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Sediment-associated mercury distribution within a major Amazon tributary: century-scale contamination history and importance of flood plain accumulation

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Abstract The sources, transport and storage mechanics, and contamination history of mercury (Hg) in the Madeira River, an important tributary of the Amazon River, were investigated from the Hg concentration and relevant geochemistry of flood plain and river sediment of one of its major Andean tributaries, the Beni River. Sediments containing clays and Al and Fe oxy-hydroxides may serve as the primary carrier for Hg and facilitate its transport and storage within the Beni River–flood plain system. We estimate an annual exchange of clay-affiliated Hg between the flood plain and the channel of 2.1 t, due to channel migration, and a net Hg deposition of 2.4 t year^{-1}, in the distal parts of the flood plain. Long-term records of sediment influx and efflux from the Beni foreland support this estimate of total Hg accumulation. Applying ^{210}Pb geochronology to flood plain cores, we find that the clay-normalized Hg concentration in sediment was constant between 1900 and 1965, and then shows an increase over the past 30 years. This trend might be explained by the recent colonization, by a new mining boom in South America and by increased deforestation of hillsides and the resulting erosion of Hg-contaminated soils.

Key words Amazon basin; Madeira tributary; mercury; sediment; flood plain; geochronology

INTRODUCTION

Mercury pollution of water and fish in the Amazon basin is a significant hazard for riparian populations, especially for people whose primary protein source is contaminated fish (Lebel *et al.*, 1999; Maurice-Bourgoin *et al.*, 2000a; Roulet & Maury-Brachet, 2001); Hg has been implicated in the irreversible damage of nervous and immune systems (Lebel *et al.*, 1998). In the Bolivian Andes, at the headwaters of the Beni River, erosion of contaminated soils and weathering of mercury-bearing rocks during the rainy season can increase the water concentration of Hg by 50 fold (Maurice-Bourgoin *et al.*, 2000b). These soils may have become contaminated through

natural crustal degasification and dissolution of Hg, and also by centuries of extensive Hg use during both the colonial and post-colonial extraction of massive quantities of gold and silver (Nriagu *et al.*, 1992). More recently, a new gold-mining boom starting in the 1970s has introduced an estimated 0.25–0.5 t $year^{-1}$ of Hg into the Beni River basin. We have estimated that in Bolivia (Maurice-Bourgoin *et al.*, 2000a), more than 330 t of mercury has been released into the environment since 1952. The mercury used can be released directly into the river itself or indirectly through the atmosphere by open-air burning of the amalgam (Malm *et al.*, 1990; Maurice-Bourgoin *et al.*, 1999). However, the major environmental impact of these mining activities is the deforestation of the exploited areas and the release of millions of tonnes of Hg-contaminated sediments and soils into affected rivers, rather than the direct release of Hg used during the last stages of gold extraction (Maurice-Bourgoin, 2001). Numerous studies have documented the distribution of Hg in water, fish, and people throughout the Amazon basin (Akagi *et al.*, 1995; Malm *et al.*, 1995; Barbosa *et al.*, 1997; Roulet *et al.*, 1999; Silva-Forsberg *et al.*, 1999; Maurice-Bourgoin *et al.*, 2000a), but the important link between Hg and sediment transport had not been fully explored. To investigate the sources, transport and storage mechanics, and contamination history of Hg for this important tributary of the Amazon, we analysed the Hg concentration and relevant geochemistry of flood plain and river sediment.

STUDY AREA

The Bolivian Amazon basin represents the Andean headwaters of the Madeira River, one of the most important tributaries of the Amazon River. In Bolivia, its drainage basin is 0.9×10^6 km^2, with 25% in the Andes, 27% on the Brazilian shield and 48% in the plain. The Beni River, the largest sediment supplier of the three major tributaries of the Madeira River (Guyot, 1993), is the focus of our study. Andean tributaries of this river drain both semiarid areas of high altitude and areas of tropical humid forest of the sub-Andes. Heights above sea level range from 6400 m at the highest headwaters to 200 m at Rurrenabaque, in the piedmont at the upper limit of the flood plain, to 115 m at the Brazilian border. At the edge of the sub-Andes, the drainage area at Rurrenabaque is 67 500 km^2 and the mean annual discharge during the sampling period, 1998–1999, averaged 2300 m^3 s^{-1}. The Beni River collects numerous Andean tributaries, half of which are exploited for their alluvial gold since the 1960s (Fig. 1).

