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Tree Rings, *Populus nigra* L., as Mercury Data Logger in Aquatic Environments: Case Study of an Historically Contaminated Environment

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Abstract In this study, a tree (*Populus nigra* L.) has been presented as data logger of mercury release in aquatic environments using tree rings chemistry to provide chronological historical monitoring of mercury discharge from a chlor-alkali industrial effluent to a coastal lagoon. Tree rings (*Populus nigra* L.) as mercury data logger is suggested by mercury accumulation trends in the tree rings reflecting the industrial plant capacity increments in the early stages of mercury discharges and enhancing industrial plant controls to minimize mercury discharges in the last two decades after imposed global regulations on mercury emissions.

Keywords Aquatic environment · Data-logger · Dendrochemistry · Mercury · Tree rings

Widespread environmental and health problems have been related to mercury (Hg) (Pacyna et al. 2001; Bindler 2003; Horvat et al. 2003; Braune et al. 2005; OJEU 2005, 2006) since the outbreak of the methylmercury poisoning—Minamata disease (Kudo et al. 1998; Ekino et al. 2007). Anthropogenic emissions have contributed with two thirds of present global Hg cycle, elevating the global concentration four to five times the background levels (Wihlborg and Danielson 2006). Environmental transport and distribution of Hg on a global scale involves the atmospheric circulation of elemental Hg vapour. On a local scale, apart from atmospheric deposition, it depends mainly on both natural and anthropogenic sources of Hg and subsequent methylation of inorganic Hg (Boening 2000).

Data on historical trends of atmospheric Hg deposition, especially on the natural conditions preceding the pollution advent, represent an important gap in the understanding of large-scale Hg pollution and Hg global cycle (Bindler 2003). Paleo-studies involving natural archives such as peat bogs, glacial ice and surface sediments have been used to fulfil this critical gap (Bindler 2003).

In this study, tree rings were used to obtain a retrospective environmental record of mercury discharges into a historically chlor-alkali mercury contaminated estuarine lagoon (Ria de Aveiro Portugal). Tree cores were taken from *Populus nigra*, located along the channel that receives the anthropogenic mercury from the industrial effluent. *P. nigra* is a specie of soft wood that prefers moist, sandy, rich soils. *Populus nigra* roots are highly invasive towards waters sources, thus they are commonly found along the borders of streams, ponds, and lakes. The most significant pathway is through the root system (Berger et al. 2004) and it is assumed that when annual rings lose function it retains and isolates a chronological record of current sap chemistry (Momoshima and Bondietti 1990). The basic assumption in tree rings chemistry (dendrochemistry) is the stability of the element distribution associated with no significant mobility after storage (Nabais et al. 1999).

Tree rings have already been used as bio-geochemical tracers to map the extent of environmental pollution due to

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anthropoge nic emissions by the different countries (Tommasini et al. 2000) and several studies have used dendrochemistry to address environmental pollution from no point sources (Satake et al. 1996; Watmough 1997; Orlandi et al. 2002; Bindler et al. 2004; Witte et al. 2004; Becnel et al. 2004). However, only a few studies have directly related trace metal levels in wood to changes in metal emissions from suspected pollution sources (Watmough 1997) and comparison with data from other natural archives such as surface sediments have not been made yet to our knowledge.

Ria de Aveiro (Portugal) is an estuarine lagoon that has been receiving anthropogenic mercury from a chlor-alkali plant for the last 50 years (Pereira et al. 1998a, b) (Fig. 1). The chlor-alkali plant, the main anthropogenic mercury contamination source in Ria de Aveiro, started its activity in the early decade of 1950 (A—Fig. 2a) presenting different stages and phases of production increments (Fig. 2a) (Pereira 1997; OSPAR 2005) and being responsible for the main Portuguese chlor and caustic production (OSPAR 2005). Mercury discharges have been tracked in sediment cores (Pereira 1997; Pereira et al. 1998a; Ramalhosa et al. 2006) presenting a peak around 1985 and decreasing until today in the surface sediments (Fig. 2c). Aquatic organisms also present an indication of mercury environmental contamination decrease in the last two decades (Lucas et al. 1986; Abreu et al. 2000).

