, focusing on water column processes.

Ria de Aveiro is a coastal lagoon, located along the Atlantic Ocean on the north-western coast of Portugal, which was subjected to a discharge of an effluent rich in mercury from a chlor-alkali industry, during more than five decades. In the last seventeen years, the industry changed its technology and the discharge of anthropogenic mercury diminished considerably. However, the dissolved total and reactive mercury concentrations, as well as the total mercury contents determined in the suspended particulate matter, obtained in a particular area of Ria de Aveiro, namely Largo do Laranjo, during the years of 1997 to 2000, are still high in comparison to other locals located world wide.

In Largo do Laranjo water column, mercury does not show a conservative behavior, due to the inexistence of a linear relationship between the dissolved total mercury concentrations and salinity. Owing to this, mercury behavior is variable and seems to result from a mixture of different phenomena. One of the most important factors that affect the dissolved mercury behavior is the dissolved organic matter, as a significant correlation is found between both parameters (r=0.788). The mercury partition evaluation performed in Largo do Laranjo water column shows that in both tide conditions, the dissolved and particulate fractions are important for mercury transport and distribution in Largo do Laranjo. However, mercury is more closely associated with the particulate phase (58 to 77%) than with the dissolved fraction.

Moreover, this case study also allows verifying that Largo do Laranjo still is a mercury source to the rest of Ria de Aveiro, as the estimated annual mean quantities of mercury that are transported in the dissolved and particulate fractions from the end of Largo do Laranjo, namely Cais do Chegado, to seaward are of 38 and 60 kg, respectively.

# Introduction

## I. Mercury: Highlights of Physicochemical and Biogeochemical Properties of Interest, and of the Main Natural and Anthropogenic Metal Sources

### a). Principal Physicochemical Properties of Mercury Compounds

Mercury and its compounds have been notoriously associated with the occurrence of several harmful situations to the environment and human health, namely, the methylmercury poisoning in Minamata (Japan), the organic mercury poisoning in Iraq, the methylmercury exposure in the Amazon (Brasil) and the elemental mercury spill in Catamarca (Peru), among other cases of contamination of air and food by both elemental and organic mercury compounds (Gochfeld, 2003).

In general, mercury is the only metal that is liquid at 25ºC, with density nearby 13.5 $g.cm^{-3}$ (Horvat, 1996) and fusion temperature of -38.89ºC (Andren and Nriagu, 1979). It has a low boiling point of 357ºC at 1 atm (Mukherjee *et al.*, 2004), presenting also low sublimation temperature (about 583ºC) (Nriagu, 1979). Inorganic mercury presents softness less than -2 and hardness (parameter related to the polarizing power of the cation) between 2.5-7.0 (Filella *et al.*, 1995). Mercury presents low electrical resistivity ($95.8\times10^{-6}$ ohm.cm at 20ºC) (Cutnell and Johnson, 1998), high surface tension (435.5 $dyne.cm^{-1}$ at 2ºC; 480 $dynes.cm^{-1}$ at 20ºC) (Weast, 1975), high thermal conductivity (0.0782 $W.cm^{-1}.K^{-1}$ at 0ºC; 0.0830 $W.cm^{-1}.K^{-1}$ at 20ºC; 0.0947 $W.cm^{-1}.K^{-1}$ at 100ºC) (Weast, 1975) and uniform volume expansion over its entire liquid range (Andren and Nriagu, 1979). These properties are the basis for choosing mercury to several industrial applications.

The concentration of mercury vapor depends on temperature, i.e. 5.5 $mg.m^{-3}$ at 10ºC, approximately 15 $mg.m^{-3}$ at 20ºC (IPCS, 1991) and 72 $mg.m^{-3}$ at 100ºC (Andren and Nriagu, 1979). At 20ºC the observed concentration is 600 times greater than the recommended health-based occupational exposure limit of 0.025 $mg.m^{-3}$ (The Japan Society for Occupational Health, 2006). Several occupational exposure limits based on biological monitoring (OEL-B) have been proposed as the reference value to the data obtained by biological monitoring at or below which the adverse health effects do not appear in most workers who are exposed to a chemical substance (Omae *et al.*, 1999). For mercury and its compounds (except alkyl mercury compounds) in urine the OEL-B is 35 $\mu g.(g\ Cr)^{-1}$ in relation to total inorganic mercury (Omae *et al.*, 1999; The Japan Society for Occupational Health, 2006).

## b). Some Natural and Anthropogenic Mercury Sources and Applications

The natural background mercury has been enormously augmented by mercury pollution resulting from a variety of human (especially industrial) activities.

The main natural sources of mercury are the Earth's crust and the upper mantle, being the volatile Hg vented into the atmosphere by volcanic activity (Gochfeld, 2003) and other degassing processes (Jackson, 1998). Mercury can also be present in rocks, being released by weathering (Jackson, 1998). Mercury deposits, which include many mercury minerals, are described in terms of composition, symmetry and typical occurrence by Nriagu (1979). However, the commercial production of mercury is made almost entirely from cinnabar, the $\alpha$-form of mercury sulfide. Cinnabar, when roasted in air, forms metallic mercury and sulfur dioxide (Deighton and Goodman, 1995). Besides, some mercury has been obtained from metacinnabar ($HgS-(HgS)_{80}(HgSe)_{20}$) (Jackson, 1998), livingstonite ($HgSb_4S_8$) and other mercury minerals, species that are found in association with cinnabar (Nriagu, 1979). Minor amounts of mercury have also been recovered from mercuriferous stibnite and tetrahedrite and as a byproduct in the smelting of some zinc ores (Nriagu, 1979). Nowadays there are strict regulations on the amount of mercury vapor that can be allowed to escape into the air during the smelting operations. The mercury mines in the European Union (EU) are situated in Italy, namely in the Tuscany region, and Spain, in Almadén (Mukherjee *et al.*, 2004). Total production of primary mercury in the EU dropped from 740 tonnes in 1993 to 313 tonnes in 2000, whereas world primary mercury production was reported to be equal to 1800 tonnes in 2000 (Mukherjee *et al.*, 2004).

Combustion of coal is another important cause of atmospheric mercury pollution, being currently the coal-fired utility boilers the largest single-known source of mercury emissions in the United States (Pavlish *et al.*, 2003), followed by incineration of solid refuse, as discussed by Jackson (1998) and Gochfeld (2003). Kolker *et al.* (2006) verified that the proportion of mercury in the coal feedstock that is emitted by stack gases of utility power stations is a complex function of coal chemistry and properties (notably Cl and S), combustion conditions, and positioning and type of air pollution control devices employed. Pavlish *et al.* (2003) refer to the fact that Western sub bituminous coals contain, on average, only about half as much mercury as Appalachian bituminous coals, but the higher chlorine content of the latter promotes mercury oxidation and results in a higher percentage of mercury capture, decreasing air contamination. Pavlish *et al.* (2003) also discussed that some iron minerals found in coal also catalyze mercury oxidation, whereas calcium and sulfur tend to impede oxidation. For a more detailed discussion of the options for mercury control from coal-fired power plants, the works of Reed *et al.* (2001) and Pavlish *et al.* (2003) are recommended for further reading.

Kilgroe (1996) stated that mercury is one of the primary pollutants of concern emitted from municipal waste combustors. Its concentration in the flue gas may range from less than 200 to more than 1000 $\mu$g/dscm, depending on the composition of the waste and technologies used. Nevertheless, mercury emissions can be reduced if powdered activated carbon is injected into the flue gas (Kilgroe, 1996).

Another industrial application of mercury has been in the chlor-alkali plants for simultaneous production of chlorine and caustic soda by the electrolysis of brine solutions, using a flowing cathode of metallic mercury (Nriagu, 1979; IPCS, 1991; Jackson, 1998). The sodium, which amalgamates at the cathode, is converted to NaOH with water and the released mercury is recycled into the cell (Nriagu, 1979). However, since this process was not entirely closed and some losses of mercury were observed, modifications of the existing plants have been performed, such as the adoption of diaphragm cells and membrane cells. Chlorine producers across Europe are progressively moving towards the membrane cell process, as this is the most environmentally sound way of manufacturing chlorine (http://www.eurochlor.org/makingchlorine). In 2004, emissions for all mercury cells across Western Europe reached an all-time low of 1.01 grams per tonnes of chlorine capacity (http://www.eurochlor.org/makingchlorine). Furthermore, a recommendation by the Parties of the OSPAR Convention of the North European region (PARCOM Decision 90/3 of 14 June 1990) has been forwarded for a total phase out of mercury process for chlor-alkali production by 2010 (Mukherjee *et al.*, 2004).

In the early 70’s the catalytic properties of mercury and many of its salts were recognized, being the conversion of acetylene to acetaldehyde (Jackson, 1998), as well as the production of polyvinyl chloride (PVC) and polyvinyl acetate (PVA) from vinyl chloride and vinyl acetate, respectively, one of the most important industrial processes applying these compounds (Andren and Nriagu, 1979; Nriagu, 1979).

Due to its ability to form amalgams or liquid metallic solutions (several metals solubility in mercury at 18-20ºC are compiled in Andren and Nriagu (1979)), mercury has been used in the industrial recovery of metals (Nriagu, 1979), such as the extraction of gold from ore, mainly in Amazon region, and in the making of dental fillings. The use of tin and silver amalgams in dental fillings dates back to the turn of the century due to their inertness, relative permanence, compressive strength, abrasion resistance and fungistatic effects (Nriagu, 1979). Lin *et al.* (1997) stated that adding Pd to a $Ag_2Hg_3$ phase in the range between 0.50 and 0.75% in dental amalgams, increased its compressive strength, increased its creep resistance and largely reduced both mercury vapor and ion release rates. In 1980s amalgam separators have been introduced in Sweden to reduce mercury emitted via dental clinic waste water. However, Hylander *et al.* (2006) studied the performance of these systems and found that mercury emissions can be reduced by improving the design of the discharge system and by implementation of high pressure water cleaning and regular maintenance (including replacement of amalgam separators and filters at certain intervals). The same study also refers that banning mercury in dentistry is the long-term way to stop mercury emissions from dental amalgam. Several studies have been performed on the effect of dental fillings on human health and Gochfeld (2003), for example, consider that the daily human exposures to methylmercury and inorganic mercury salts due to dental amalgams are negligible, with exposures lower than 0.1 $\mu g.day^{-1}$. In recent years amalgam use for tooth filling has been discouraged in European society and has been replaced by improved carbonations of metal oxide and silica nanoparticles in polymeric material (Mukherjee *et al.*, 2004).

Mercury has been used in the manufacturing of measuring devices, control instruments, electrical apparatus, batteries and boilers, mainly due to properties such as: liquid at ordinary temperatures, high surface tension, uniform volume expansion and inability to wet and cling to glass. Mercury has found commercial use in the production of fluorescent and high intensity arc discharge lamps, rectifiers, oscillators, power control switches, hot-cathode tubes and pool-cathode tubes for high-frequency applications (Nriagu, 1979; IPCS, 1991). Amalgams of Bi–Pb–Hg and Bi–Pb–Au–Hg have been attempted in compact fluorescent lamps in order to control the mercury vapour pressure inside the lamps, with satisfactory results at temperatures in the range of 60 to 150ºC (Lankhorst *et al.*, 2000). However, the use of mercury in lamps and batteries is declining, and, for example, the Nordic Countries, Germany and Austria have strict regulations on the use of amalgam and mercury thermometers (Mukherjee *et al.,* 2004).

Mukherjee *et al.* (2004) discussed and quantified the mercury containing wastes in the European Union, including batteries, lamps, mining and smelting industry, coal combustion products, chlor-alkali production, sewage sludge, landfills, urban waste and incinerator slag. The quantity of mercury estimated was around 990 tonnes for the year 1995 but this amount could be 2 to 4 times higher if more complete information was made available.

Due to the high toxicity of mercury, as well as of its compounds, has led to their widespread use as bactericides, fungicides, insecticides and pharmaceuticals, as diurectics, antiseptics, skin preparations and preservatives (Nriagu, 1979; IPCS, 1991). However, mercury is being effectively replaced by other less toxic materials.

Mercury is also a useful coolant due to its high thermal conductivity and it is highly rated as an electrical conductor because of its low electrical resistivity (Nriagu, 1979). Nowadays an emerging research area is the synthesis and preparation of mercury based superconductors and semiconductors. Several mercury based superconductors have been studied and reported in the literature, namely, the high temperature superconductors mercury based cuprates, such as, $Hg_{1-x}Tl_xBa_2(Ca_{0.86}Sr_{0.14})_2Cu_3O_{8+\delta}$ ($x=0.25$, 0.50, 0.75) (Hur *et al.*, 1994), $Hg_{0.8}V_{0.2}Ba_2CuO_{4+\delta}$ (Maignan *et al.*, 1995), $Hg_{0.8}V_{0.2}CaCu_2O_{6+\delta}$ (Maignan *et al.*, 1995), $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Bryntse and Kareiva, 1995; Bertinotti *et al.*, 1995), $HgBa_2CuO_{4+\delta}$ ($\delta>0$) (Bertinotti *et al.*, 1996; Hyatt *et al.*, 1999), $Hg_{1-y}V_yBa_{2-x}Sr_xCuO_{4+2y+\delta}$ ($x = 0, 0.25, 0.5, 0.75, 1$ and 1.25) (Knízek *et al.*, 1997), $HgBa_2CuO_{4+\delta}$ (Marucco *et al.*, 1997; Knízek *et al.*, 1998), (Hg, Bi)$Ba_2Ca_2Cu_3O_y$ (HgBi1223) (Sastry *et al.*, 1998), $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ with $n$=1–5 (Itskevich, 1998), $Hg_{1-x}Pb_xBa_{2-y}Sr_yCa_{n-1}Cu_nO_{8+\delta}$ ($x$~0.2–0.3, $0.5\leq y\leq 1.5$) (Klimonsky *et al.*, 2004), and Re-doped Hg-1223 ($HgBa_2Ca_2Cu_3O_8$) thin films (Moriwaki *et al.*, 1998). In terms of thin superconducting mercury based films, Valeriánová *et al.* (2006) gives an important insight on their formation mechanisms. As semiconductors, several mercury dots and films have been synthesized, namely, the chalcopyrite semiconductor - mercury thiogallate ($HgGa_2S_4$) (Schunemann and Pollak, 1997; Ricci *et al.*, 2003), the HgSe semiconductor thin films (Hankare *et al.*, 2003) and the mercury selenide and its ternary and quaternary modifications in the form of Hg(A,B)Se with A, B as magnetic ions (Tran-Anh *et al.,* 2004).

