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HYDROLOGICAL CONTROL ON THE TEMPORAL VARIABILITY OF MERCURY IN SURFACE WATERS OF THE UPPER MADEIRA BASIN RIVERS, BOLIVIA

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ABSTRACT

Mercury contamination of waters and soils is an environmental problem of increasing concern throughout the Amazon River basin. In order to better understand the sources of Hg in a major tributary to the Amazon, a monthly time series spanning an entire hydrological cycle has been measured for two rivers of the Upper Madeira drainage basin. At both gauging stations, we observe a hydrological control on the temporal variability of the dissolved and the total mercury (THg) concentrations: they increase in phase with increasing discharge and we observe the highest THg concentrations at the peak stage. Mercury associated with particles represents more than 90% of the THg in high-water period, and tends to decrease only slowly with falling river stage. This suggests that weathering processes are still active during this last stage. One of the principal factors controlling the distribution of Hg in Andean waters is apparently the process of soil erosion.

INTRODUCTION

The biogeochemical cycle of mercury in the Amazon basin is a topic covered by many recent papers, but it is still poorly understood. Mercury released from gold-mining activities was commonly thought responsible for the Hg contamination of aquatic ecosystems (Malm *et al.*, 1990 ; Nriagu *et al.*, 1992). But recent studies have shown the importance of the pre-anthropogenic sources in the elevated mercury concentrations measured in the superficial mineral horizons of the Tapajós basin (Roulet *et al.*, 1998). In order to quantify the cycle of mercury in the study basins, a monthly time series covering a whole hydrological cycle, from December 1998 to July 1999, has been collected at 2 gauging stations of the Upper Madeira river, in Bolivia (Fig. 1). Elevations range from 6400 m at the headwaters to 200 m at Rurrenabaque. The first sampling station is located in the subAndes, on the Coroico river, at 450 m above sea level. The drainage basin area at this station is 4700 km² and the annual mean discharge during the 1998-2000 period was 220 m³ s⁻¹. The second sampling station is located at the edge of the Andean piedmont at the beginning of the Amazonian plain, on the Beni river at Rurrenabaque. This lower station has an associated drainage area of 67500 km² and a mean annual discharge during the sampling period of 2300 m³ s⁻¹. It collects numerous Andean tributaries some of which are largely exploited for their alluvial gold (Fig. 1).

This paper evaluates the importance of the erosion process in determining the variability of the Hg concentrations in surface waters of a 'white waters' tributary of the Amazon river.



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METHODS

Water samples were collected using Teflon bottles and all handling operations were performed using 'ultra-clean' techniques (Ahlers *et al.*, 1990), including a portable laminar flow hood to avoid contamination. Mercury in the both dissolved and particulate fraction of the water samples was analysed by CV-AFS after reduction to elemental mercury by addition of SnCl_2 . Analyses were conducted in triplicate. Reproducibility was 0.1 to 2% and detection limit was 0.23 ng l^{-1} . The reactive blanks reached 5 to 9 pg Hg ; the acid blanks averaged 140 pg l^{-1} . The accuracy of the particulate Hg analysis was limited by the standard deviation of membrane blanks, which reached 12 and 50 pg Hg .

RESULTS AND DISCUSSION

In the Andean tributary

The Coroico River is considered as a 'clear-water' river, slightly mineralised with a conductivity ranging from 20 to $50 \mu\text{S cm}^{-1}$ and a steady neutral pH. The temporal variation of conductivity is out of phase with the hydrograph in contrast to the suspended particulate matter which follows the water level. Since 1997, the Coroico valley has been highly perturbed by anthropogenic activities: the construction of a major mountain road and increased agricultural practices (such as deforestation and burning) both favour accelerated erosion processes. The steep slope (5.8 %) and recent anthropogenic activities may explain the high concentrations of suspended particulate matter (SPM) measured in this river. The annual load of suspended sediments estimated for the 1998 and 1999 years averages $5.3 \cdot 10^6$ tons of which 72% is exported during the rainy season.