MATERIAL AND METHODS

In order to study the century-scale Hg contamination and to better understand the sources and the behaviour of Hg within a major Amazon tributary, a sampling survey was conducted along the entire Beni River in August–September, 1999. Water samples were collected using Teflon bottles and all procedures were performed using "ultra-clean" techniques (Nolting & De Jong, 1994; Gaudet *et al.*, 1995). Sediment cores were sampled 1.3 m deep into the flood plain at different locations along the Beni River (Fig. 1); they were frozen in the field and subsequently dried and processed in the laboratory. The total Hg (T-Hg) was determined by atomic fluorescence spectrometry

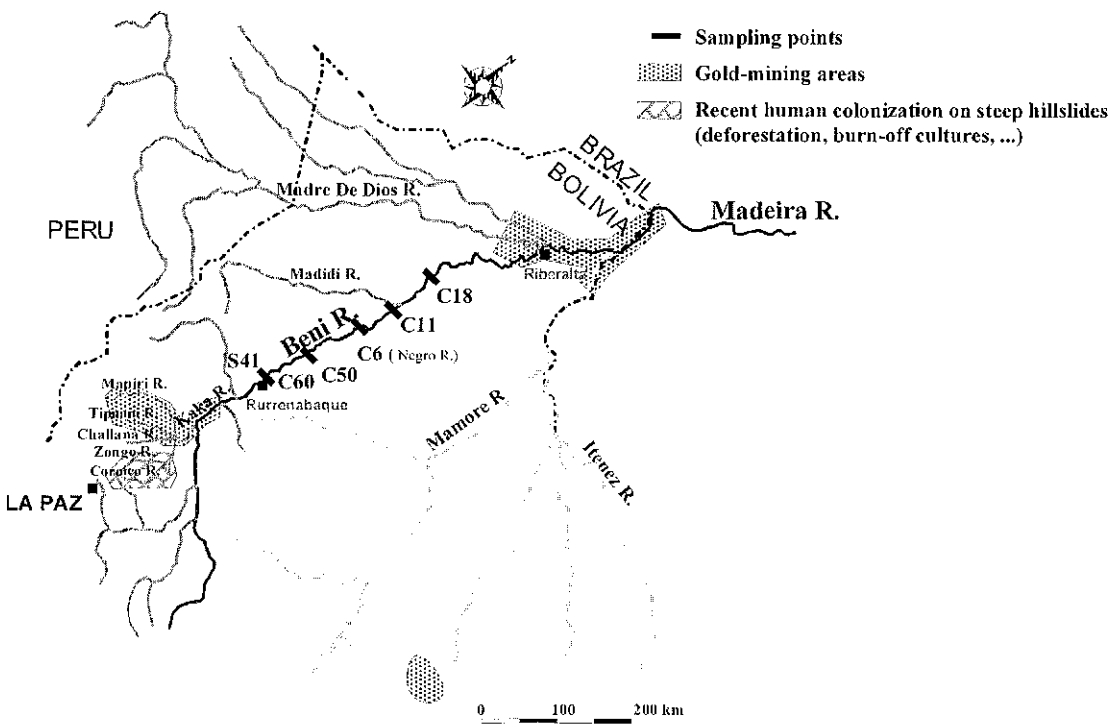

Fig. 1 Hydrological map of the Madeira tributaries, location of the sample sites and distribution of the recent anthropogenic disturbance (deforestation, mining, road construction).

after reduction with Sn(II); the detection limit was 2 ng g^{-1}. The accuracy and reproducibilty of the method were calibrated by the analysis of a reference standard; the mean T-Hg concentration obtained was 92 ± 4 ng g^{-1} (dw) for a recommended value of 92 ± 9 ng g^{-1} (dw). The concentrations of T-Hg, organic carbon and nitrogen, iron (Fe_{cdb}) and aluminium (Al_{cdb}) substituted into oxy-hydroxides, as associated with the granulometry and ^{210}Pb activity within the same sediment cores, were used to characterize the main geochemical processes controlling the deposition of Hg within the flood plain.