### c). Biogeochemical Aspects: Inorganic Mercury Reactions and Transformations; Organomercury Compounds Properties, Formation and Decomposition

Mercury can be found in three oxidation states: 0 (elemental), 1+ (mercurous) and 2+ (mercuric) (Andren and Nriagu, 1979; Jackson, 1998), such as in $Hg^0$, $Hg_2^{2+}$ and $Hg^{2+}$, respectively, depending on the environmental redox conditions (Horvat, 1996). Specifically, Hg(0) has the unique distinction of being a volatile liquid at most Earth-surface temperatures, rather unreactive and with a very slow oxidation to HgO by oxygen (though thermodynamically favored) (Jackson, 1998). Therefore, it can persist for significant lengths of time in contact with air (Jackson, 1998). Compounds such as $Hg_2Cl_2$ (calomel) are not paramagnetic but contain fairly strong mercury-mercury bonds (Carty and Malone, 1979). However, the $Hg_2^{2+}$ form is unstable in most natural environments and can suffer dismutation (Jackson, 1998), which implies Hg(0) and Hg(II) formation, when the counter ion bonded to the mercurous ion forms an insoluble Hg(II) salt (Carty and Malone, 1979) or in the presence of ligands that can bind Hg(II) (Jackson, 1998). Hg(II) is the principal form of mercury in aquatic environments, having strong tendency to form extremely stable coordination complexes and organometallic compounds (Jackson, 1998). Unlike most other metals, mercury exhibits higher tendency to form covalent rather than ionic bonds (Andren and Nriagu, 1979), due to the combination of high polarisability (reflection of size and number of electrons) with high polarizing power (resulting from poor shielding by the $4f^{14}$ shell) (Carty and Malone, 1979; Jackson, 1998).

Mercury might form several complexes with different ligands, such as sulphur (Leermakers *et al.*, 1995; Lobinski, 1998), namely thiol groups (Carty and Malone, 1979; IPCS, 1991) and sulphides (Jackson, 1998), nitrogen (e.g. $R\text{-}NH_2$), phosphorous or carbon (Jackson, 1998). Mercury has low affinity to oxygen ligands (Carty and Malone, 1979), but Hg (II) can be complexed with O-bearing ligands (e.g. R-COO-, OH- and $H_2O$), including ligands of amino acids and nucleic acids (Jackson, 1998), in the form of less stable bonds than in sulphides.

Owing to the formation of these kind of complexes with mercury, several biopolymers, as well as other compounds, have been evaluated as feasible adsorbents for mercury removal from artificially and/or natural aqueous solutions, namely, chitosan (Shafaei *et al.*, 2007), due to its free amino groups, cationic exchange resin of carboxyl banana stem (Anirudhan *et al.*, 2007), activated carbon from sago industry waste (Kadirvelu *et al.*, 2004), 1,5-diphenylcarbazide (DPC) functionalized sol–gel silicas (DPCSG) (Khan *et al.*, 2006), ground discarded tires (Gunasekara *et al.*, 2000), carbonaceous adsorbents prepared from rubber from tyre (Manchón-Vizuete *et al.*, 2005), porous cellulose carriers modified with polyethyleneimine (Navarro *et al.*, 1996), silica chemically modified with zirconium(IV) phosphate (Nagata *et al.*, 1998) and silica gel-immobilized-dithioacetal derivatives (X=H, $CH_3$, $OCH_3$, Cl and $NO_2$) (Mahmoud and Gohar, 2000).

The performance of activated carbon prepared from several matrixes, such as raw and demineralised lignite (Skodras *et al.*, 2007a), pine and oak wood, olive seed and tire wastes (Skodras *et al.*, 2007b), has also been evaluated for gas-phase Hg(0) removal. Vidic and Siler (2001) studied the adsorption capacity of a commercially available granular activated carbon (BPL) impregnated with copper chloride (BPL-C), β-aminoanthraquinone (BPL-A), 2-(aminomethyl)pyridine (BPL-P) and 2-aminoethanethiol (BPL-T) (which are less cost-effective than the chloride- or sulfur- impregnated carbons). However, the impregnation with thiol was the only promising approach that could originate effective mercury sorbents at room temperature, diminishing its dynamic adsorption capacity at 140ºC. Li *et al.* (2002) studied the role of surface moisture in capturing Hg(0) by two activated carbons, namely a bituminous-coal-based activated carbon (BPL) and an activated carbon fiber, and verified that moisture plays a critical role in retaining Hg(0). The adsorbed water is closely associated with surface oxygen complexes, which are the reactive sites for mercury bonding. Li *et al.* (2003) further studied the effect of changing the physicochemical properties of two activated carbons (BPL[1], WPL[1]) and suggested again that oxygen surface complexes, possibly lactone and carbonyl groups, are the active sites for Hg(0) capture.

Rooney (2007) recently stated that low molecular weight thiols, i.e. sulfhydryl containing molecules such as cysteine, are emerging as important factors in the transport and distribution of mercury throughout the body due to the phenomenon of “Molecular Mimicry” (Bridges

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[1] BPL and WPL are bituminous-coal-based activated carbons.

and Zalups, 2005), whereby the bonding of metal ions to nucleophilic groups on certain biomolecules results in the formation of organo-metal complexes that can behave or serve as a structural and/or functional homolog of other endogeneous biomolecules or of the molecule to which the metal ion has bonded.

Finally, mercury can also form very stable complexes with organic matter, namely humic substances, which are among the most common, abundant and effective complexing agents in soil, water and sediments (Jackson, 1998).

Mercury is classified as a dangerous chemical in the European Union (EU) and if present on waste, this is classified as hazardous (Mukherjee *et al.*, 2004). However, in terms of toxicity, organomercury compounds are the ones that cause more concern. It must be enhanced that the complexes formed with organic matter originally present in the aquatic systems do not belong to this group of compounds. The organomercury compounds can be divided into two groups: one in which mercury atom is linked to an organic radical, and another group to that mercury is linked to two organic radicals (Benes and Havlík, 1979).

The compounds that belong to the first group are soluble in water, dissociating in the $R\text{-}Hg^+$ cation and $X^-$ anion, being the most common the $Cl^-$, $OH^-$, $NO_3^-$ and $SO_4^{2-}$ anions (Benes and Havlík, 1979). Poorly coordinating anions such as $ClO_4^-$, $NO_3^-$, $PF_6^-$ and $BF_4^-$ anions confer an ionic character to $RHg^+X^-$ salt (Carty and Malone, 1979), and are correspondingly more hydrophilic (Jackson, 1998), while $Cl^-$, $Br^-$ and $I^-$ anions confer on a linear covalent character (C-Hg-X) (Carty and Malone, 1979), being these methylmercury halides among the more lipophilic methylmercury species (Jackson, 1998).

Methylmercury is one of the most hazardous mercury species, due to its high stability in combination with its lipid solubility and ionic properties, leading to a high ability to penetrate membranes in living organisms (Beijer and Jernelöv, 1979), in contrast to inorganic mercury, which is mainly accumulated in visceral tissues (Meili, 1997). Several works have been published in this domain, presenting Boening (2000) a general review over the ecological effects, transport and fate of mercury in aquatic receptors (microorganisms, aquatic plants, aquatic invertebrates, fish and marine mammals), amphibia and terrestrial receptors (birds, plants, soil invertebrates and mammals). Methylmercury presents a physiological fractionation factor, related to its turnover, of about 5-10, which implies that the depuration of methylmercury is several times slower than the metabolization of biomass (Meili, 1997). In terms of the biomagnification factor, that corresponds to the concentration increase for each trophic transfer, it is about two- to fivefold for various aquatic ecosystems and to all typical trophic levels, being an order of magnitude higher than the one for inorganic mercury (Meili, 1997).

On contrary, other organic mercury compounds like phenylmercury and the alkoxy-alkyl mercurials, that also belong to the first group, decompose rapidly in the environment and thus behave more like inorganic mercury (Beijer and Jernelöv, 1979).

The second group includes compounds such as dimethylmercury and diphenylmercury (Benes and Havlík, 1979). Due to the fact of having covalent bonds, these compounds are volatile, non polar and have low solubility in water (Benes and Havlík, 1979; Carty and Malone, 1979; Jackson, 1998), not being affected by air, and weak acids and bases (Andren and Nriagu, 1979). Dimethylmercury is extremely lipophilic and highly volatile, and hence readily escapes into the atmosphere (Jackson, 1998), whereas in solution diphenylmercury may undergo a photoredox decomposition, which is induced by ligand-to-metal charge transfer excitation (Kunkely and Vogler, 2004).

The organomercury compounds RHgX and $R_2Hg$ are broad-spectrum biocidal agents acting via diverse mechanisms in biological systems. Organomercurials are supposed to induce membrane associated oxidative stress in living organisms through different mechanisms, including the enhancement of the lipid peroxidation and intracellular generation of reactive oxygen species (ROS) (Milaeva, 2006). The perturbation of the antioxidative defense system and the peroxidation of unsaturated fatty acids in membrane lipid bilayer are consequences of this impact (Milaeva, 2006). On the other hand, the formation of active free radicals $R^{\bullet}$, as a result of carbon to metal bond's homolytic cleavage in the oxidative/free radical medium, is also responsible for the promotion of the lipid peroxidation (Milaeva, 2006).

Organomercury compounds are stable due to the existence of weak intramolecular interaction (Jiang *et al.,* 2000). These authors verified that the ligands which coordinate with mercury may be atoms that contain lone pairs (nitrogen, halogen), or $\pi$ bonds (erene), or $\pi$ electrons in the conjugated systems. Wong (2007) summarizes the recent progress in the developments of novel organomercurial materials, namely, linear mercury-based metallaynes, as well as, their long-chain oligomers and polymers, which exhibit interesting properties to optoelectronic and analytical applications. In fact, the linear geometry of the alkynyl unit and its $\pi$-unsaturated character have led to an increase of interest on mercury (II) alkynyls, which have become attractive building blocks for molecular wires and organometallic functional materials, which possess interesting properties such as optical nonlinearity, luminescence and chemosensing and mercurophilicity (Wong, 2007).

Since 60-70's, several methylation mechanisms are known. Methylmercury can be formed naturally in the aquatic environment by two general pathways: chemical methylation (abiotic processes) and microbial metabolism (biotic processes) (Celo *et al.,* 2006). On the whole, chemical methylation of mercury will only occur in the aquatic environment if suitable methyl donors are present (Celo *et al.,* 2006). In general, chemical reagents thought to cause abiotic methylmercury formation include small organic molecules, such as methyliodide and dimethylsulfide, and larger organic components of dissolved organic matter, such as fulvic and humic acids (Celo *et al.,* 2006). In relation to methyliodide, this compound does not methylate oxidized mercury and so its role is only significant in reducing/anaerobic conditions. Methyliodide only methylates reduced forms of metals, being the oxidative addition ($Hg(0) + MeI \rightarrow MeHgI$) the presumably mechanism evolved (Celo *et al.,* 2006). Jackson (1998) refers that $CH_3Hg^+$ can be generated abiotically by humic substances and by acetate ions in the presence of sunlight or UV radiation. Nagase *et al.* (1982; 1984) verified that extracts of humic substances in river sediment have the ability to methylate mercury, as well as fulvic acids. Only three humic substances identified by GC-MS, namely 2,6-di-tert-butyl-4-methylphenol (BHT), *p*-xylene and mesitylene had the ability to methylate at pH 3.5 (Nagase *et al.*, 1984). At pH 7, only BHT produced methylmercury (Nagase *et al.,* 1984). In terms of fulvic acids, all of them, fractionated by molecular weight, were able to methylate inorganic mercury, being the lower molecular weight compounds (M.W. 200) the most active (Nagase *et al.,* 1982). Transmethylation reactions involving organometallic complexes such as methylcobalamin, methyllead or methyltin compounds have also been considered as possible pathways for chemical methylation of mercury in the aquatic environment (Celo *et al.,* 2006). Filippelli and Baldi (2004) verified that the reaction products of methylcobalamin and ionic mercury were methylmercury and dimethylmercury. The first specie to be formed is the former, being the first methylation rate two times faster than the second. Chen *et al.* (2007) studied the methylation of inorganic mercury by methylcobalamin in aquatic systems and identified methylmercury as the reaction product, having the salinity and pH of the aquatic system great effects on its formation and even occurring in highly saline solutions. It is suggested that inorganic mercury acts as an electrophile to attack methylcobalamin with a subsequent transfer of a carbanion methyl group to the higher oxidized state of Hg(II) (Chen *et al.*, 2007). However, Celo *et al.* (2006) refer that methylcobalamin is apparently unreactive towards chloride complexes of Hg(II) and so, is unlikely to methylate Hg(II) in moderately or highly saline environments. Another recognized effective methylator for mercury is the trimethyllead (Beijer and Jernelöv, 1979; Ebinghaus and Wilken, 1996). The methylation of mercury (II) by trimethyltin cation was found to be a bimolecular reaction, decreasing the reaction rate with increasing chloride concentration (Bellama *et al.*, 1988). However, as stated by Jackson (1998), all of these "abiotic" mechanisms are indirect consequences of biological activity, as humic matter, acetate, methyltin and $H_2S$ are by-products of microbial decomposition of the remains of organisms.

In biological systems, there are three major coenzymes which are known to be involved in methyl transfer: *S*-adenosylmethionine, 5-methyltetrahydrofolate (THF) and methylcorrinoid derivatives (vitamin $B_{12}$) (Beijer and Jernelöv, 1979; Reichardt, 1996). D'Itri (1991) mentions several works in which is referred that the *S*-adenosylmethionine and THF cannot transfer directly methyl groups to mercuric ions because both of these coenzymes can only transfer a methyl group as $CH_3^+$ (carbonium ion). On the contrary, methylcobalamin, which is an active form of vitamin $B_{12}$, appears to be the only biological methylating agent capable of transferring a methyl group to an inorganic mercuric ion, in the form of a carbanion ($CH_3^-$) and a methylradical ($CH_3^\bullet$) to produce methylmercury and dimethylmercury under both aerobic and anaerobic conditions (D'Itri, 1991; Jackson, 1998). Still in relation to THF role, Choi *et al.* (1994) observed that methylmercury synthesis in *Desulfovibrio desulfuricans* LS from this compound, was an enzymatically catalyzed process, involving two steps instead of one, being the sequence of the methyl transfer from THF $\rightarrow$ corrinoid protein $\rightarrow$ $Hg^{2+}$. Beyond these, other biochemical pathways have been observed, as reported by Ebinghaus and Wilken (1996) and Jackson (1998). However, the previous ones are the most studied.

Organisms capable of mercury methylation have been found among anaerobes, facultative anaerobes and aerobes, and the potential for microbial methylation thus exists both under aerobic and anaerobic conditions (Beijer and Jernelöv, 1979). The product is mainly monomethylmercury under neutral and acidic conditions, while formation of dimethylmercury is predominant under basic conditions (Beijer and Jernelöv, 1979). In a number of aquatic ecosystems (e.g. estuaries), sulphate-reducing bacteria are the dominant methylators in sediments and water column under anoxic conditions, provided that the ambient sulphate levels are low enough to be limiting, thus compelling the bacteria to live by fermentation rather than anaerobic respiration (Jackson, 1998). In fact, when the sulphate levels are high enough to sustain production of $H_2S$ the methylating activity declines due to sulphide interference (Jackson, 1998). The bioavailability of Hg for methylating bacteria tends to decrease as sulfide concentrations increase, since dissolved mercury tends to form non-neutral complexes with S (Hines *et al.*, 2006). Neutral HgS complexes in pore water, for example, which tend to dominate at low sulfide concentrations, are capable of readily passing through bacterial membranes and be methylated to methylmercury, yet this form is replaced by non-neutral complexes as dissolved sulfide concentrations increase (Hines *et al.*, 2006). Some microbes may also convert methylmercury to dimethylmercury and inorganic Hg(II) (Jackson, 1998). It must always be remembered that the factors that affect mercury methylation can be separated into those that affect the bioavailability of mercury to the methylating organisms and those that affect the activity of the mercury methylating bacteria (Heyes *et al.*, 2006). The relative importance of these categories with regard to controlling mercury methylation in estuaries is difficult to assess, as, for example, dissolved organic carbon concentration and composition could impact both mercury bioavailability and microbial activity (Heyes *et al.*, 2006). The processes that alter mercury methylation by affecting microbial activity are related to temperature (Heyes *et al.*, 2006), pH, redox potential and to the presence of inorganic and organic complexing agents (Celo *et al.*, 2006).