Materials and Methods

Three trees (*Populus nigra* L.) located along the margins of the channel (Esteiro de Estarreja) that receives the industrial effluent have been selected to sample the tree cores (Fig. 1). Cores were taken at breast height ($\sim$1.5 m) from each tree using a stainless steel borer (5 mm in diameter and 300 mm in length). One of the trees (tA) has about 90 cm in diameter at breast height and it is located in the left margin directly in front (<5 m) of the industrial effluent discharge point (Fig. 1). The second tree (tB) has about 70 cm in diameter at breast height and is located in the right margin 100 m upstream of the industrial effluent discharge point. The third tree (tC) has about 50 cm in diameter at breast height and it is located in the right margin 1.6 km downstream the discharge point.

Cores were sectioned into 1 cm segments corresponding to $\sim$2-years intervals, a shorter period compared to other studies presenting 5-years intervals (Berish and Ragsdale 1985). Mercury was quantified in every segment using atomic absorption spectrometry after integrated pyrolysis of samples (without pre-treatment). Compared to traditional methods of analysis, such as atomic absorption or atomic fluorescence where a time consuming sample pre-digestion process would lead towards a mercury dilution in the digested sample solution, this methodology quantifies mercury directly from the combusted sample, requiring small amounts of sample, thus allowing the direct quantification of mercury in shorter core segments, meaning mercury quantification in shorter time periods.

Replicate blanks and the reference material NIST-SRM 1575a 39.7 ± 0.9 ng g^{-1} Hg, on a dry basis) were analysed for quality control purposes. Precision of the measurements, determined on replicate digestions of SRM ranged between 2.2% and 5.6%. Results, expressed on a dry weight basis, were reported considering corresponding