A new model has been developed for ^{210}Pb geochronology on river flood plains, termed Constant Initial Reach Clay Activity and Unknown Sedimentation rate (CIRCAUS) and has been applied to more than one hundred locations throughout the Beni and Mamore systems (Aalto, 2002; Aalto & Nittrouer, submitted). The approach employs discrete down-core, clay-normalized measurements of ^{210}Pb activity and is coupled with a geomorphic model of the input concentration of ^{210}Pb in sediment during large floods. The numerical modelling approach is supplemented with an empirical determination of the supported ^{210}Pb activity, the meteoric input of ^{210}Pb, and the clay-normalized ^{210}Pb activity in fresh sediment for that reach of river. The sediment age is determined from the "decay" age of any activity plateaus (zones of uniform activity found in most cores), as well as independently calculated from the excess "meteoric cap" ^{210}Pb activity above the activity of the plateau.

RESULTS AND DISCUSSION

Efflux of sediments and associated mercury to the Beni flood plain

The T-Hg concentrations in the Beni River range from 19 ng l^{-1} during the dry season to 460 ng l^{-1} at peak flood stage. The Hg associated with the particles represents 59 and 98% of the T-Hg, respectively. In this Andean tributary, the importance of soil erosion during the rainy season in controlling the mercury concentrations of freshwater has been previously demonstrated (Maurice-Bourgoin *et al.*, 2000b). For the 1999 water year, from surface water samples, we estimated a total suspended particulate matter (SPM) efflux at Rurrenabaque of 302 × 10^6 t; 97% of this material was transported during the first four months of high water and about 40% is later deposited in the Amazonian flood plain (Maurice-Bourgoin *et al.*, 2001); these results concur with the