In terms of dimethylmercury formation, this can occur through a dismutation reaction of methylmercury in the presence of $S^{2-}$ ions (Craig and Moreton, 1983; Berman and Bartha, 1986; Compeau and Bartha, 1987; Fitzgerald and Mason, 1997), by methylmercury methylation (Horvat *et al.*, 1993; Johnson, 1998) and by elemental mercury methylation by the carbocation ($CH_3^+$) (Fitzgerald and Mason, 1997). Symmetrisation ($RHgX + RHgX \leftrightarrow R_2Hg + HgX_2$) can also play an important role in dimethylmercury formation (Carty and Malone, 1979), as the anionic (e.g., $I^-$) and neutral (e.g., phosphines) ligands can induce this kind of reaction, which is also an important formation process of other monoorganomercury derivatives ($R_2Hg$) (Carty and Malone, 1979).

Beyond these organomercurial formations, methylmercury can be decomposed by light (Jackson, 1998) or by various free-living demethylating microbes, or demethylators (IPCS, 1990; Ebinghaus and Wilken, 1996), ranging from anaerobes to aerobes (Jackson, 1998). Nowadays it is known that demethylation of methylmercury in sediments can occur via a number of mechanisms, being the two major microbial mechanisms the reduction by *mer* operon-mediated pathways and the oxidative demethylation pathway (Whalin *et al.*, 2007). The *mer*-coded enzymes catalyze the reductive demethylation of methylmercury, originating $CH_4$ (Hines *et al.*, 2006). The *mer* system can harbor genes for both an organomercurial lyase and a mercury reductase, that reduces Hg(II) to Hg(0) (broad-spectrum resistance), or for a reductase alone (narrow-spectrum) (Hines *et al.*, 2006). Bacteria with broad spectrum ability can degrade methylmercury and reduce Hg(II) (Hines *et al.*, 2006). In relation to the oxidative demethylation pathway, which implies the degradation of the methyl moiety of methylmercury to $CO_2$, is thought to be analogous to the decomposition of other $C_1$ compounds, such as methylamines, methanol or methyl sulfides, and has been shown to occur in a variety of habitats and by a diverse microflora (Hines *et al.*, 2006). Although $CO_2$ production is indicative of oxidative demethylation, one would expect the production of both $CO_2$ and $CH_4$ during oxidative demethylation by methanogenic bacteria, since these are the products of $C_1$ metabolism by methanogens (Hines *et al.*, 2006). Hines *et al.* (2006) refer that it has been suggested that the oxidative degradation of methylmercury is more prevalent in anaerobic habitats, whereas the reductive path is most active in oxidizing environments. In fact, although the oxidative path can occur during $O_2$ reduction, it tends to be favored in the absence of $O_2$ when alternate electron acceptors are used, such as $NO_3^-$ or $SO_4^{2-}$ (Gray *et al.*, 2006). However, there are few data to support this premise. Another detoxification strategy that can be found in microbes, include the transformation of inorganic Hg(II) or methylmercury to dimethylmercury (Jackson, 1998), resulting in mercury removal from the microbe´s immediate vicinity. In conclusion, methylation may meet the detoxification requirements of some microbial species, whereas demethylation is more satisfactory for others (Jackson, 1998).

## II). Biogeochemical Cycling of Mercury in the Water Column of Natural Waters

Owing to the fact of some general reviews concerning the biogeochemistry of mercury in the aquatic ecosystems have already been published, such as the ones written by Jackson (1998) and Meili (1997), that have yielded important insight into mercury behavior, only some aspects over the estuarine behavior of mercury in the water column will be discussed in this section.

In the water column it is necessary to distinguish between the dissolved and particulate fractions. The dissolved phase is typically defined as the fraction that includes all the forms of an element capable of passing through a filter of 0.45 μm porosity (Schroeder, 1989; Lund, 1990; Kennish, 1998; Town and Filella, 2002). However, there is no perfect way to distinguish between what is dissolved and what is nondissolved, because: *a)* although most particles, larger than a given pore size are normally retained, many smaller particles (sometimes 10-1000 times smaller than the pore size) may also be retained; *b)* coagulation may occur in the bulk sample and in the filter; and *c)* interaction of solutes can occur with the filter material and the retained particles (Stumm and Morgan, 1981).

The dissolved fraction includes hydrated ions, ionic pairs, quelates, humates and metal oxides (Laxen and Harrison, 1981; Millward and Turner, 1995). A part of the colloidal fraction, which includes particles between 0.003 and 1 μm, is also considered in the dissolved phase. Therefore, the filtrates obtained with filters of 0.45 μm porosity include the colloidal and the true dissolved fractions (Stordal *et al.*, 1996). The colloids present in fresh and saline waters are normally of organic nature, heterogeneous, and polifunctional (Stordal *et al.*, 1996), showing high affinity for metals. In the common conditions of redox potential and pH observed in well oxygenated freshwaters, the most stable are likely to be the iron and manganese oxides and clay particles, coated with humic material (Florence, 1982). However, colloids can suffer conformational alterations due to salinity and pH gradients, observed along estuaries (Stordal *et al.*, 1996), playing an important role on metal partition between the dissolved and particulate fractions.

In relation to particulate fraction, in estuarine systems the suspended particulate matter concentrations are generally high and variable, due to the changeability of the particulate material that is discharged with river waters and due to the complex interaction existent between the tides and the residual currents observed in these aquatic habitats, capable of remobilizing recently deposited material (Turner and Millward, 1994). The principal constituents of the suspended particulate matter are clays, quartz, feldspar and carbonates, sometimes associated to iron and manganese hydroxides and organic matter of marine and terrestrial origins (Förstner, 1989). In this way, the fine-grained suspended particles are a heterogeneous mixture of both organic and inorganic components (Filella *et al.*, 1995). The surfaces of the particulate matter have ionizable groups and the retention of a metallic ion ($M^{z+}$) can be described such as one competition with protons by the surface sites ($S\text{-}OH$) (Millward and Turner, 1995): $S\text{-}OH + M^{z+} \Leftrightarrow S\text{-}OM^{(z-1)+} + H^{+}$, with $S$ as an iron, aluminum or manganese oxide, as well as, carbon of a functional group of humic substances. These last compounds proceed from the organic matter degradation and consist on a mixture of several composites with various molecular weights (Benes and Havlík, 1979), showing great tendency to form complexes with metallic cations. This is due to the existence of several functional groups (Förstner, 1989), as for example, carboxylic acids, phenolic and alcoholic hydroxyl, and keto functional groups (Hintelmann *et al.*, 1997). By definition, the humic substances that precipitate in acid medium are designated humic acids, while those that remain in solution are denoted fulvic acids (Hintelmann *et al.*, 1997).

Much of the solid material present in the estuaries can have anthropogenic origin, proceeding from industrial discharges and domestic sewages. However, some solid material is produced *in situ* by chemical (flocculation) and biological (primary production) processes or originated from natural processes of erosion (Millward and Turner, 1995), being the sediments composition similar to the suspended particulate matter. Telmer *et al.* (2006), for example, collected suspended material from the plume of River Creporí (Brazilian Amazon), analyzed it by SEM micrograph and found out that this suspended material is formed by agglomerations of superfine clay particles.

In relation to mercury, when this metal is introduced into natural waters, it is rapidly and efficiently scavenged by the fine-grained suspended particles (Filella *et al.*, 1995), being the suspended particulate matter essential to the mercury transport through horizontal and vertical directions (Ebinghaus *et al.*, 1994; Ebinghaus and Wilken, 1996). Afterwards, most of the introduced mercury accumulates in clay- and silt- sized bottom sediments, although a small and highly variable proportion of it remains in solution, or is resolubilized in the form of different ionized and uncharged aqueous species and complexes (Jackson, 1998). If the binding agents are scarce, as in a highly oxidizing environment where most of the particulate matter consists of mineral detritus, the Hg(II) is sorbed by mineral particles, principally by Fe and Mn oxyhydroxides (Jackson, 1998). The role of the suspended particulate matter over mercury behavior has already been reported several times. However, in a recent study performed in Thau Lagoon (France), it was once more stated this relationship, but it was also referred that the vertical structures of mercury species in the water column indicate that (Muresan *et al.*, 2007): *a)* a large proportion of mercury is associated with the particulate phase, especially during the productive period within the photic layer, and *b)* the concentration increase in several mercury species near the bottom, reveals an effect of the benthic layer by particulate matter resuspension or/and by diffusive processes at the sediment-water interface.

Sediment resuspension can also be responsible for the high total suspended solids and particulate mercury concentrations found and reported in some works (Lacerda and Gonçalves, 2001; Kim *et al.*, 2004). As referred by Munteanu and Munteanu (2007) in the Dniester River (Ukraine), the total mercury content in the water column is determined by the interaction of phases in the “bottom sediments – water” system and the intensity of the mercury transition from bottom sediments to water and vice versa is determined by many factors, like the hydrochemical composition of the liquid phase, the physico-chemical and biochemical state of the solid phase, temperature, redox-potential, etc. In its turn, the stability and continuity of these factors is also highly determined by the hydrological regime of the reservoir (Munteanu and Munteanu, 2007). Nevertheless, the total suspended solid load, as well as sediment resuspension, can be influenced by several external factors, changing mercury partition in the water column. Ullrich *et al.* (2007), for example, stated that during one sampling campaign at Lake Balkyldak (Kazakhstan), the surface water samples were turbid, with a high suspended solid load, due to strong winds and waves, which had led to the resuspension of highly contaminated bed sediments, which originated higher mercury concentrations in the water column.

In the dissolved fraction the principal mercury species encountered depend on pH and chloride concentration. In seawater, the tri- and tetrachloride complexes (i.e. $HgCl_3^-$ and $HgCl_4^{2-}$) are more abundant (Turner, 1987), augmenting the dichloride complex importance when salinity decreases (Fitzgerald and Mason, 1997). In short, $HgCl_2$ and $Hg(OH)_2$ are probably the main inorganic Hg species in oxygenated, sulphide-free fresh waters and pH range of ~4 to 6 or 7, becoming increasingly important the $HgCl_3^-$ and $HgCl_4^{2-}$ species with rising $Cl^-$ level (Jackson, 1998). If pH increases from ~6 or 7 to 11, an increase in $Hg(OH)_3^-$ concentration will be predicted (Jackson, 1998). In terms of sulphides, if present at picomolar concentrations, they can also form complexes with mercury (Fitzgerald and Mason, 1997), such as $Hg(SH)_2$ (Jackson, 1998), and if reducing conditions exist, formation of mercury sulphide on the bottom can occur and tend to trap and accumulate mercury (Jackson, 1998). The organic complexation of mercury has also an important role, dominating the organic complexes over the inorganic in estuarine habitats (Fitzgerald and Mason, 1997). As a rule, Hg(II) is strongly and preferentially bound to inorganic sulphides and thiol groups of humic and non-humic organic substances (Jackson, 1998). Lacerda and Gonçalves (2001) suggested that 98% of the total dissolved mercury, determined in eleven coastal lagoons of Rio de Janeiro (Brazil), was strongly bound to dissolved complexes, which were probably refractory organic colloids. In regard to colloids, mercury, as many heavy metals, may be strongly adsorbed to these particles, being these "pseudocolloidal" forms of the heavy metals the main dissolved species present in natural waters (Florence, 1982). However, as already referred, these colloidal particles in suspension in the estuaries may be removed by destabilization and consequent aggregation and flocculation that occur when these particles encounter waters with higher quantity of cations, namely waters with high salinity (Hunter and Leonard, 1988), carrying down with them most of the adsorbed metals.

The dissolved fraction can also contain dissolved gaseous mercury, which includes elemental mercury and dimethylmercury (Coquery *et al.,* 1997; Fitzgerald and Mason, 1997; Amouroux *et al.,* 1998). The elemental mercury present in the water column might result from bacteriological reduction of inorganic mercury and methylmercury, and from the reduction of the dissolved mercury by phytoplankton (Leermakers *et al.,* 1995; Ebinghaus and Wilken, 1996; Fitzgerald and Mason, 1997; Baeyens and Leermakers, 1998). Dimethylmercury is rarely detected on freshwaters, on contrary to seawaters (Fitzgerald and Mason, 1997). This is probably due to an increase in dimethylmercury stability originated by the low luminosity and high pH values, characteristics of deeper oceanic waters (Fitzgerald and Mason, 1997). In fact, this specie is spontaneously converted to methylmercury under acidic conditions ($pH < 5.6$) (Jackson, 1998).

Changes in mercury partition on water column can be observed when a shift from freshwater to marine conditions occur, including partial desorption and solubilization of the bound mercury by the formation of water-soluble Hg-Cl complexes, as well as flocculation of mercury-bearing clay and humic matter owing to the increase in salinity (Jackson, 1998). In the Scheldt Estuary, for example, dissolved Hg is predominantly bound to strong complexing ligands (organic substances) in the upper estuary, but this fraction decreases with increasing salinity (Leermakers *et al.,* 1995). In Douro estuary (Portugal), the bottom waters that present higher salinities and lower particulate organic matter, also presented higher concentrations of dissolved reactive mercury probably due to the formation of chlorocomplexes (Ramalhosa *et al.,* 2005a). On the other hand, Plaschke *et al.* (1997) observed that as suspended particles moved down the Derwent Estuary (Australia) in contact with water containing dissolved mercury species, the level of mercury per particle increased in a direct relationship with salinity, as the scavenging process continued. Another important parameter that may also change the existent equilibriums is pH. A change in the pH of water column in one unit can cause the difference between complete adsorption or dessorption of heavy metals (Florence, 1982). Besides, the nature of the particles has also an important role on metal partition. Jackson (1998) points out that several works suggest that under acidic conditions the sorption capacities of mineral particles decline sharply with decreasing pH, whereas organic matter shows only a slight decline. Along the gradual migration of mercury in a estuary, several other processes may occur. For example, the mercury sorbed to FeOOH coatings on suspended clay and silt transported by fluvial currents, can be deposited if it encounters an anoxic basin, rich in sulphides and organic matter. In spite of this, FeOOH will be reduced and solubilized, liberating the mercury. Although, mostly of the mercury might be immobilized by sulphide and thiols, it will also be, to some extent, mobilized as dissolved sulphide and thiol complexes, hydrolysis products, etc., and again recycled into the water (Jackson, 1998). These results show that each ecosystem must be regarded individually. Besides, it cannot be forgotten that every system is dynamic and subjected to a great number of intrinsic and extrinsic factors, originating great variability on mercury pathways.