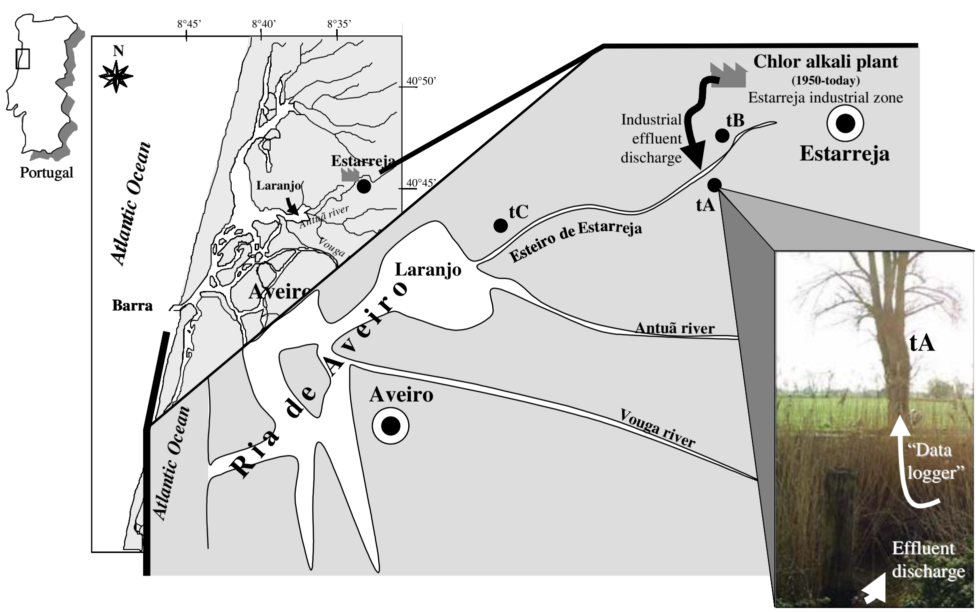

Fig. 1 Study site and trees (tA, tB, and tC) location

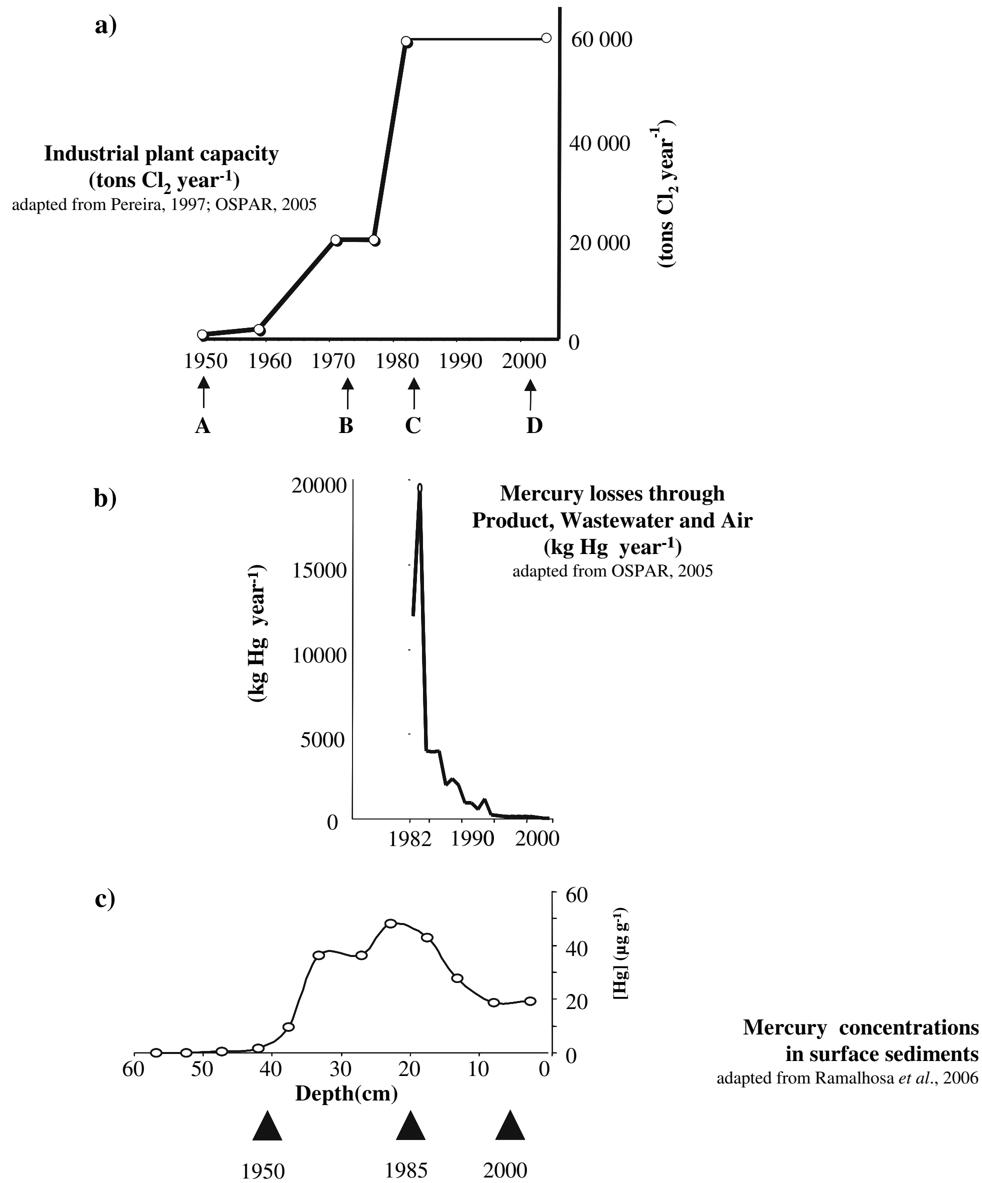

Fig. 2 (**a**) Industrial plant production (tons Cl_2 year^{-1}), date of unit implant (A) and moments (B and C) of changes introduced into the industrial plant system to minimize mercury discharges, and (D) last changes to membrane cells technology (January 2002) adapted from Pereira (1997), European Commission (2001), and OSPAR (2005). (**b**) Mercury losses through product, wastewater and air by the chlor-alkali industry in Portugal, after the imposed regulations on mercury emissions (adapted from OSPAR 2005). (**c**) Pattern of mercury discharges obtained from mercury concentrations in surface sediments (adapted from Ramalhosa et al. 2006)

precision percentage obtained in reference material analysed at same time.