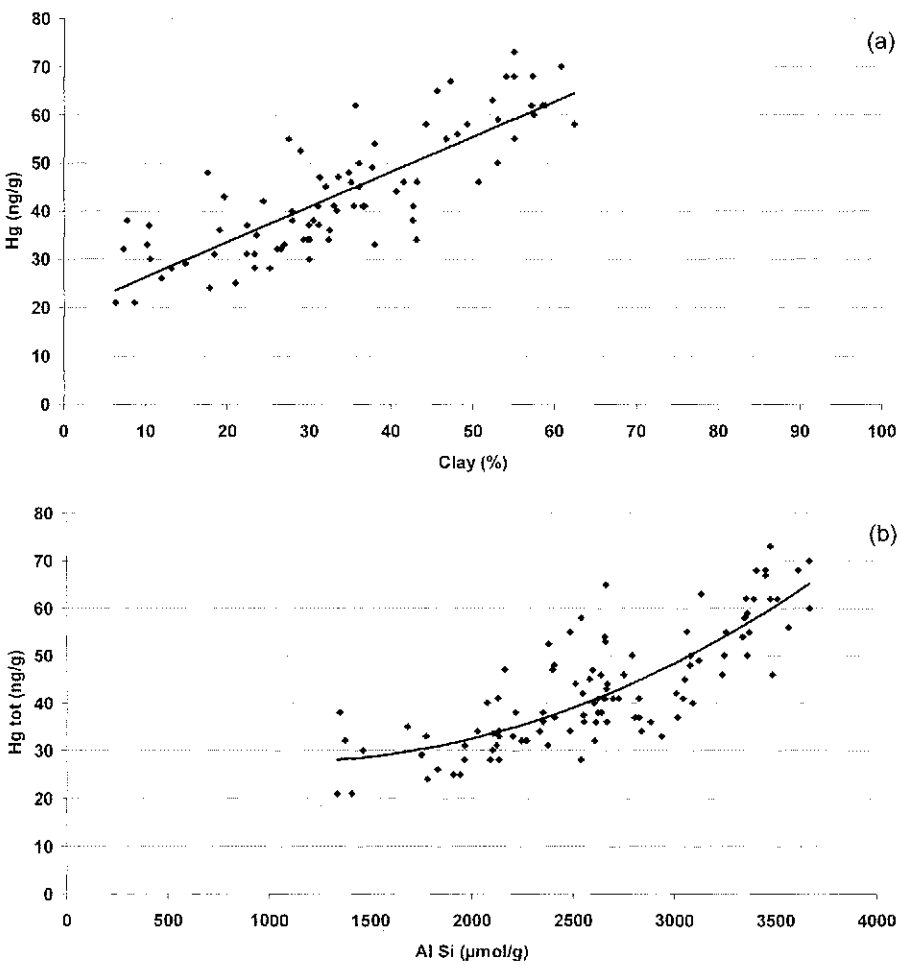

Fig. 2 Correlations between T-Hg concentrations and (a) the clay content (%) and (b) the Al incorporated in clay minerals (Al_{Si}) concentrations (µmol g^{-1}) in the Beni flood plain sediments.

values published by Guyot (1993). The total Hg (T-Hg) flux associated with sediment reached 33 t, 96% of which was particulate Hg (P-Hg). During the wet season, from November to March, Hg-contaminated particles are transported from the Andean sub-basins characterized by steep slopes and by an accelerated erosion rate driven by recent agriculture practices and the ongoing construction of a major road. Due to the high adsorption capacity of mercury on fine particles (clays) in the white water rivers (in contrast to organic-rich "black waters"), most of the mercury is transported on SPM. In the Beni River basin, a depth-integrated average of 35% of the deposited sediment collected in the flood plain is composed of clays, and these contain most of the sediment-borne mercury.

Century-scale contamination history and importance of sediment transport, channel–flood plain interchange, and flood plain accumulation

For the 139 sediment samples analysed (n = 114 for clay defined as particles smaller than 4 μm), we observe (Fig. 2) a strong correlation between T-Hg and clays content (r^2 = 0.74), Al_{tot} (r^2 = 0.65), Fe_{tot} (r^2 = 0.64) and with Fe incorporated in clay minerals, Fe_{Si} (r^2 = 0.53) concentrations. This confirms that clays and Al and Fe oxy-hydroxides in sediments may serve as the primary carrier and facilitate the transport and storage of Hg within the Beni river–flood plain system. By utilizing results from a detailed model for the transport and deposition of river sediment (including clays) along the Beni river–flood plain system as it crosses a large foreland basin (Aalto, 2002), we estimate, using the observed Hg–Clay relationship (Fig. 2), an annual exchange of clay-affiliated Hg between the flood plain and the channel of 2.1 t Hg, primarily due to channel migration. This exchange has been estimated by subtracting the net Hg deposition of 2.4 t $year^{-1}$, primarily lost into the distal flood plain, from the total deposition of 4.5 t $year^{-1}$. Long-term records of sediment influx into and efflux from the Beni foreland support this estimate of total sediment loss and associated Hg accumulation within the foreland.

In many of our cores, we observe an increase of the T-Hg concentrations in sediments with depth (Fig. 3). Applying the CIRCAUS model to date the sediment within our flood plain cores, we find that the ratio of observed Hg concentration to expected Hg concentration (as derived from measured clay abundance or from measured Al incorporated in clay minerals, Al_{Si}) is approximately 1 from 1900 to 1965 and then increases starting in the 1970s (Fig. 4). This increase is most evident for the clay-normalized Hg content where we observed a best correlation between these two elements. This suggests that the clay, and in a less extend Al-normalized Hg concentration in sediment is constant from 1900 to 1965, and then shows an increase over the past 30 years, most likely because of a new input of Hg in the Andean drainage basins. This influx of Hg can be attributed to accelerated erosion of Hg-enriched soils, due to increased gold-mining activities, recent colonization, and new agriculture practices (e.g. burning after deforestation), road construction, and other human activities. A substantial increase in the price of gold during the 1970s, with a maximum in 1980, sparked a new gold boom in various tropical countries, and especially in Latin America (Cleary, 2000). Other authors (Roulet *et al.*, 2000) observed an increase in sediment Hg concentrations