The total Hg (THg) concentrations range from 16 ng l^{-1} in dry season to 169 ng l^{-1} at high stage (Fig. 2) and the Hg associated with the sediment particles represents 49 and 92% of the THg, respectively. The dissolved Hg concentration varies from 5.3 ng l^{-1} in dry season to 67.6 ng l^{-1} at the first peak stage of the seasonal flood where maximum values are measured. We observe that the temporal variability the Hg adsorbed on the particles (in ng g^{-1}) is out of phase with the concentration of the SPM (Fig. 2). This enrichment of particulate Hg at the end of the rainy season can be explained by a decreased of the efficiency of the erosion process from the first peak stage to the end of the annual flood.

At the edge of the subAndes

The Beni River constitutes one of the 'white-water' tributaries of the Madeira R. Its conductivity ranges from $5.3 \mu\text{S cm}^{-1}$ to $180 \mu\text{S cm}^{-1}$, respectively, during the rainy and dry seasons; this variability is inversely proportional to the water level and its neutral pH does not vary with the hydrology. At the long-term sampling station, this river is composed of six Andean tributaries half of which are exploited for their alluvial gold. The suspended sediment flux at this station, reached in 1998 and 1999, averages $240 \cdot 10^6$ tons per year. Approximately, 80% of this material is transported during the 3 months of high water and about 40% is later deposited in the Amazonian floodplain (Guyot, 1993).

The THg concentrations range from 19 ng l^{-1} in dry season to 460 ng l^{-1} at the peak flood stage (Fig. 3) and the Hg associated with the particles represents 59 and 98% of the THg, respectively. The concentrations of Hg adsorbed to the suspended particles are in opposite phase to the suspended sediment concentrations, with the highest values measured during the early part of the dry season (Fig. 3). At this station, we observe i) some of the highest values of precipitation in Bolivia, ii) a subsident zone which favour the deposition of sediment particles transported from the Andes and iii) upstream source basins characterised by sediments mainly composed of clays and soils enriched in iron oxy-hydroxydes. During the wet season, from November to March, contaminated particles are transported from the Andean sub-basins (characterised by steep slopes and by an accelerated erosion rate driven by

recent agriculture practices and the construction of a road) to the Amazonian plain. The high adsorption capacity of mercury on fine particles (clays) is one of the reasons why, in any river basin, most of the mercury is transported on particulate matter (Benes and Havlik, 1979; Maurice-Bourgoin *et al.*, 1999). This mainly occurs during the rainy season, when soil erosion is the most significant. In the white waters of the Andean rivers, an average of 15% of the SPM in the Beni river at Rurrenabaque is composed of clays. This fraction ranges as high as 70% to 80% of the SPM in one of the Beni tributaries exploited for alluvial gold, the K'aka river (Guyot, 1993).

CONCLUSION

It appears that mercury concentrations measured in suspended matter indicate that mercury is preferentially released into the river during the rainy season, mainly during the first peak stage. Mercury is primarily adsorbed on the many fine particles in great abundance in Andean rivers, and is consequently transported downstream with these particles. Mercury contamination affects drainage basins downstream characterised by high precipitation, high sedimentation rate, and by soils and sediments enriched in clays and iron oxy-hydroxides. Even if the hydrodynamic conditions in this area were instead to favour the transport and dispersion of mercury in particulate form, mercury pollution could still be a problem in the Bolivian Amazonian basin because of the high fish consumption by indigenous riparian communities as a primary source of protein (Maurice-Bourgoin *et al.*, 2000).