As already discussed in the previous section, it cannot be forgotten that in aquatic environments, inorganic mercury can be microbiologically transformed into the lipophilic organic compound “methylmercury” (Zahir *et al.,* 2005). As methylmercury was not determined in Ria de Aveiro, the case study described in the next section, its behavior in natural waters will only be slightly discussed. For a deeper understanding in the aqueous methylmercury speciation and over the factors that influence the oxidation, reduction, methylation and demethylation of mercury species in coastal waters, it is recommended the reading of Jackson (1998) and Whalin *et al.* (2007) works, where the theme is largely described.

Whalin *et al.* (2007) preliminary results point out to a high stability of methylmercury in coastal waters, suggesting that this may be an important source of methylmercury to open ocean waters. In natural waters, methylmercury is thought to be mostly complexed to inorganic and organic sulphide ligands, or, if these are absent, to $OH^-$ or $Cl^-$ ions, although methylmercury may be released from sulphide complexes under acidic conditions or at high $Cl^-$ concentrations (Jackson, 1998). In aerobic systems with low sulfide concentrations, the dissolved organic matter can also play an important role, as it can be responsible for the scavenging of dissolved methylmercury (Jackson, 1998). Methylmercury-humic substances complexes dominate at pH values below 7, becoming important the sulfide complex under alkaline conditions where the hydroxide complex becomes measurable, too (Hintelmann *et al.,* 1997). In terms of methylmercury partition, the suspended particulate matter has also an important role on this specie behavior. In a recent study performed by Monperrus *et al.* (2007) in Thau Lagoon (France), which envolved isotopically enriched mercury species, with the aim of determining the methylation rates of mercury in both surface sediments and water column, the major part of the formed methylmercury was mainly recovered in the particulate phase, corroborating the fact of methylmercury association to phytoplankton and/or bacteria.

This higher methylmercury affinity with the suspended matter was explained by the greater affinity of methylmercury towards biogenic particles, whereas inorganic mercury tends to bind more strongly to mineral particles and detrital organic matter (Monperrus *et al.*, 2007).

In the dissolved phase, methylmercury behavior also depends on colloids presence. Ikingura and Akagi (1999), for example, performed several laboratory experiments involving sediment-water systems with or without fish and observed that approximately 50-100% of the methylmercury present was dissolved in water or associated with the colloidal fraction < 1 μm, after analysis of whole water and filtered water. In fact, methylmercury shows strong binding capacity towards low molecular weight of dissolved organic carbon, being almost entirely found in the lower molecular weight fraction of the colloids and in the truly dissolved fraction (Cai *et al.*, 1999). In surface waters collected in Florida Everglades, for example, Cai *et al.* (1999) also refer that methylmercury is primarily associated to the smaller molecular weight colloidal fractions (<10 kDa) and to the truly dissolved fraction (< 3 kDa), in contrast to total mercury, which is mainly associated with colloidal forms (0.22 μm to 3 kDa) in the dissolved phase, showing both species different distribution patterns. However, it cannot be forgotten that methylmercury production is kept in check by the process of demethylation performed by various microorganisms (Jackson, 1998) or by sunlight, if irradiation is high (Meili, 1997). The highest demethylation seems to be observed in oxic waters, while methylation appears to be more intense in the combined presence of steep redox gradients and high microbial activity (Meili, 1997).

In conclusion, the net rate of methylmercury production depends on the abundance of bioavailable inorganic Hg(II) species and the activities of methylating and demethylating microbes (Jackson, 1998), being higher if there are inorganic Hg(II) species available and the activities of methylators surpass the ones related to demethylators.

## Ria de Aveiro (Portugal) as a Case Study

### I) General Description of the Studied Area and of the Methodology Followed

Ria de Aveiro is a coastal lagoon, located along the Atlantic Ocean north-western coast of Portugal that covers an area of 43 km$^2$ at low tide, with islands and channels that originate a complex circulation of water and particles. This lagoon connects to the sea through a single artificially maintenance entrance. Some areas are currently used for fish-farming and as popular recreational resorts.

During more than five decades a chlor-alkali industry, which started operating in Estarreja around 1950, has been discharging an effluent rich in mercury in a remote branch of the lagoon (Esteiro de Estarreja) that ends in the bay of Largo do Laranjo (Figure 1). In the last seventeen years, the industry changed their technology and the discharge of anthropogenic mercury diminished considerably (Pereira, 1996). However, in some areas of the lagoon, the mercury pollution continues to be significant.

Since 80’s, several works have been carried out in Ria de Aveiro related to sediments (Lucas *et al.*, 1986; Hall *et al.*, 1987; Pereira, 1996; Pereira *et al.*, 1998a; Ramalhosa *et al.*, 2001; Ramalhosa *et al.*, 2005b; Ramalhosa *et al.*, 2006a; Ramalhosa *et al.*, 2006b), water (Pereira *et al.*, 1995 and 1998b; Ramalhosa *et al.*, 2001 and 2006b) and organisms (Lucas *et al.*, 1986; Abreu *et al.*, 2000; Ramalhosa *et al.*, 2001). However the results reported for the water column, are related to particular situations that were studied in order to evaluate, for example, the seasonal variability in mercury concentrations and fluxes in Ria de Aveiro (Pereira *et al.*, 1995), the tidal export of particulate mercury from Largo do Laranjo to the rest of the lagoon (Pereira *et al.*, 1998a) and the export across the sediment-water interface in Largo do Laranjo (Ramalhosa *et al.*, 2001; Ramalhosa *et al.*, 2006b).

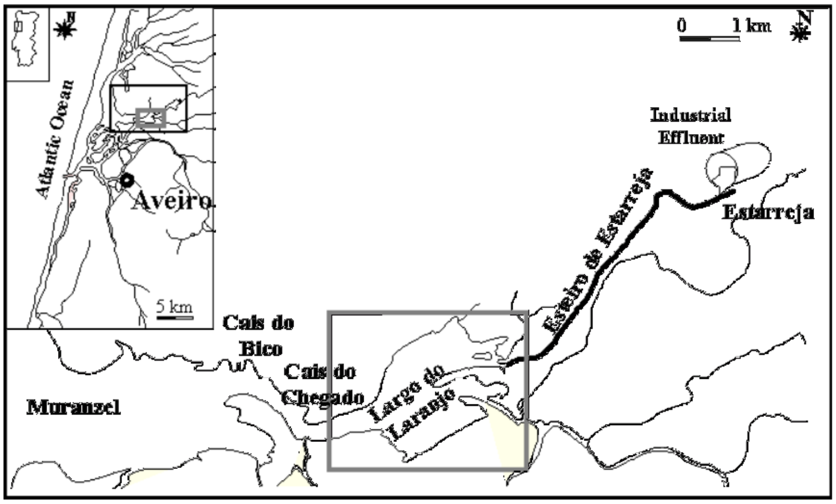

Figure 1. General plan of Ria de Aveiro, Esteiro de Estarreja and Largo do Laranjo.

In this section of the present work a detailed characterization of Ria de Aveiro water column will be performed, using the values recorded during these last ten years of study. It must be referred that a higher number of sampling campaigns were realized during the years of 1997 to 2000, included in the project with Ref. nº PEAM/C/SEM/540/95 and the PhD scholarship Ref. PRAXIS XXI/BD/11153/97, developed in order to acquire more knowledge about mercury behavior in this habitat, mainly in Largo do Laranjo.

In order to determine mercury concentrations in the dissolved and particulate fractions of the water column of Largo do Laranjo, several surface water samples were collected in various places around Largo do Laranjo at different times of the year and during several years at low and high tides, trying to cover the most possible huge area. The sampling methodology adopted was to carry out short and consecutive samplings, acquiring data that allowed spatial interpolations.

In each campaign, several parameters were measured *in loco*, namely, pH, temperature, salinity and dissolved oxygen. The samples of surface water were collected manually under a boat, by submerging acid-cleaned polyethylene bottles approximately 20-50 cm under the water surface. The samples were rapidly transported to the laboratory under refrigeration, where they were immediately processed.

In the laboratory, the water samples were filtered through Millipore filters, type HA of 0.45 $\mu$m porosity, in order to obtain the dissolved and particulate fractions. The filtration was always performed using an adequate water volume (500 to 5000 $cm^3$) in order to observe particles deposition over the filter. After filtration, the filtrates were acidified to a pH less than 2 with nitric acid (conc., "mercury-free") and placed at 4ºC in glass bottles until analysis. The filters were dried at 70ºC in Petri dishes, until reach constant weight. Duplicates were always analyzed and a similar volume of ultrapure water was carried through the filtration apparatus as a blank procedure.

The acidified filtrates were analyzed by cold-vapor (tin chloride reduction: 2% (m/v) $SnCl_2$ in 10% (v/v) HCl) – atomic fluorescence spectrophotometry (CV-AFS) in order to determine the reactive mercury. This procedure was similar to the one adopted by Cossa *et al.* (1988) and Dalziel (1995), and permit the quantification of the dissolved inorganic mercury, dissolved Hg(0) and the labile mercury complexes with organic matter (Cossa *et al.*, 1988; Gill and Bruland, 1990; Fitzgerald and Mason, 1997). The total mercury, including the reactive and the non-reactive mercury species, namely mercury compounds that have covalent bonds of the type C-Hg (such as in methylmercury) (Gill and Bruland, 1990) and non-labile complexes of mercury with organic matter, was analyzed in a similar way as described before for the reactive mercury, but previously an oxidation was performed. Potassium peroxodissulfate was added to the samples and these were submitted to ultraviolet radiation, in a similar way as described by Mucci *et al.* (1995). The filters were analyzed in terms of total mercury after digestion with nitric acid 4 $mol.dm^{-3}$ and using cold-vapor (tin chloride reduction: 5% (m/v) $SnCl_2$ in 10% (v/v) HCl) – atomic absorption spectrophotometry (CV-AAS), in a similar way as described in Pereira (1996) and Pereira *et al.* (1998b).

The organic matter contents present in the dissolved and particulate fractions of the water samples were also determined. The methodology used was the following: the water samples were filtered through glass fiber filters (GF/C), previously cleaned at 450ºC during at least 24 hours. The filtrates were transferred to quartz cells of 10 cm optic length and analyzed by ultraviolet spectrophotometry at 330 nm. This wavelength was used to estimate the dissolved organic carbon concentrations present in the water samples, as referred by Moore (1987). The filters were oxidized by potassium dichromate in the presence of sulfuric acid, in order to determine the particulate organic carbon. In this method, the oxidant is added in excess to the samples, being this determined by a Fe(II) solution.

## II) Physico-Chemical Characterization of Largo do Laranjo Water Column

Salinity, temperature, pH, dissolved oxygen, absorbance at 330 nm, suspended particulate matter (SPM) and particulate organic carbon (POC) values determined on the sampling campaigns performed on Largo do Laranjo are described in Table 1. Not always all the parameters were determined because some of their analytical methodologies were developed later on. The sampling campaigns realized on Autumn/Winter are shaded on grey.

**Table 1. Physico-chemical parameters, namely salinity, temperature, pH, dissolved oxygen (%), absorbance at 330 nm, suspended particulate matter (SPM) (mg.dm$^{-3}$) and particulate organic carbon (POC) (%), determined on the sampling campaigns performed in Largo do Laranjo during the years of 1997 to 2000 (Median ± Range).**

| Date of the sampling campaign | Tide condition | Salinity | Temperature | pH | Dissolved oxygen (%) | Absorbance at 330 nm | SPM (mg.dm$^{-3}$) | POC (%) |
|---|---|---|---|---|---|---|---|---|
| April 1997 | Low | 19.4 ± 10.0 | 21.8 ± 3.2 | 7.41 ± 0.57 | 83 ± 27 | -- | 42.4 ± 36.2 | 2.92 ± 3.62 |
| | High | 24.6 ± 12.1 | 19.4 ± 0.8 | 7.55 ± 0.37 | 76 ± 17 | -- | 36.6 ± 20.7 | 2.42 ± 2.95 |
| December 1997 | Low | 2.0 ± 1.3 | 12.1 ± 0.2 | 6.61 ± 0.31 | 73 ± 3 | -- | -- | -- |
| | High | 11.7 ±7.0 | 12.7 ± 0.2 | 7.43 ± 0.73 | 87 ± 3 | -- | -- | -- |
| February 1998 | Low | 5.2 ± 3.5 | 11.6 ± 0.6 | 6.93 ± 0.31 | 86 ± 26 | -- | 14.9 ± 4.3 | 5.11 ± 4.43 |
| | High | 18.1 ± 6.1 | 13.5 ± 1.0 | 7.77 ± 0.23 | 89 ± 2 | -- | 26.7 ± 19.3 | 3.39 ± 1.52 |
| June 1998 | Low | 16.5 ± 11.3 | 22.4 ± 1.9 | 7.22 ± 0.75 | -- | 0.580 ± 0.420 | 28.5 ± 27.4 | 5.60 ± 9.00 |
| | High | 26.6 ± 10.7 | 21.4 ± 2.4 | 7.65 ± 0.53 | -- | 0.150 ± 0.260 | 34.1 ± 35.2 | 4.30 ± 2.00 |
| June 1999 | Low | 22.2 ± 5.0 | 22.7 ± 2.6 | 7.22 ± 0.47 | 88 ± 74 | 0.520 ± 0.240 | 27.9 ± 16.4 | 5.05 ± 7.40 |
| | High | 30.7 ± 0.9 | 22.4 ± 0.8 | 7.48 ± 0.03 | 94 ± 6 | 0.295 ± 0.090 | 21.4 ± 5.7 | 3.84 ± 1.51 |
| January 2000 | Low | 8.8 ± 5.3 | -- | 7.31 ± 0.25 | 92 ± 21 | 0.215 ± 0.039 | -- | -- |
| | High | 19.0 ± 7.8 | -- | 8.05 ± 0.26 | 82 ± 76 | 0.183 ± 0.066 | -- | -- |
| February 2000 | Low | 15.7 ± 10.6 | 13.5 ± 1.1 | 7.31 ± 0.22 | 82 ± 40 | 0.234 ± 0.073 | 33.81 ± 38.27 | 5.27 ± 1.21 |
| | High | 24.0 ± 6.4 | 13.7 ± 0.4 | 7.64 ± 0.32 | 76 ± 48 | 0.170 ± 0.061 | 35.99 ± 31.88 | 4.86 ± 3.28 |

Generally, in Largo do Laranjo, the lowest salinities are observed during the sampling campaigns performed on Autumn/Winter, due to the higher dilution effect felt in these seasons. Autumn and Winter are characterized by higher rainfalls and an higher quantity of fresh water discarded on Esteiro de Estarreja, which flows into Largo do Laranjo, explaining the obtained values.