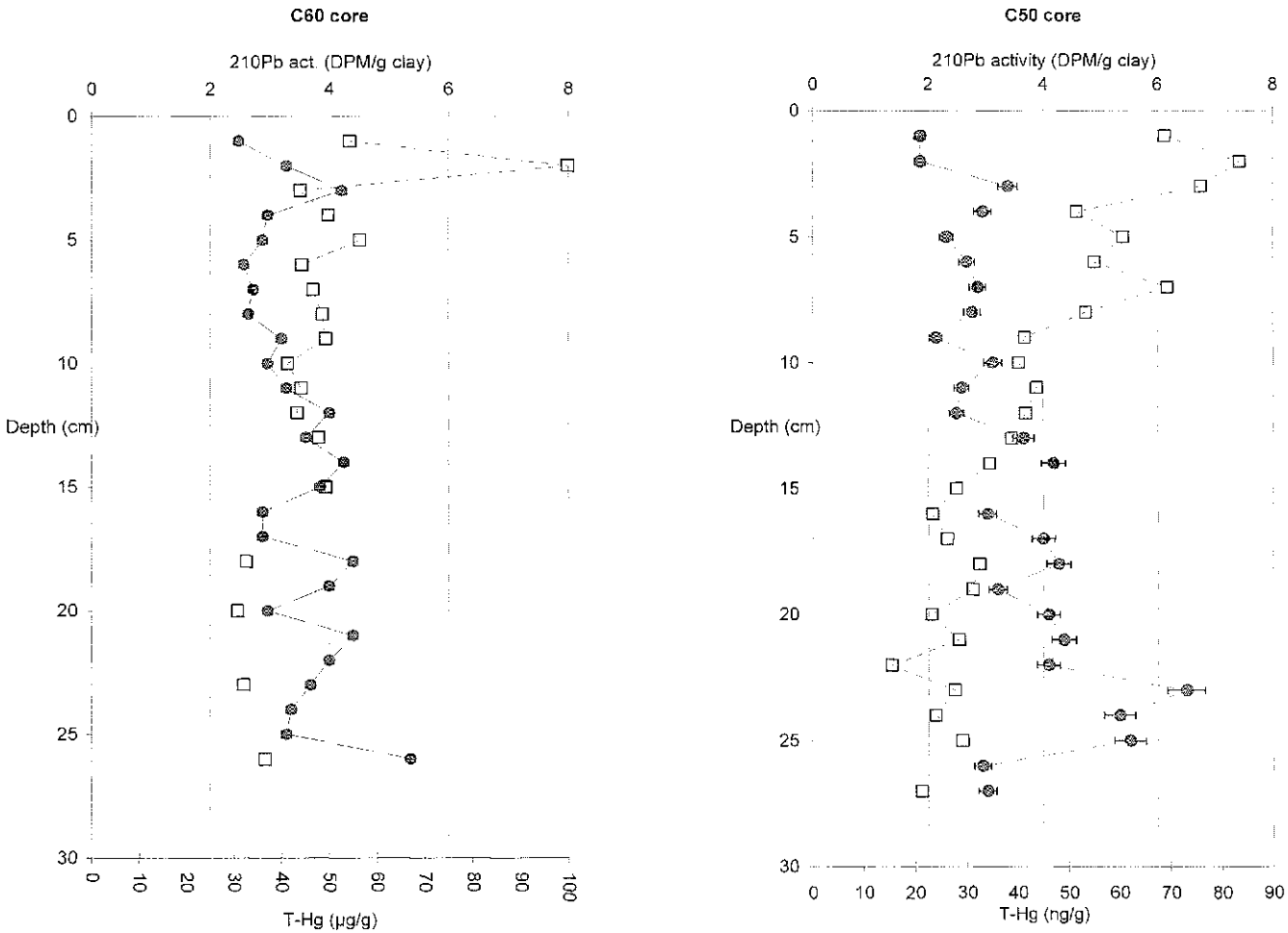

Fig. 3 Vertical distribution of T-Hg concentrations (●) and ^{210}Pb activity (□) in two sediment cores collected in the Beni River flood plain (C50 and C60).