Results and Discussion

Mercury concentrations in the annular tree rings obtained in the three trees (tA, tB and tC) show different mercury accumulation levels but similar trends (Fig. 3). Mercury accumulation levels depend on the tree location, exhibiting tA (on the opposite margin directly in front of the industrial effluent discharge point) comparatively higher mercury concentrations. Cores sampled upstream discharge point (tB) reflect lower mercury accumulation, probably associated with tidal reflux reflecting the fraction of metal transport upstream. Cores sampled downstream (tC) indicate mercury dilution away from the discharge point and mercury transport towards the rest of the lagoon. Mercury concentration standard deviations are mainly due to ring growth differentiation occurred during the environmental recording (data logging) period.

Cores sampled in tA (length of approximately 25 cm) corresponds to an annual growth of about 5 mm year^{-1} in agreement to the radial grow of *P. nigra* (Helle and Scheser 2004) therefore reflecting about 50 years of environmental record (Fig. 4a). Mercury accumulation trends in the tree rings reflect industrial plant capacity evolution trend (kt Cl_2 year^{-1}) (Pereira 1997; OSPAR 2005) and chlor-alkali discharge events chronology, enhancing trees as data loggers (Fig. 4).

Mercury concentration in the inner annular tree rings (tA), environmental record—data logging—of first

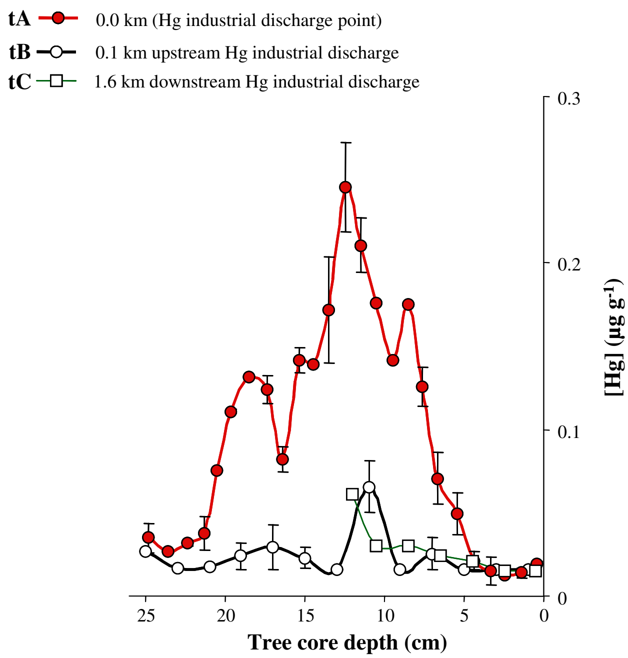

Fig. 3 Mercury concentration in the annular tree rings sampled from the three trees: tA—directly in front of the effluent discharge, tB—0.1 km upstream the effluent discharge, and tC—1.6 km downstream the effluent discharge

discharges, shows low mercury accumulation (<40 ng g^{-1}), followed by an increment of mercury accumulation in the following tree rings, recording the industrial plant capacity increase and subsequent production trend reflecting not only the mercury discharges into the environment but also the minimization measures to reduce the discharge of mercury into the environment, according to the regulations on mercury emissions imposed on the chlor-alkali industry in the early 1970s by the Paris Commission and the European Community (Yarime 2003). The industrial plant begun producing chlor and caustic soda in the early decade of 1950, increasing its production up 20,000 tons $year^{-1}$ in the decade of 1970, when the discharge system it was changed from an open effluent (until 1975) to a closed pipe work system having the outlet almost directly (<5 m) to the root environment of "our data logger"—tA.