In relation to the tide, during the sampling campaigns performed on high-tide, the salinity values determined are fairly high, showing that the sea penetration is significant over Largo do Laranjo and is felt during all the year.

In relation to temperature, Largo do Laranjo is an ecosystem that does not suffer high variations with respect to this parameter. In Spring and Summer, the temperature varies between 19 and 23ºC, and in Autumn and Winter, between 11 and 14ºC.

Taking into account the pH medians determined for each campaign, higher values are measured during the high tide than low tide. Besides, during all the sampling campaigns the highest pH values are observed in the zones with higher salinities. This behavior is expected, as the common pH value found in sea water is between 8.1 and 8.5, which corresponds to a narrow range of pH, controlled by bicarbonate and borate concentrations (Knezovich, 1994). Moreover, the estuarine waters have lower pH values than sea water due to the lowest base concentrations and highest levels of acidic humic material present in these waters (Knezovich, 1994).

Normally the concentrations of dissolved oxygen are high and both tide conditions give similar results. However, in some sampling campaigns, namely June 1999 and January 2000, in some locals a significant decrease on the dissolved oxygen is observed, being measured low values around 22 and 35%, respectively. This phenomenon has already been reported in a previous study performed in Esteiro de Estarreja (Pereira, 1996) (Figure 1) and is due to the sporadic discharge of domestic sewage and effluents proceeding from slaughterhouses, rich in organic matter.

As already mentioned, the absorbance determined at 330 nm permitted to estimate the dissolved organic carbon, as suggested by Moore (1987). In January 2000 twelve water samples were collected in Largo do Laranjo and the absorbance at 330 nm were determined, as well as the corresponding dissolved organic carbon concentrations, determined by the wet persulfate/ultraviolet oxidation method, namely “Method 415.3” of USEPA. A linear relationship was encountered ($y=11.3x$, $r=0.820$), meaning that both parameters are in fact correlated. After application of this equation, the DOC concentrations in all sampling campaigns performed in that ecosystem varied between 1.6 and 9.7 $mg.dm^{-3}$.

Generally, in Largo do Laranjo the absorbance at 330 nm values are higher in low tide (mean equal to 0.405 and standard coefficient of 52%) than in high tide (mean equal to 0.211 and standard coefficient of 31%), due to the smaller dilution effect of sea water, which has less organic matter. The high standard coefficient determined on low tide is consequence of the fact of the sampling campaigns performed in Winter (January 2000 and February 2000) had provided lower values of absorbance (mean equal to 0.266 and standard coefficient of 10%) than the ones realized during Summer (June 1998 and June 1999) (mean equal to 0.559 and standard coefficient of 30%). These results can be due to a simple dilution phenomenon, as Winter sampling campaigns are associated to higher rainfalls. However, after plotting the values of absorbance at 330 nm in relation to salinity, it was observed that the values of salinity determined in Winter were included in the ones relative to Summer (Figure 2). This means that the lower values obtained for the dissolved organic carbon in Autumn and Winter are due to the existence of less organic matter in those campaigns and not to an higher quantity of fresh water, proceeding from precipitation that would decrease the salinity values. In Summer the probability of existing an higher quantity of DOC is also larger due to the occurrence of phytoplankton blooms.

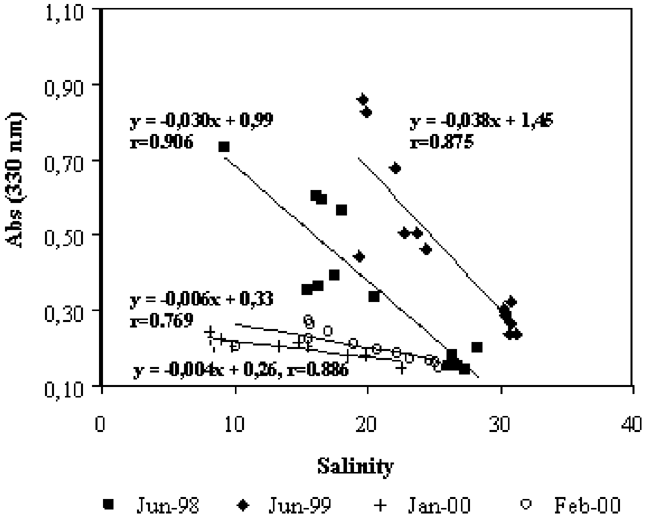

Figure 2. Linear relationships encountered between the absorbance at 330 nm and salinity.

In terms of SPM, this parameter varied along the different sampling campaigns in the way depicted in Figure 3.

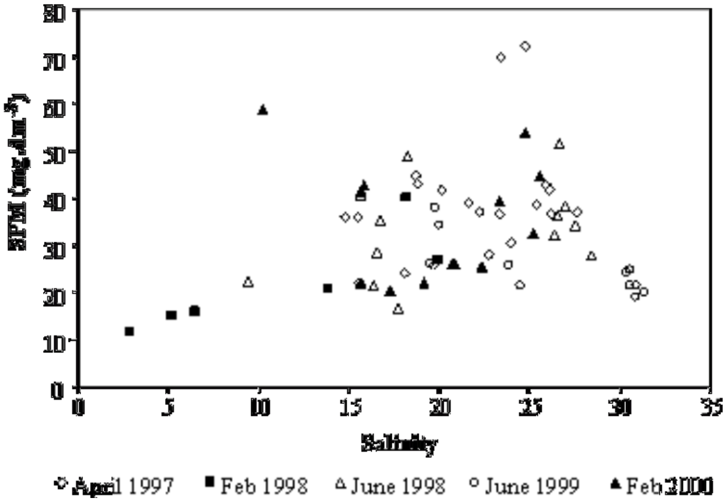

Figure 3. SPM (mg.dm$^{-3}$) determined in Largo do Laranjo during several sampling campaigns in function of salinity.

All campaigns showed a similar behavior, being not detected any significant difference between the Autumn/Winter and Spring/Summer sampling campaigns, unlike what is observed in Scheldt estuary where the suspended matter concentrations are generally higher in winter than in the summer months (Baeyens *et al.,* 1998). In Largo do Laranjo, the maximum of SPM varies according to the sampling campaign. For example, in April 1997 the maximum was observed on salinity equal to 23, and in February 1998, June 1998, June 1999 and February 2000 around salinities of 18, 27, 20 and 10, respectively. This increment in SPM can be due to the introduction of SPM proceeding from other areas of Ria de Aveiro, as for example from Antuã River, or due to surface sediments ressuspension induced by the tide. This area where the highest SPM concentrations are found can be classified as the maximum turbidity zone. In estuaries where the tide influence is significant, this zone can be formed by periodic ressuspension of local surface sediments, induced by strong tide current (Millward and Turner, 1995), whereas in estuaries where the tide influence is small, this zone occurs due to a density of gravitational circulation that maintains particles in suspension (Allen, 1980).

In Largo do Laranjo, both tide conditions gave equivalent results. In fact at low tide and high tide, the medians were 34.8 and 32.4 mg.dm$^{-3}$, respectively, with minimums of 11.5 and 16.5 mg.dm$^{-3}$ and maximums of 72.1 and 54.1 mg.dm$^{-3}$. It was not also observed a significant decrease on SPM concentrations with the salinity increase that would result from dilution caused by sea water less rich in SPM. However, the number of sampling points performed in the zone of the biggest salinity was small, do not permitting to see this behavior.

In terms of particulate organic carbon (POC), both tide conditions, as well as seasons (Spring/Summer and Autumn/Winter), gave similar results, being the highest values determined on low tide and in June 1998, June 1999 and February 1998. For the low tide and high tide, the medians were 5.1 and 3.8 %, with minimums of 1.2 and 0.5 % and maximums of 13.8 and 7.1 %, respectively. It was not found any direct relationship between SPM and POC, meaning that in the zone where SPM reaches the highest values, the larger SPM quantity results from surface sediments ressuspension and not to the entrance in Largo do Laranjo of particles enriched in organic matter. These results were corroborated by the fact that after determination of iron species extracted with hydroxylamine hydrochloride in some SPM, a significant negative linear relationship (r= -0.872) was encountered between this parameter and SPM, suggesting that in the maximum turbidity zone, the highest SPM values are not also due to the entrance of particles rich in iron, but may result from the ressuspension of the surface sediments, which are less rich in iron oxi/hydroxides than SPM (results not shown).

## III) Mercury Behavior in the Dissolved and Particulate Fractions of Largo do Laranjo Water Column

Once the chlor-alkali industry changed the production process to membrane cells and due to the implementation of an effluent treatment plant by the same industry, it was expected that mercury concentrations determined in Largo do Laranjo water column, during the studied period, decreased along the years. However, no significant reduction on the dissolved reactive mercury concentrations was observed during the period of 1997 to 2000, as represented in Figure 4.

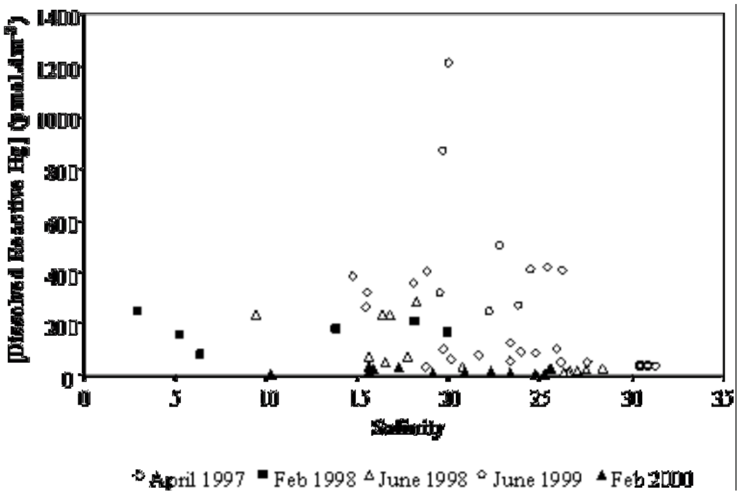

Figure 4. Dissolved reactive mercury concentrations (pmol.dm$^{-3}$) determined in Largo do Laranjo in function of salinity.

The highest concentrations of dissolved reactive mercury were determined in June 1999 campaign. The two samples for which elevated reactive mercury concentrations were determined, also presented very low concentrations of dissolved oxygen, namely 22 and 26%, and the highest absorbance at 330 nm, corresponding to waters with high organic matter content.

Generally, higher values of dissolved reactive mercury are determined during low tide than high tide, with medians equal to 195 and 37 pmol.dm$^{-3}$, minimums of 7.4 and 5.2 pmol.dm$^{-3}$, and maximums of 1211 and 422 pmol.dm$^{-3}$, respectively. This is probably due to a dilution process caused by the sea water, less rich in mercury, during high tide.

It was also stated that the lowest dissolved reactive mercury concentrations are not always determined in the sampling campaigns performed in Winter, as sometimes in Spring/Summer campaigns values of the same order of magnitude are obtained. However, due to higher water flows observed in winter, the probability of obtaining lower dissolved reactive mercury concentrations is higher.

Mercury is rapidly distributed along Largo do Laranjo because it is not detected a significant decrease on the dissolved reactive mercury concentrations with salinity. This is probably due to the faster transport of mercury associated to this fraction. This behavior suggest that the precipitation of dissolved humic substances, which would bring about the precipitation of metals associated to these compounds (Willey, 1984), must be insignificant in this zone of Ria de Aveiro. However, it must also be considered that in sea water the magnesium concentrations are higher than in fresh waters and the stability constants magnesium-organic complexes are significative. Magnesium may change with trace metals bound to organic ligands during estuarine mixing, being these metals released and subsequently precipitated (Willey, 1984). However, Andren and Harriss (1975) refer that mercury is not changed considerably with other cations when crossing the estuarine zone from low to high salinities, but if Fe(III) is present in sufficient quantity, it can change with mercury. Additionally, higher dissolved reactive mercury concentrations can be determined in the area of higher salinities due to the formation of chloride complexes. However, Cossa *et al.*

(1988) in St. Lawrence Estuary and Coquery *et al.* (1997) in Loire and Sena Estuaries, did not detect any increase in the dissolved reactive mercury concentrations when salinity increased, in a similar way as observed in Largo do Laranjo.

Comparing Largo do Laranjo dissolved reactive mercury concentrations with the values reported for other estuaries, it can be concluded that the values determined in this ecosystem are high (Table 2).

**Table 2. Dissolved reactive mercury concentrations (pmol.dm$^{-3}$) reported in other works.**

| **Reference** | **Sample Description** | **[Reactive Mercury] (pmol.dm$^{-3}$)** |
|---|---|---|
| Cossa *et al.*, 1988 | S. Lawrence Estuary | $2.9^{a}$ |
| Dalziel, 1992 | Scotian Shelf | $2.2^{a}$ |
| Leermakers *et al.*, 1995 | Scheldt Estuary<br>June 1993<br>February 1994 | <br>$<10^{a}$<br>$< 7.5^{a}$ |
| Bonzongo *et al.*, 1996 | Carson River – Lahontan Reservoir System | $2 – 61.2^{a}$ |
| Coquery *et al.*, 1997 | Loire Estuary<br>Sena Estuary | $0.40–1.1^{b}$<br>$0.40 – 2.1^{b}$ |
| Plaschke *et al.*, 1997 | Derwent Estuary | $< 25^{c}$ |
| Lacerda and Gonçalves, 2001 | Coastal lagoons of Rio de Janeiro | $0.18 – 0.43^{b}$ |
| Monperrus *et al.*, 2007 | Thau Lagoon | $3.24\pm0.12^{a}$<br>$4.09 \pm 0.17^{d}$ |
| This work | Largo do Laranjo<br>Low tide<br>High tide | <br>$7.4–1211^{a}$<br>$5.2 – 422^{a}$ |

a – Filtered and acidified samples;
b – Filtered but non acidified samples;
c – Unfiltered and non acidified samples;
d – Unfiltered but acidified samples.

In terms of dissolved total mercury concentrations, it was also not detected a significant decrease during the three years analyzed (June 1998, June 1999 and February 2000). The maximum concentrations were determined in June 1999, namely 2.86 and 2.97 nmol.dm$^{-3}$, corresponding to the points with also the greatest dissolved reactive mercury concentrations.

In the low tide, higher dissolved total mercury concentrations are determined than in the high tide, as the medians are equal to 389 and 194 pmol.dm$^{-3}$, minimums of 87.5 and 78.3 pmol.dm$^{-3}$, and maximums of $2.97\text{x}10^{3}$ and 444 pmol.dm$^{-3}$, respectively. This is due to an inferior dilution effect caused by sea water during low tide.

Mercury in Largo do Laranjo does not show conservative behavior, as can be observed in Figure 5. It must be referred that only the common values of dissolved total mercury concentrations encountered in Largo do Laranjo are represented, having been neglected the two samples with the highest total mercury values determined in June 1999.