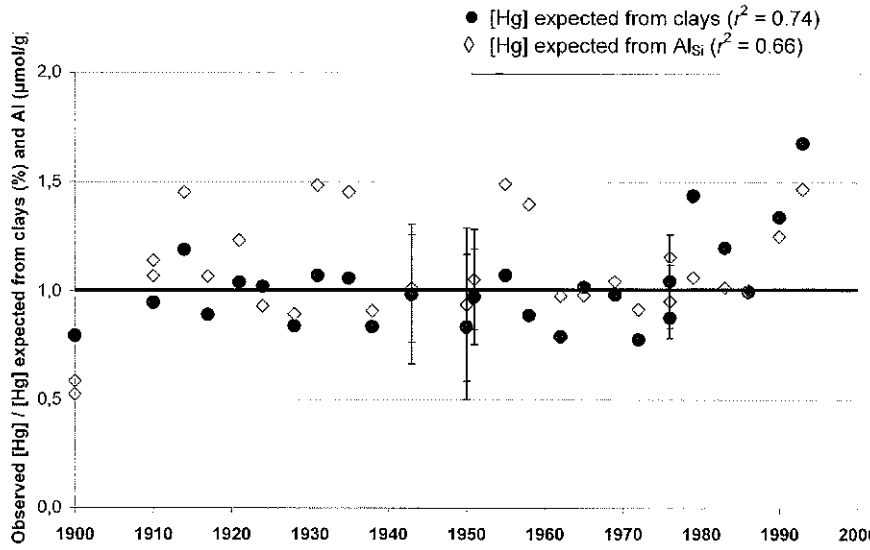

Fig. 4 Observed Hg concentration/expected Hg ratio from measured clay abundance, and from Al incorporated in clay minerals, in the Beni River sediments over the last century.

in the surface sediments of the Tapajós and Ariapiuns Rivers; although their study is not based on substantial geochronological data, they concluded that between the 1950s and 1970s, the significant colonization of the Amazon drainage basins and the growing development of new parcels of land disturbed mineral and organic matter cycles, including the Hg distribution within sediments.

CONCLUSION

The substantial increase of clay or Al_{Si}-normalized Hg concentration in the sediments of an important tributary of the Amazon during the last 30 years might be explained by a recent gold mining boom and also by increased deforestation of steep hillsides and the resulting erosion of Hg-contaminated soils. Our dating methodology is based on a recently-developed ^{210}Pb technique for flood plains, including extensive documentation for sediment deposition across the Beni River flood plain (over 90 activity profiles processed to date); therefore, this study represents the first geochronological determination of heavy metal pollution history from flood plain sediments. These results underscore the importance of river sediment as a carrier of Hg, and the key role of channel–flood plain sediment interchange in regulating the transport and accumulation of any sediment-associated pollution.

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REFERENCES

Aalto, R. (2002) Geomorphic form and process of sediment flux within an active orogen: denudation of the Bolivian Andes and sediment conveyance across the Beni foreland. PhD Dissertation, University of Washington, Seattle.

Aalto, R. & Nittrouer, C. A. (submitted) Application of fallout ^{210}Pb geochronology to river–flood plain systems: a flexible new methodology. Submitted to *Chem. Geol.*

Akagi, H., Malm, O., Branches, F. J. P., Kinjo, Y., Kashima, Y., Guimaraes, J. R. D., Oliveira, R. B., Haraguchi, K., Pfeiffer, W. C., Takizawa, Y. & Kato, H. (1995) Human exposure to mercury due to goldmining in the Tapajós River basin, Amazon, Brazil: speciation of mercury in human hair, blood and urine. *Wat. Air Soil Pollut.* **80**, 85–94.

Barbosa, A. C., Garcia, A. M., & de Souza J. (1997) Mercury contamination in hair of riverine populations of Apiacas Reserve in the Brazilian Amazon. *Wat. Air Soil Pollut.* **97**, 1–8.

Cleary, D. (2000) Small scale gold-mining in Brazilian Amazonia. In: *Amazonia at the Crossroads* (ed. by A. Hall), 58–72. Institute of Latin America Studies, London.

Gaudet, C., Lingard, S., Cureton, P., Keenleyside, K., Smith, S. & Raju, G. (1995) Canadian environmental quality guidelines for mercury. *Wat. Air Soil Pollut.* **80**, 1149–1159.

Guyot, J. L. (1993) Hydrogeochemistry of the Bolivian Amazonian rivers. PhD Dissertation. ORSTOM, Paris, France.

Lebel, J., Mergler, D., Branches, F., Lucotte, M., Amorim, M., Larribe, F. & Dolbec, J. (1998) Neurotoxic effects of low-level mercury contamination in the Amazonian basin. *Environ. Res.* **A79**, 20–32.