Tree rings also record the industrial plant production increment up to 60,000 tons $year^{-1}$ in the early 1980s, leading mercury concentration in annular rings from 0.02–0.03 µg g^{-1} to 0.22–0.28 µg g^{-1}.

A decrease in the tree ring mercury accumulation it was also recorded reflecting the decrease in mercury discharge into the environment due to the implement of new technology such as close circuits and hermetic cells (in the 1980s), and diaphragm membranes (in the 1990s) (Pereira 1997), until the last replacement by membrane cells in January 2002 (OSPAR 2005). The peak of mercury in the annular tree rings occurs in central segments of the tree cores and it is consistent with the increase of production in the 1980s, showing the peak of mercury discharge into the environment before last minimization measures have taken place.

Overall data obtained in the tree cores show similar trends representing chronological historical record of anthropogenic mercury discharge into the estuarine lagoon. In the period before the 1980s, mercury concentration in the tree rings and data on industrial plant production presented a strong positive correlation ($p < 0.001$), supporting the use of *P. nigra* as mercury "data loggers". After the 1980s, mercury concentration in the tree rings also reflects similar trend to mercury losses through product, wastewater and air (Fig. 2b) (OSPAR 2005).

Mercury concentration in the annular tree rings also follows the pattern obtained in sediment cores (sampled at the end of the channel that receives the effluent discharge—about 4 km downstream) (published data from Ramalhosa et al. 2006). The similar pattern (Fig. 4b) enhances annular tree rings as "data loggers", despite mercury concentration in the tree rings being 25 times lower then mercury concentration in the sediment core. The pronounced decrease of mercury concentration obtained in the annular rings for the last decade could represent a more reliable record of the mercury discharge (point source) into the environment, contrary to the moderate decrease observed in the first layers from the sediment core, where the arrival of contaminated particles from upstream areas may postpone the decrease of mercury in the surface sediments.

Considering the pattern of mercury accumulation in all tree cores and the decrease of the trees mercury burden in relation to the distance from the industrial effluent discharge point, it is assumed that mercury present in the samples has mostly entered via the root system.

Some authors have stated that tree-ring chemistry is not a useful indicator and some tree species are better spatial indicators of pollution than historical monitors (Watmough 1997; Nabais et al. 1999) due to radial translocation of elements, radial tendencies in element concentration from pith to bark, physiological differences between heartwood and sapwood, or even bias soil uptake (Bindler et al. 2004). Therefore, the adequacy of dendrochemistry to historical environment monitoring seems to be strongly dependent on the choice of the tree specie and on the elements to be studied. Although these uncertainties associated with the method, Becnel et al. (2004) found a good correlation (0.85 ± 0.03) between Hg in tree rings and lichens and there are many reports published where the analysis of tree-ring chemistry have been successfully used to reconstruct trace-metal deposition from a variety of sources (Watmough 1997; Orlandi et al. 2002; Witte et al. 2004), using tree rings (Orlandi et al. 2002) or tree bar pockets (Satake et al. 1996).