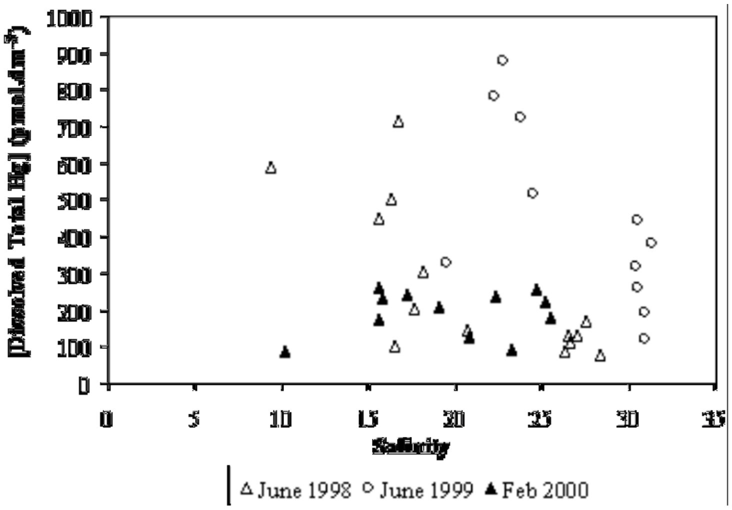

Figure 5. Dissolved total mercury concentrations (pmol.dm$^{-3}$) in function of salinity.

Conservative behavior results in a linear relationship between the two parameters due to a simple dilution phenomenon. In the majority of estuaries, the behavior of the dissolved constituents is non-conservative, occurring positive deviations when metal dissolves from particles, metals diffuse from pore waters, industrial discharges that are rich in metals occur, variation on metal concentrations in tributaries of the estuary are observed (Ferrara and Maserti, 1992) or metal mobilization from suspended particulate matter during fresh water/sea water mixing occurs (Jingsheng *et al.*, 1995). The negative deviations to linearity are due to adsorption, precipitation and/or flocculation of colloidal particles (Millward and Turner, 1995).

In Largo do Laranjo, mercury behavior seems to be a mixture of all of these phenomena, because it is not observed an evident positive or negative deviation in the dissolved total mercury concentrations in view of the salinity increase. This situation is similar to the one described by Coquery *et al.* (1997) in Loire and Sena estuaries, who suggested the existence of possible anthropogenic sources superimposed to temporal variations in mercury concentrations present in the rivers, related to fluctuations in water discharge. Guentzel *et al.* (1996) and Benoit *et al.* (1998) also detected a non-conservative behavior for total dissolved mercury in Ochlockonee and Patuxent Estuaries, respectively.

Largo do Laranjo presents high concentrations of total dissolved mercury after comparison with other estuaries (Table 3). Only the results reported for Carson River – Lahontan Reservoir System (Bonzongo *et al.*, 1996), Anacostia River (Mason and Sulivan, 1998), III River Basin (Probst *et al.*, 1999) and Nura River (Heaven *et al.*, 2000) are of the same order of magnitude of the determined in Largo do Laranjo. However, the samples were not always processed in the same way. In relation to Scheldt Estuary, a ten fold decrease was observed in ten years, being the values determined in 1991-1994 much lower than the ones obtained in 1981-1983 period and in Largo do Laranjo.

Largo do Laranjo total dissolved mercury concentrations do not exceed the European Union’s suggested maximum allowable concentration of 1 μg.dm$^{-3}$, corresponding to 5 nmol.dm$^{-3}$, for inland surface waters, or the WHO (1984) guideline value for the maximum acceptable concentration of mercury in drinking water, also set at 1 μg.dm$^{-3}$.

**Table 3. Dissolved total mercury concentrations (pmol.dm$^{-3}$) reported in other works.**

| Reference | Sample Description | [Total Mercury] (pmol.dm$^{-3}$) |
|---|---|---|
| Cossa *et al.*, 1988 | S. Lawrence Estuary | 8.5 – 11[a] |
| Leermakers *et al.*, 1995 | ScheldtEstuary<br>1981-1983<br>1991-1994 | <br>75–249[a]<br>5 – 15[a] |
| Bonzongo *et al.*, 1996 | Carson River –Lahontan Reservoir System | 11.3 – 281[b] |
| Guentzel *et al.*, 1996 | Ochlockonee Estuary<br>1993<br>1994 | <br>5.0–30[a]<br>5.0 – 25[a] |
| Stordal *et al.*, 1996 | Texas Estuaries | 0.32 – 8.18[a] |
| Coquery *et al.*, 1997 | Loire Estuary<br>Sena Estuary | 2.0–6.2[a]<br>1.8 – 21.2[a] |
| Baeyens *et al.*, 1998 | Scheldt Estuary | < 15 |
| Benoit *et al.*, 1998 | Patuxent River Estuary | < 2.5 – 30[a] |
| Mason and Sullivan, 1998 | Anacostia River<br><1.7m$^3$/s<br>1.7–14m$^3$/s<br>> 14 m$^3$/s | NE arm NW arm<br>43.5±2.7 22.2±13.8[a]<br>152±141 144±65[a]<br>197±73 154±70[a] |
| Roulet *et al.*, 1998 | Tapajós River Basin<br>Wet season<br>Dry season | <br><8.5[c]<br>< 9.5[c] |
| Mason *et al.*, 1999 | Chesapeake Bay | < 15, except in locals nearby urban sites |
| Probst *et al.*, 1999 | III River Basin (France)<br>February 1996<br>July 1996 | <br>LD–120[a]<br>>80 – 842[b] |
| Heaven *et al.*, 2000 | Nura River | 6.5 x10$^2$ – 12.4x10$^3$[c] |
| Lacerda and Gonçalves, 2001 | Coastal lagoons of Rio de Janeiro | 18.2 – 55.2[c] |
| Muresan *et al.*, 2007 | Thau lagoon<br>Summer<br>Winter | <br>2.9–5.5[a]<br>1.4 – 2.5[a] |
| This work | Largo do Laranjo<br>Low tide<br>High tide | <br>87.5 – 2.97x10$^3$[b]<br>78.3 – 444[b] |

a – Unfiltered but acidified samples;
b – Filtered and acidified samples;
c – Filtered but non acidified samples.

After calculation of the percentage of reactive mercury, as the ratio between the dissolved reactive mercury concentration and the dissolved total mercury content, it was stated that in low tide the values dispersion is higher, with a median equal to 32% and a minimum and maximum of 8 and 97%, respectively, than in high tide, with a median of 13% (minimum and maximum of 2 and 36%, respectively). In Krka river estuary (Croatia) the proportion of reactive to total mercury also changed, depending on salinity, seasonal and weather changes, not only in fresh water and at the freshwater/seawater interface but in some cases in seawater down to the bottom (Bilinski *et al.*, 2000). In Thau lagoon the percentage of reactive mercury also varied between 12 and 67%, with the highest level found in surface water in winter (Muresan *et al.*, 2007).

As the median values of the reactive mercury percentages are not high, these results point out the fact that in Largo do Laranjo the dissolved mercury is normally in a non-reactive state. This behavior is similar to the one reported by Cossa *et al.* (1988) in S. Lawrence Estuary, who determined a dissolved reactive mercury percentage around 30% in the low salinity zone. Besides, Coquery *et al.* (1997) also refer dissolved reactive mercury percentages less than 5 to 24% in Loire and Sena Estuaries. In coastal lagoons of Rio de Janeiro, the reactive mercury comprises less than 2% of the total dissolved mercury (Lacerda and Gonçalves, 2001).

In Largo do Laranjo, an increase in the dissolved reactive mercury percentage with salinity was not observed, suggesting that the chloro-complexes formation is not yet significant in this zone of Ria de Aveiro. This behavior is different to the reported to the lower Scheldt Estuary in Winter where chlorocomplexes of mercury dominate the speciation (Baeyens *et al.*, 1998). However, it is also suggested that the percentage of reactive mercury is also influenced by other dissolved mercury species (Baeyens *et al.*, 1998).

In relation to particulate mercury, total mercury and reactive mercury extracted with a solution of HCl 3 mol.dm$^{-3}$ were determined. This kind of solution permits to extract metals associated to carbonates, oxides and sulphides (Casas and Crecelius, 1994; Jingsheng *et al.*, 1995). However, in other studies performed in estuaries the concentration used is lower, meaning that the present results must be regarded carefully and are merely indicative. A significant linear relationship was encountered between both parameters (r=0.971), representing the mercury extracted with this solution a high fraction of the total mercury, around 71 to 79%.

After plotting the particulate total mercury concentrations determined in all sampling campaigns performed in Largo do Laranjo, as represented in Figure 6, it was not detected a significant decrease on the particulate total mercury concentrations along the studied time period.

However, these results show that as salinity increases, the total mercury concentrations decrease. This relationship can be due to several factors. On the one hand, passage from particulate total mercury to the dissolved fraction can be occurring, justifying the positive deviations observed on the non-conservative behavior detected and referred in the dissolved fraction of Largo do Laranjo. The decrease of particulate total mercury in relation to the salinity increase is gradual, because, in general, the dissolution and dessorption processes are slower than precipitation and sorption, implying that when a metal is discharged in the environment it cannot stay immediately associated to the dissolved fraction after its introduction in the system (Benson *et al.*, 1994). On the other hand the observed decrease on particulate total mercury concentrations can be due to the deposition of enriched particles during their circulation in Largo do Laranjo or to the dilution effect provoked by the entrance of particles less rich in mercury in the system. However, this hypothesis was not corroborated with the data obtained so far because none significant relationship was encountered between particulate total mercury and SPM. So, the lowest particulate total mercury concentrations are not always observed with the highest SPM values, situation that would point out to the entrance in the system of particles less rich in the metal.

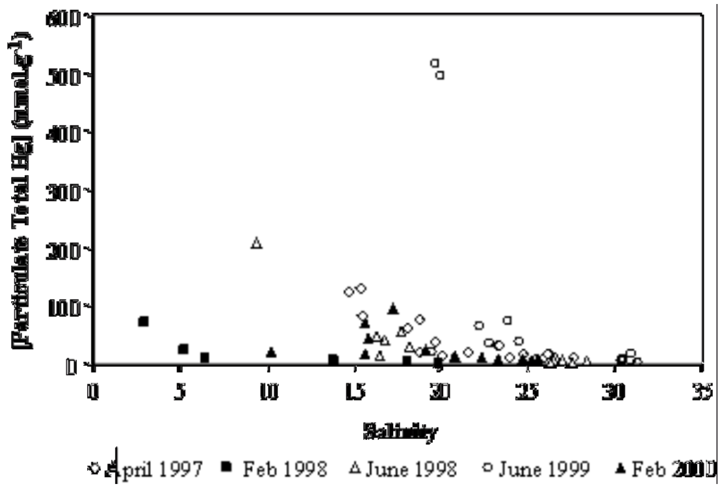

Figure 6. Particulate total mercury concentrations (nmol.g$^{-1}$) determined in Largo do Laranjo in function of salinity.

The highest values of particulate total mercury concentrations are determined in low tide, with a median equal to 37 nmol.g$^{-1}$, minimum of 8.1 nmol.g$^{-1}$ and maximum of 516 nmol.g$^{-1}$. At high tide the obtained values are 8.4, 1.3 and 63 nmol.g$^{-1}$, respectively. In Yalujiang Estuary, for example, a decrease in particulate total mercury concentrations was also detected in high tide (Jingsheng *et al.,* 1995), being this phenomenon explained by the existence of some desorption process during this tide condition or by the fact that periods with higher salinity imply an increase in the horizontal velocity of water, letting that fine material less rich in mercury stay in suspension.

The particulate total mercury concentrations determined in Largo do Laranjo are high in comparison to others places, as described in Table 4, with the exception of Elba River (Wilken and Hintelmann, 1991). However, the available data refer to 1989-1990 period, meaning that nowadays the actual concentrations can be different. In fact, in Scheldt Estuary a decrease in particulate total mercury concentrations of almost ten times was observed after ten years (Leermakers *et al.,* 1995).

In general, these results indicate a relevant mercury contamination of Largo do Laranjo in comparison to other places.

**Table 4. Particulate total mercury concentrations (nmol.g$^{-1}$) reported in other works.**

| Reference | Sample Description | [Total Mercury] (nmol.g$^{-1}$) |
|---|---|---|
| Wilken and Hintelmann, 1991 | Elba River<br>1989-1990 | 25 - 498 |
| Leermakers *et al.*, 1995 | ScheldtEstuary<br>1981-1983<br>1991-1994 | <br>50–10<br>7.5 – 1.0 |
| Coquery *et al.*, 1997 | LoireEstuary<br>Sena Estuary | 0.32–1.6<br>2.8 – 7.98 |
| Baeyens *et al.*, 1998 | ScheldtEstuary<br>June 1993 to August 1994 | 0.2 – 8.0 |
| Cai *et al.*, 1999 | Florida Everglades | 0.47 – 0.79 |
| Lacerda and Gonçalves, 2001 | Coastal lagoons of Rio de Janeiro | 3.5 - 14 |
| This work | Largo do Laranjo<br>Low tide<br>High tide | <br>7.5 – 234[a]<br>1.3 - 85 |

a – In some situations values around 500 nmol.g$^{-1}$ can be determined.

## IV) Inter-Parameter Relationships

As already stated in the previous section, in the dissolved fraction of Largo do Laranjo water column, mercury seems to be in a non reactive form, as the reactive mercury percentages determined are low. One possible responsible for these low values is the organic matter. The relationships encountered between the reactive and total mercury with the dissolved organic matter, estimated by the absorbance at 330 nm, are represented in Figure 7.

Both reactive and total mercury shows a linear relationship with organic matter. However, reactive mercury loses this linear behavior for absorbances at 330 nm higher than 0.40, represented by the circular area, corresponding to waters with high organic matter content. The obtained results indicate that total mercury present in Largo do Laranjo water column is associated to the dissolved organic matter present and one part of the Hg-organic matter complexes are labile. These results are similar to the ones reported for S. Lawrence Estuary where 50 to 85% of the dissolved mercury is associated to organic matter (Cossa *et al.*, 1988).

In terms of particulate total mercury none relationship was encountered between this parameter and POC, as well as with iron species extracted with hydroxylamine hydrochloride. This solution allows the extraction of iron oxides and hydroxides (as for example, FeOOH), that may exist in the particulate and colloidal forms in oxic water-sediment systems (Meyer *et al.*, 1994). These species can adsorb trace metals that are in a reactive form. These results suggest that POC and iron species are not responsible for mercury behavior in Largo do Laranjo, indicating that the particulate total mercury concentration only depends on the mercury quantity discharged by the industrial effluent.