Lebel, J., Roulet, M., Mergler, D., Lucotte, M. & Larribe, F. (1999) Fish diet and mercury exposure in a riparian Amazonian population. *Wat. Air Soil Pollut.* **97**, 31–44.

Malm, O., Pfeiffer, W.C., Souza, C. M. M. & Reuther, R. (1990) Mercury pollution due to gold mining in the Madeira river basin, Brazil. *Ambio* **19**(1), 11–15.

Malm, O., Branches, F. J. P., Akagi, H., Castro, M. B., Pfeiffer, W. C., Harada, M., Bastos, W. R. & Kato, H. (1995) Mercury and methylmercury in fish and human hair from the Tapajós river basin, Brazil. *Sci. Total Environ.* **175**; 141–150.

Maurice-Bourgoin, L. (2001) Le mercure dans les eaux de surface du bassin amazonien—transfert du mercure des sols aux milieux aquatiques—spéciation, transport et sédimentation dans les rivières et plaines d'inondation. In: *Le Mercure en Amazonie: Rôle de l'homme et de l'environnement* (ed. par J. P. Carmouze, M. Lucotte & A. Boudou), 167–200. IRD Publ. (Expertise Collégiale), Paris, France.

Maurice-Bourgoin, L., Quiroga, I., Guyot, J. L. & Malm, O. (1999) Mercury pollution in the upper Beni River basin, Bolivia. *Ambio* **28**(4), 302–306.

Maurice-Bourgoin, L., Quiroga, I., Chincherros, J. & Courau, P. (2000a) Mercury distribution in waters and fishes of the Upper Madeira rivers and mercury exposure in riparian Amazonian populations. *Sci. Total Environ.* **260**, 73–86.

Maurice-Bourgoin, L., Fraizy, P., Alanoca, L., Seyler, P. & Guyot, J. L. (2000b) Hydrological control on the temporal variability of mercury in surface waters of the Upper Madeira basin, Bolivia. In: *25th Int. Conference on Heavy Metals in the Environment* (ed. by J. Nriagu). Contribution no. 1282, University of Michigan, School of Public Health, Ann Arbor, Michigan (CD-rom).

Maurice-Bourgoin, L., Aalto, R., Fraizy, P., Barnaud, V. & Guyot, J. L. (2001) Modulation of mercury transport through fluvial systems by channel–floodplain interaction: a case study for the Beni River, Bolivian Amazonia. In: *6th Int. Conference on Mercury as a Global Pollutant.* Akagi, Minamata, Japan.

Nolting, R. F. & de Jong, J. T. M. (1994) Sampling and analytical methods for the determination of trace metals in surface seawaters. *Int. J. Environ. Anal. Chem.* **57**, 189–196.

Nriagu, J. O., Pfeiffer, W. C., Malm, O., Souza, C. M. M. & Mierle, G. (1992) Mercury pollution in Brazil. *Nature* **356**, p. 389.

Roulet, M., Lucotte, M., Farella, N., Serique, G., Coelho, H., Sousa Passos, C. J., De Jesus da Silva, E., Scavone de Andrade, P., Mergler, D., Guimaraes, J. R. D. & Armorim, M. (1999) Effects of recent human colonization on the presence of mercury in Amazonian ecosystems. *Wat. Air Soil Pollut.* **112**, 297–313.

Roulet, M., Lucotte, M., Canuel, R., Farella, N., Guimarães, J.-R. D., Mergler, D. & Amorim, M. (2000) Increase in mercury contamination recorded in lacustrine sediments following deforestation in central Amazonia. *Chem.Geol.* **165**, 243–266.

Roulet, M. & Maury-Brachet, R. (2001) Le mercure dans les organismes aquatiques amazoniens. In: *Le Mercure en Amazonie: Rôle de l'homme et de l'environnement*, (ed. par J. P. Carmouze, M. Lucotte & A. Boudou), 203–271. IRD Publ. (Expertise Collégiale), Paris, France.

Silva Forsberg, M. C., Forsberg, B. R., & Zeidemann, V. K. (1999) Mercury contamination in humans linked to river chemistry in the Amazon basin. *Ambio* **28**(6), 519–521.