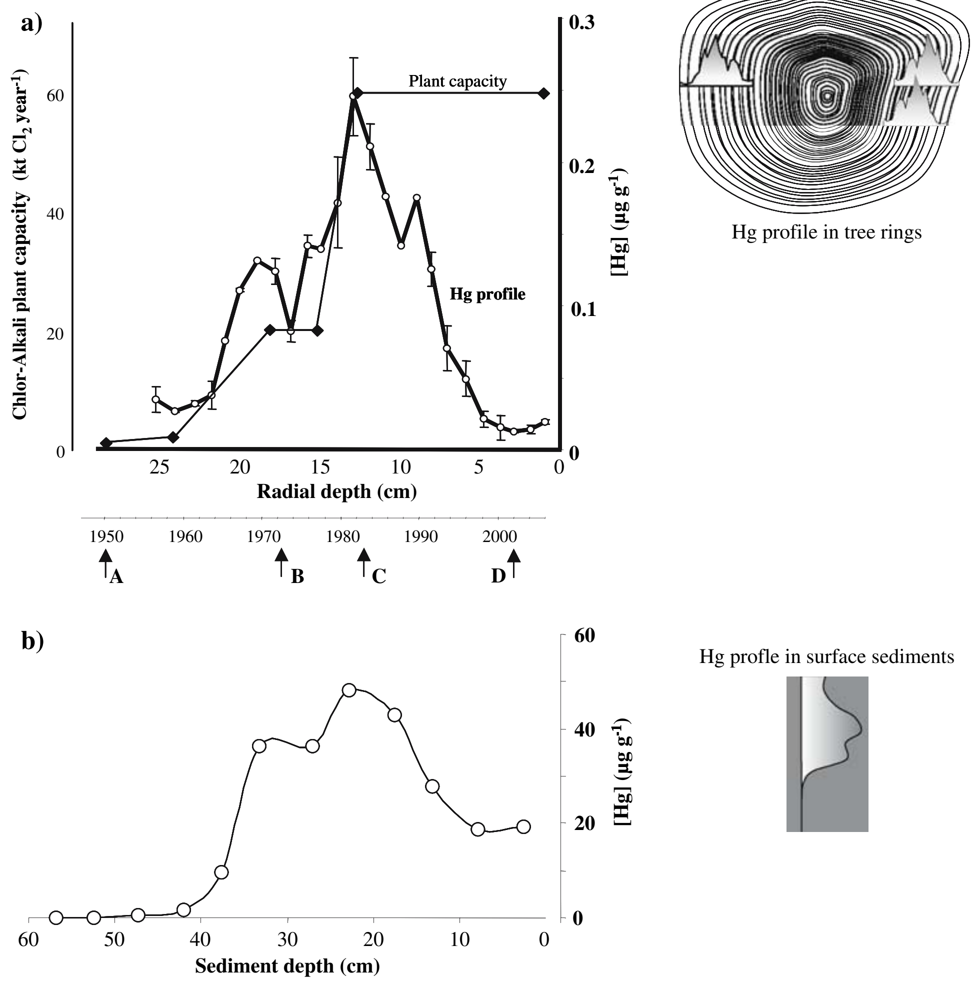

Fig. 4 (**a**) Mercury concentration in the annular tree rings (tA) sampled from the tree directly in front of the effluent discharge comparing to industrial plant capacity and (**b**) mercury concentration in the sediment cores sampled at the end of the channel ($\sim$4 km downstream) that receives the effluent discharge

The shared trends between trees suggest that variations in Hg are related to factors common to all trees and could potentially reflect changes in local environmental conditions. Mercury accumulation in the annular rings is able to mimic not only historical discharges of mercury, enhancing trends and peaks of production, but also tracks the moments of the industrial plant efforts controlling mercury discharges. The analysis of the time-trend of mercury in the tree rings (before introduction of new technologies in the 1980s) is in agreement with data on industrial plant production, therefore representing chronological historical trend record of anthropogenic mercury discharge into the aquatic environment (the estuarine lagoon Ria de Aveiro). Mercury concentration in the tree cores agrees with published results on mercury concentration in sediment core profiles, indicating the 1980s as the peak of anthropogenic mercury discharges into the lagoon, followed by a sudden decrease until present, and also reflecting and “recording” the industrial plant efforts in order to minimize mercury discharges.

Contrary to sediment core profiles (exposed to dynamic resuspension and sedimentation processes), annular tree rings present a chronological reliable matrix providing support to historical recording of environmental contamination.

Despite a more detailed understanding of nutrient and metal cycling in trees is needed (Smith 2003), the application of dendrochemistry in environmental monitoring and its use as environmental recorders—data loggers acting trees as “quite sentinels”—seem to be promising, not only to monitor historical changes in soil and atmospheric pollution but also to record trends of metal discharges into the aquatic environment provided the specificity of the tree location.

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