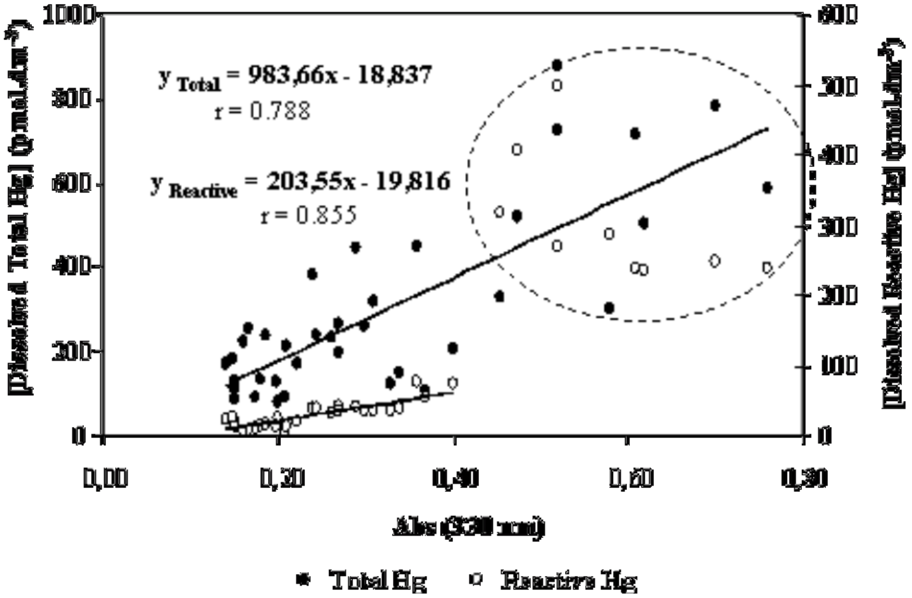

Figure 7. Dissolved total mercury and reactive mercury concentrations (pmol.dm$^{-3}$) determined in Largo do Laranjo water column in function of organic matter content, estimated by the absorbance at 330 nm.

Another important aspect is that the smallest suspended particles, retained by filters with 0.1 μm of porosity, present in the water column of Largo do Laranjo may have a mercury enrichment of 13 to 35% in relation to the largest. In fact, in April 1997 sampling campaign, water column of Largo do Laranjo was filtered through 0.1 and 0.45 μm filters, being analyzed in terms of particulate total mercury. A linear relationship (y= 1.24x ; r=0.97) was encountered between both parameters with a confidence interval for the slope equal to 1.13 to 1.35. These enriched small particles constitute the colloidal mercury. After comparison with other locals, the importance of colloidal particles in Largo do Laranjo is small. In Texas Estuaries, for example, the colloidal mercury represents 12 to 93% of the mercury that passes through the filters with porosity of 0.45 μm (Stordal *et al.*, 1996) and in Ochlockonee Estuary the colloidal mercury represents 35 to 87% (Guentzel *et al.*, 1996).

## V) Mercury Partition in Largo do Laranjo Water Column

The solid-solution interactions have been quantified by the distribution coefficient ($K_d$), defined by the ratio of the particulate metal (w/w) and dissolved metal (w/v) concentrations. This parameter is important in order to elucidate the role of removal mechanisms and to identify the predominant factor that determines the partitioning between phases, as well as, in understanding the residence time of certain elements (Turner *et al.*, 1992; Turner and Millward, 1994; Pereira, 1996). It also has particular interest in the geochemical modulation and in the evaluation of environmental pollution. A high value of $K_d$ means a significant metal affinity by the particulate fraction (Coquery *et al.*, 1997). However, $K_d$ presents some limitations, linked to the determination method of metal concentrations in the particulate and dissolved fractions and to the assumption of the existence of equilibrium and sorption phenomena totally reversible, that might not be the real case.

The total mercury associated to the particulate fraction in function of suspended particulate matter concentration (expressed in log), for the several sampling campaigns performed in Largo do Laranjo, in both tide conditions, are represented in Figure 8. The isolines for equal values of log $K_d$ are also represented. The mercury percentage associated to the particulate fraction was determined by the following equation:

$$\%\ Hg\ associated\ \ to\ particles = \frac{[Total\ \ Hg\ ]_{particulat\ \ e}(\mu g.g^{-1}) \times 100}{[Total\ \ Hg\ ]_{particulat\ \ e}(\mu g.g^{-1}) + \dfrac{[Total\ \ Hg\ ]_{dissolved}\ (ng\ .dm^{-3})}{Suspended\ \ \ Particulat\ \ e\ Matter\ \ (mg\ .dm^{-3})}}$$

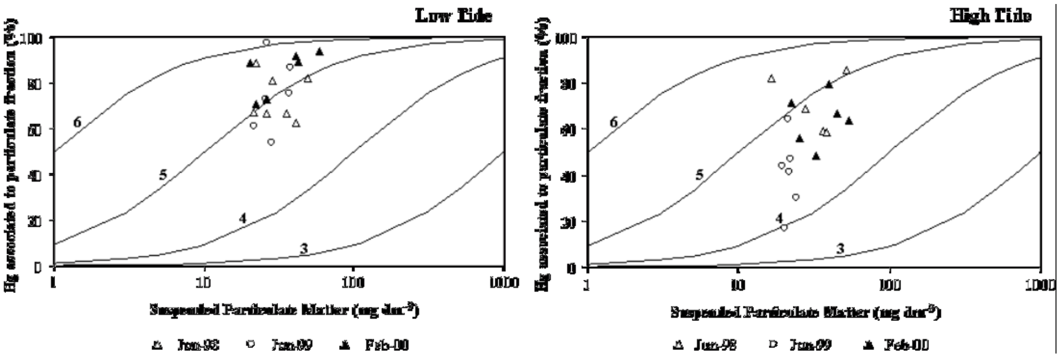

Figure 8. Mercury associated to suspended particles (%) in function of the suspended particulate matter (mg.dm$^{-3}$) in low and high tides in Largo do Laranjo. Note: The total mercury concentrations determined for the dissolved and particulate fractions were used in the calculations.

In Largo do Laranjo, it was not detected any difference between the sampling campaigns performed in Summer (June) and Winter (February). In relation to tide conditions, at low tide the $K_d$ values varied between $4.1\times10^4$ to $1.5\times10^6$ dm$^3$.kg$^{-1}$, or in terms of log $K_d$ between 4.6 and 6.2. $K_d$ values of this order of magnitude indicates that the total mercury transport is done 54 to 98% by the suspended particulate matter (mean equal to 77%, with variation coefficient of 16%). At high tide, the $K_d$ values varied between $1.0\times10^4$ to $2.8\times10^5$ dm$^3$.kg$^{-1}$, or in terms of log $K_d$ between 4.0 and 5.4, pointing out that total mercury transport is done 17 to 86% by the suspended particulate fraction (mean equal to 58%, with variation coefficient of 32%). Largo do Laranjo $K_d$ values are similar to the reported for other places, namely, Patuxent River Estuary of $6\times10^4$ to $5\times10^5$ dm$^3$.kg$^{-1}$ (Benoit *et al.*, 1998), Scheldt Estuary of $4\times10^5$ to $7\times10^5$ dm$^3$.kg$^{-1}$ (Baeyens *et al.*, 1998) and coastal lagoons of Rio de Janeiro of $6\times10^4$ to $5.5\times10^5$ dm$^3$.kg$^{-1}$ (Lacerda and Gonçalves, 2001), as well as in terms of log $K_d$ that are equal to 4.6 to 5.2 in Galveston Bay (Stordal *et al.*, 1996), 5.5±0.3 in Loire Estuary and 5.9±0.3 in Sena Estuary (Coquery *et al.*, 1997), 3.2 to 5.9 in Anacostia River (Mason and Sullivan, 1998) and 4.80 to 5.11 in Florida Everglades (Cai *et al.*, 1999).

In relation to the obtained percentages of mercury transported by the particulate fraction on both tide conditions, namely equal to 77% in low tide and 58% in high tide, and after comparison with other places, these values can be considered low. In Loire and Sena Estuaries, 87 and 95% of the transported mercury is associated to suspended particles, respectively (Stordal *et al.*, 1996), being these results of the same order of magnitude to the ones reported by Coquery *et al.* (1997) which determined that the particulate fractions represent more than 95% of the total mercury for those estuaries, in Carson River – Lahontan

Reservoir System 94 to 99% of the total mercury is associated to the particulate fraction (Bonzongo *et al.*, 1996) and in Scheldt Estuary the value is around 90% (Leermakers *et al.*, 1995; Baeyens *et al.*, 1998). In Tapajós River Basin and Baltimore Harbor, the obtained percentages are a little lower, equal to 40 to 80% (Roulet *et al.*, 1998) and 35 to 75% (Mason *et al.*, 1999), respectively. On contrary, in Florida Everglades, Nura River and Thau lagoon, much lower percentages were determined. In fact only 14.3 to 23.5% (Cai *et al.*, 1999), 6 to 37% (Heaven *et al.*, 2000) and 42 to 66% (Muresan *et al.*, 2007) of the total mercury is linked to the particulate fraction, respectively.

Largo do Laranjo $K_d$ values also suggest that in both tide conditions, mercury is a little more associated to the particulate fraction than to the dissolved. However, in this ecosystem, none significant relationship was encountered between the log $K_d$ and POC (r=0.223), meaning that the organic matter content present in the particles is not the only factor responsible for mercury distribution between dissolved and particulate fractions. Nevertheless, there are some situations that the dissolved fraction plays an important role, mainly in high tide. In fact it is in this tide condition that the lowest percentages of mercury associated to the particulate phase are determined, suggesting the occurrence of dissolution and dessorption processes along Largo do Laranjo.

## VI) Mercury Transport Evaluation in the Dissolved and Particulate Fractions of the Water Column from Largo do Laranjo to the Rest of the Lagoon

In order to evaluate the mercury quantity that Largo do Laranjo exports to the rest of the estuarine system, mercury fluxes from Largo do Laranjo to the rest of Ria de Aveiro were determined. This kind of results permits to infer if there is accumulation or dispersion of the metal in Ria de Aveiro, and to evaluate the need to implement preventive measures that avoid the contamination of other areas located far away from the source contamination (Pereira, 1996).

The local chosen to perform these measures was located 6000 m from the industrial effluent discharge point in Chegado Channel, nearby “Cais do Chegado” (see Figure 1). Water samples were collected hourly along a tide cycle (12 hours). In these samples, suspended particulate matter, particulate total mercury and dissolved reactive mercury concentrations were determined. This sampling campaign was performed in April 1999 because previously another similar sampling campaign was realized in April 1994 (Pereira, 1996), allowing results comparison. However, in this last campaign none dissolved mercury concentrations were determined due to the inexistence of a sensitive analytic technique in that moment.

As referred by Pereira (1996), this season permits the evaluation of metal transport in an almost stationary situation, that is after flooding periods associated to Winter and before Summer, that also corresponds to another extreme situation.

The depth profile determined by Pereira (1996) for Cais do Chegado was used in this study.

### a). Tide Intensity, Salinity and Suspended Particulate Matter Concentrations Evaluation in a Tide Cycle

The water velocity determined in Cais do Chegado in April 1999 is represented in Figure 9. The water velocity varied between 0.02 to 0.84 $m.s^{-1}$, obtaining the highest values in low tide. Both tide conditions originate approximately sinusoidal curves.

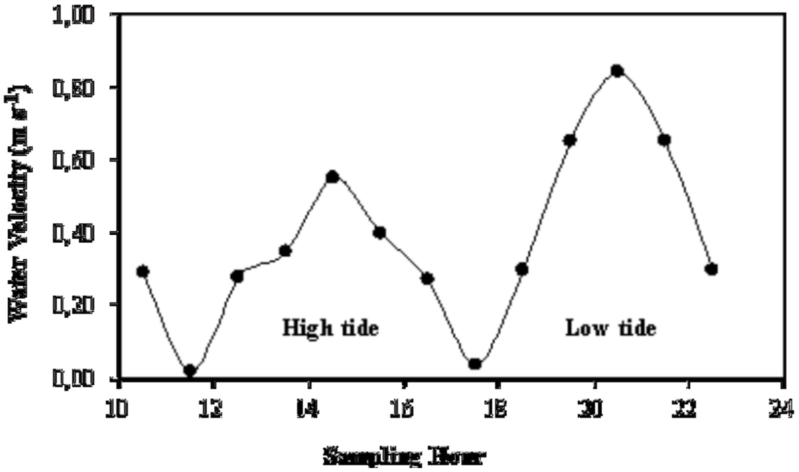

Figure 9. Water velocity ($m.s^{-1}$) determined in Cais do Chegado in April 1999 in function of sampling hour.

During the tide cycle, the salinity values were always high (superior to 19) due to sea proximity (Figure 10). The maximum (28.6) occurred in the situation of the highest water column height and the minimum (19.4) in the situation of the lowest water column height.

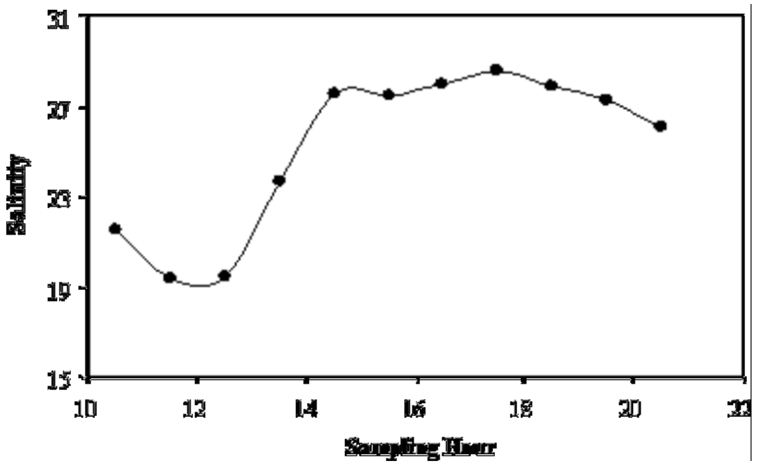

Figure 10. Water salinity values determined in Cais do Chegado in April 1999 in function of the sampling hour.

After comparison of the suspended particulate matter and water velocity curves (Figure 11), it can be observed the important role of the tide in the behavior of particles in suspension and probably over the metals transport associated to the particulate fraction. As represented in Figure 11 the suspended particulate matter concentrations increase with water velocity. This originates ressuspension of the deposited particles and contributes to the observed increment on suspended particulate matter load.

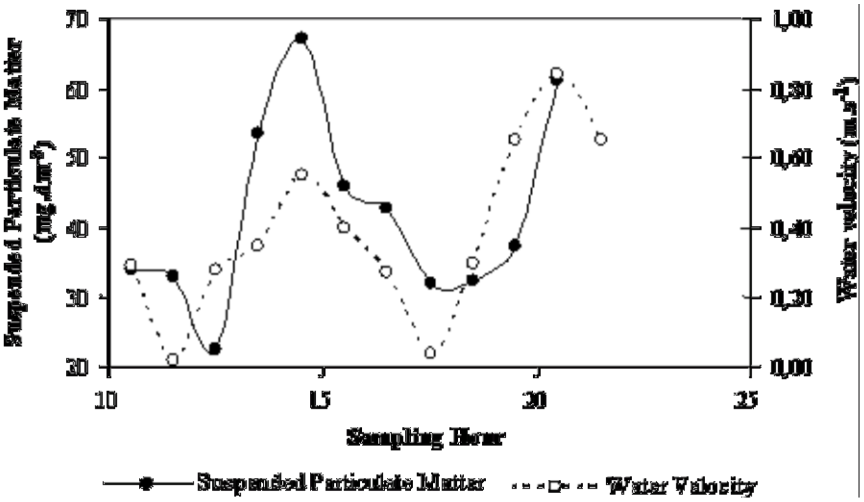

Figure 11. Suspended particulate matter (mg.dm$^{-3}$) and water velocity (m.s$^{-1}$) determined in Cais do Chegado in April 1999 in function of sampling hour.

These results point out that coastal lagoons are unstable environments probably due to their relative shallowness. As observed in Largo do Laranjo, a major result of this is a rapid variation on water column conditions. In some particular situations the effect of physical forces, such as winds, tides, storm events and relative sea level changes can even provoke higher modifications (Lacerda and Gonçalves, 2001).

### b). Particulate Total Mercury and Dissolved Reactive Mercury during a Tide Cycle

The particulate total mercury varied as represented in Figure 12, allowing the statement of the occurrence of temporal variations during a tide cycle. The highest value of mercury concentration (35 nmol.g$^{-1}$) was determined for one of the lowest suspended particulate matter concentration. Furthermore, low particulate total mercury contents were associated to high suspended particulate matter concentrations. However, the correlation encountered between both parameters was not significant (r=-0.251). Similar situation was observed in April 1994 (Pereira, 1996), meaning that in spite of the important influence of the induced water movement by the tide over particles ressuspension, the particulate total mercury concentration is not directly influenced by this phenomenon.

The particulate total mercury varied between 2.7 and 35 nmol.g$^{-1}$, values that are superior to the determined in April 1994, which varied between 1.6 and 8.5 (nmol.g$^{-1}$) (Pereira *et al.*, 1998b), showing again that during this period, a none significant decrease on total mercury concentrations was verified.

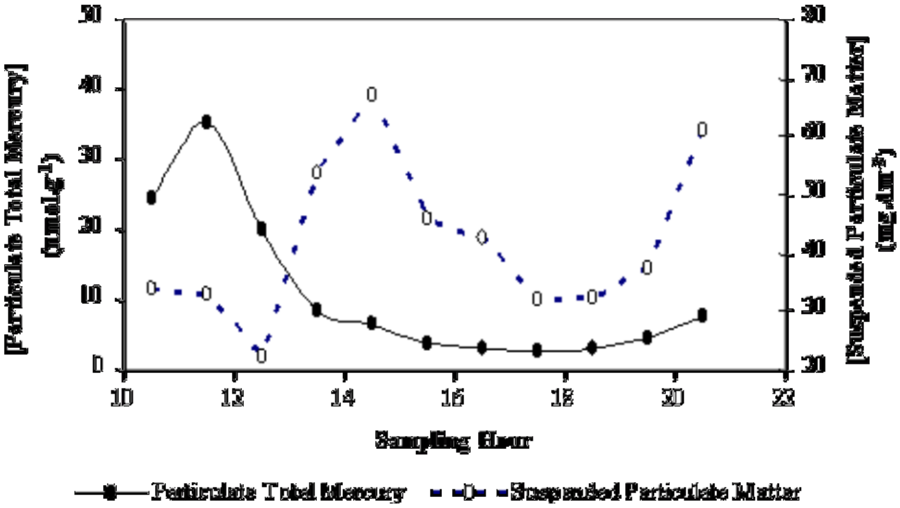

Figure 12. Particulate total mercury (nmol.g$^{-1}$) and suspended particulate matter (mg.dm$^{-3}$) concentrations in Cais do Chegado in April 1999 in function of sampling hour.

As already mentioned, on contrary to April 1994, in April 1999 it was possible to determine the dissolved reactive mercury concentrations (Figure 13). As the particulate total mercury, the dissolved reactive mercury varied along time and between 21 and 221 pmol.dm$^{-3}$. It can also be stated that, for the two first points correspond water samples with high levels of reactive mercury in the dissolved fraction and of total mercury in the particulate fraction. These samples were collected in low tide, as can be observed in Figure 9.

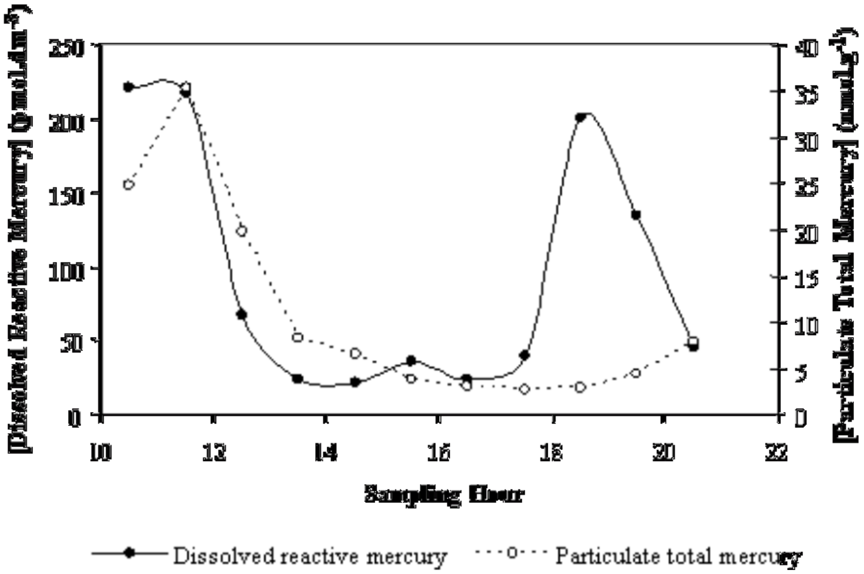

Figure 13. Dissolved reactive mercury (pmol.dm$^{-3}$) and particulate total mercury (nmol.g$^{-1}$) concentrations determined in Cais do Chegado in April 1999 in function of sampling hour.

Afterwards, according to salinity increase due to high-tide (Figure 9), both mercury concentrations decrease. The dissolved reactive mercury concentrations decrease possibly due to the dilution effect caused by sea water less rich in mercury, while the particulate total mercury concentrations decrease due to ressuspension of surface sediments, less enriched on mercury. This contributes to the observed increase in suspended particulate matter concentration (Figure 11), originating a dilution and further decrease on total mercury concentrations associated to the particulate fraction.

High dissolved reactive mercury concentrations were again determined between 18:30 and 19:30 hours (200 and 134 pmol.dm$^{-3}$, respectively), in low tide. Previously, around 10:30 and 11:30 hours, the highest concentration of dissolved reactive mercury was observed, in the same order of magnitude (221 pmol.dm$^{-3}$) and tide condition.

These results point out to the fact that the highest dissolved reactive mercury concentrations are always determined in low-tide caused by the smaller sea water dilution effect. The particulate total mercury has a different behavior. Not always in low tide, high particulate total mercury concentrations are observed because the water velocity can be high enough to originate ressuspension of deposited particles, less rich in this metal, contributing to a decrease in mercury concentration in the particulate fraction.

### c). Particulate and Dissolved Mercury Fluxes Evaluation in Largo do Laranjo

Before proceeding to the evaluation of the particulate and dissolved mercury fluxes in Largo do Laranjo, the water and suspended particulate matter amounts that enter and go out from this area were estimated. The determined value of the water quantity that goes out from Largo do Laranjo per day through Cais do Chegado was equal to $6.4\times10^5$ m$^3$.day$^{-1}$, corresponding to an average flow of 7.4 m$^3$.s$^{-1}$. The value of $6.4\times10^5$ m$^3$.day$^{-1}$ was determined through the balance performed between the water quantity that leaves Largo do Laranjo during the low tide and that enters during the high tide.

The suspended particulate matter amount was estimated by the following equation:

$$Suspended\ Particulate\ Matter\ (g.h^{-1}) = \sum_{t=0}^{t=n} 3600 \times \frac{v_t S_t SPM_t + v_{t+1} S_{t+1} SPM_{t+1}}{2}$$

with $t$ equal to the determination time, varying between 0 and 12 hours, $v_t$ to water velocity (m.s$^{-1}$), $S_t$ to the transversal area (m$^2$), $SPM$ to suspended matter concentration (g.m$^{-3}$) and 3600 to the conversion factor of seconds to hours.

The exported suspended particulate matter from Largo do Laranjo was equal to 1 tonne *per* tide cycle or to 730 tonnes *per* year. This high value determined for the suspended particulate matter that goes out Largo do Laranjo to the rest of the lagoon through Chegado Channel, explains the observed silting in this zone and the necessity of performing dredging actions with some frequency in that area.

The particulate total mercury fluxes ($Q_{particulate}$) that circulates through Cais do Chegado was determined by the following equation:

$$Q_{particulate}(nmol.h^{-1}) = \sum_{t=0}^{t=n} 3600 \times \frac{v_t S_t SPM_t [Hg]_t + v_{t+1} S_{t+1} SPM_{t+1} [Hg]_{t+1}}{2}$$

where [Hg] corresponds to the particulate total mercury concentration (nmol.g$^{-1}$).

The dissolved reactive mercury fluxes ($Q_{dissolved}$) were determined by the following equation:

$$Q_{dissolved}(pmol.h^{-1}) = \sum_{t=0}^{t=n} 3600 \times \frac{v_t S_t [Hg_D]_t + v_{t+1} S_{t+1} [Hg_D]_{t+1}}{2}$$

where [Hg$_D$] corresponds to the dissolved reactive mercury concentration (pmol.m$^{-3}$).

In terms of particulate mercury, the annual quantity transported in sea direction was equal to 299 mol or 60 kg. In terms of dissolved mercury, the corresponding annual quantity was 189 mol or around 38 kg. These values show that 61% of the transferred mercury to the rest of Ria de Aveiro, through Cais do Chegado, occurs through the particulate fraction and 39% by the dissolved fraction. The obtained results indicate that both, particulate and dissolved phases, play an important role in mercury transport to zones of Ria de Aveiro far away from the contaminated area. Largo do Laranjo appears such as a continuous source of mercury to the rest of the lagoon, as described in Figure 14.

The estimated mercury quantity transported by the particulate fraction determined in the present work (60 kg) is similar to the one determined in April 1994, which was equal to 70 kg *per* year (Pereira, 1996), suggesting that over two years, none significant alterations occurred.

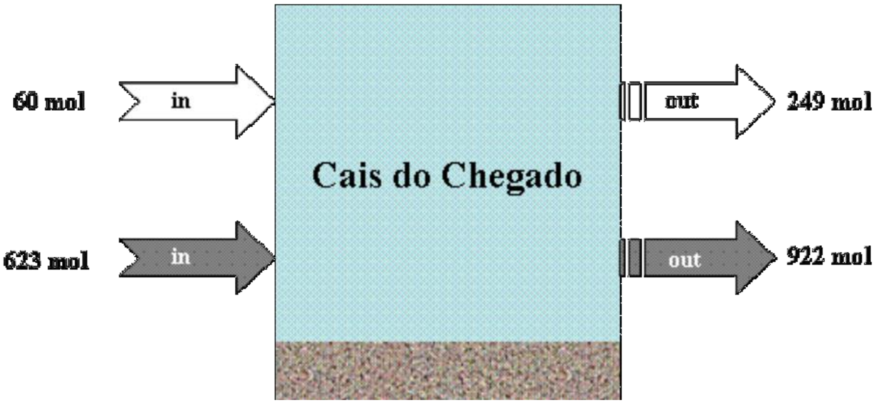

Figure 14. Mean annual quantities of mercury (mol) transported in the dissolved (white arrows) and particulate (grey arrows) fractions of Largo do Laranjo water column from this area to the rest of the lagoon.

## Conclusion

Mercury is a metal that has been known as a toxic substance for centuries. As previously discussed, mercury has interesting properties, such as low electrical resistivity, high surface tension and high thermal conductivity, that are the basis for choosing mercury for several industrial applications. However, nowadays due to health and environmental concerns and to implementation of more strict legislation, there has been several constraints to its use, which has diminished considerably.

As referred in other published works, mercury has a high affinity to ligands that contain sulphur, nitrogen, phosphorous or carbon, being these bonds are partly responsible for the mercury participation in some reactions that occur, for example in the environment, and specifically in the water column. In general, mercury that is introduced into natural waters is rapidly and efficiently scavenged by the fine-grained suspended particles. However, mercury partition between the dissolved and particulate phases is highly variable and dynamic, changing along the estuary due to several factors and conditions.

In this chapter a case study performed in Ria de Aveiro is also presented. Ria de Aveiro is a coastal lagoon, which has been subjected to mercury pollution due to the discharge of an effluent rich in this metal from a chlor-alkaly plant located nearby. Nevertheless, in the last seventeen years, the industry changed its technology and the discharge of anthropogenic mercury diminished considerably. However, the dissolved total and reactive mercury concentrations, as well as the total mercury contents determined in the suspended particulate matter, obtained in a particular area of Ria de Aveiro, namely Largo do Laranjo, during the years of 1997 to 2000, are still high in comparison to other locals located world wide. In the Largo do Laranjo water column, the highest dissolved total and reactive mercury concentrations are found in low tide, being the reactive mercury a relatively low fraction of the total in both tide conditions: 32% at low tide and 13% at high tide, respectively. Mercury shows a non-conservative behavior, as no linear relationship between the dissolved total mercury concentrations and salinity is found. Mercury behavior in Largo do Laranjo dissolved phase is variable. Sometimes positive deviations are observed, probably due to metal dissolution from particles and metal diffusion from pore waters, beyond other processes, as well as, negative deviations originated from adsorption, precipitation and/or flocculation of colloidal particles. Organic matter plays a very important role in mercury dissolved behavior, as significant correlations between dissolved total and reactive mercury with this parameter are found (r= 0.788 and 0.855, respectively). In relation to particulate fraction and in a similar way as the dissolved phase, the particulate fraction shows higher total mercury concentrations at low tide than at high tide. No significant relationships were encountered between this parameter, POC and iron species extracted with hydroxylamine hydrochloride, indicating that the particulate total mercury concentration only depends on the mercury quantity discharged by the industrial effluent.

The distribution coefficients, based on total mercury concentrations in the particulate and dissolved fractions, varied between $4.1\times10^4$ and $1.5\times10^6$ $dm^3.kg^{-1}$ at low tide, and between $1.0\times10^4$ and $2.8\times10^5$ $dm^3.kg^{-1}$ at high tide. These values show that almost 77% and 58% of the mercury present in Largo do Laranjo water column is transported by the particulate fraction at low tide and high tide, respectively, demonstrating that mercury is more closely associated with suspended particulate matter than with the dissolved fraction. However, in some situations, particularly in high tide, the role of this fraction can be important.

The case study performed in Ria de Aveiro also allows us to verify that the tide can play a relevant role in the dynamics of particles in suspension. The estimated annual mean quantity of mercury that is transported in the dissolved and particulate fractions from the sampling local to seaward is of 38 and 60 kg, respectively. These values indicate that 61% of the mercury that is transported from Largo do Laranjo to the rest of the lagoon occurs through the particulate fraction and 39% through the dissolved fraction, indicating that both are important to mercury transport and dispersion from Largo do Laranjo to more remote areas, less contaminated in mercury. Owing to this, Largo do Laranjo continues to be a possible mercury source to other areas of Ria de Aveiro.

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