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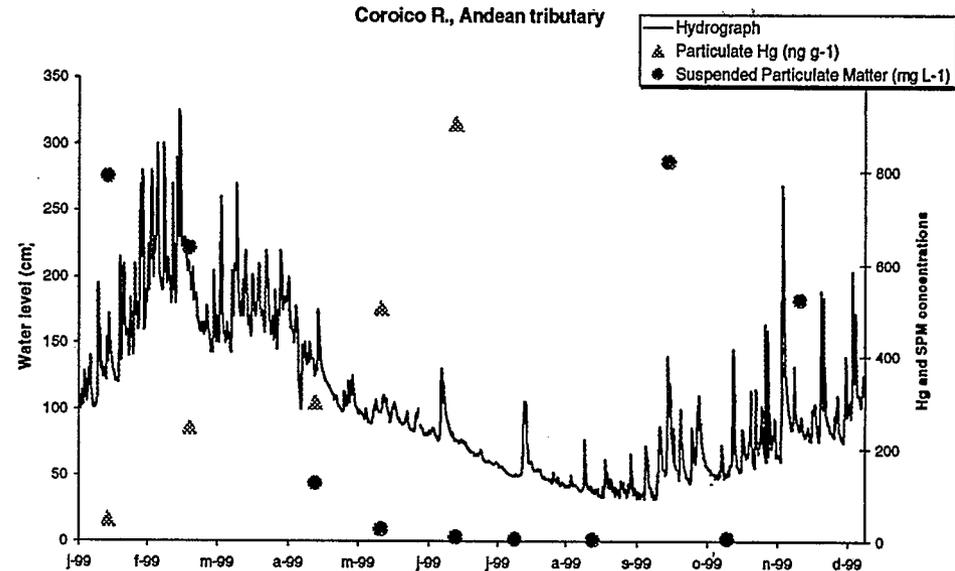
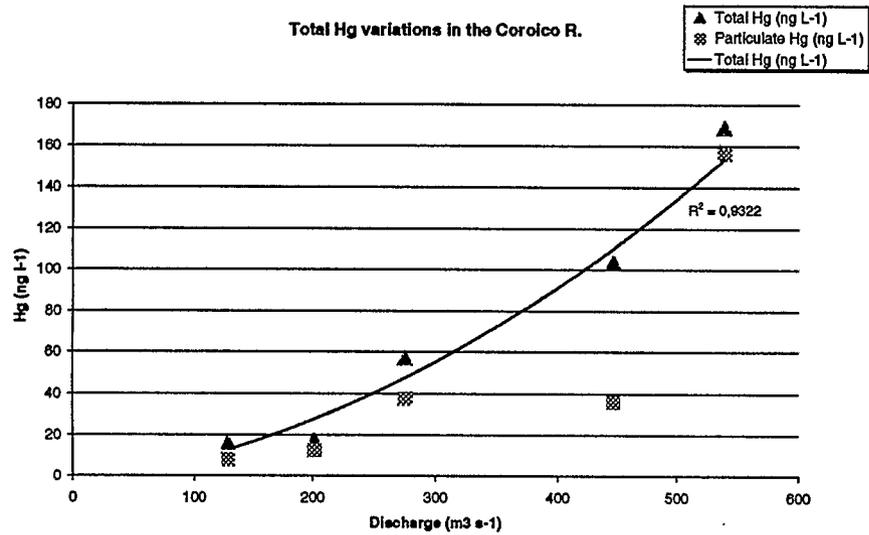


Figure 2. Temporal variability and hydrological control of the total and particulate mercury in the Coroico River, Bolivian subAndes.

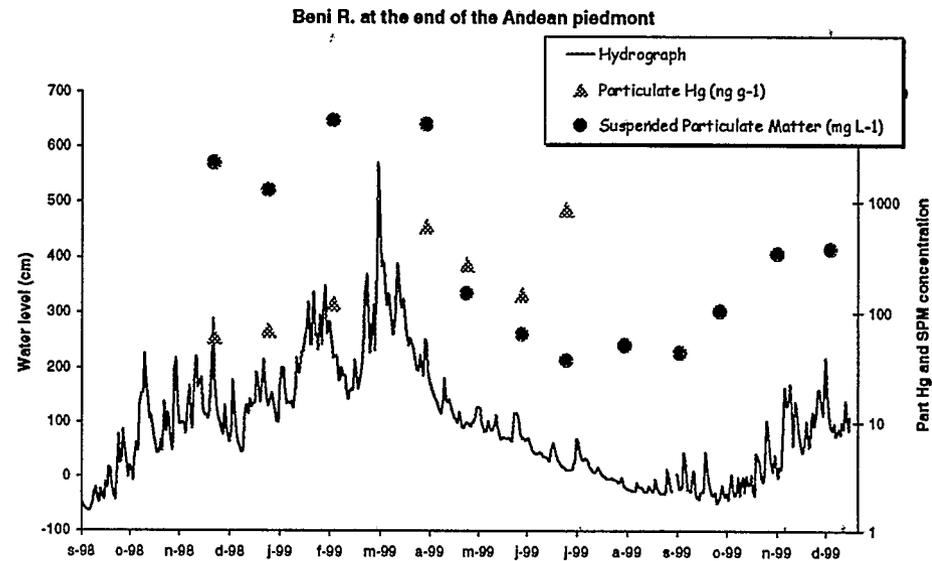
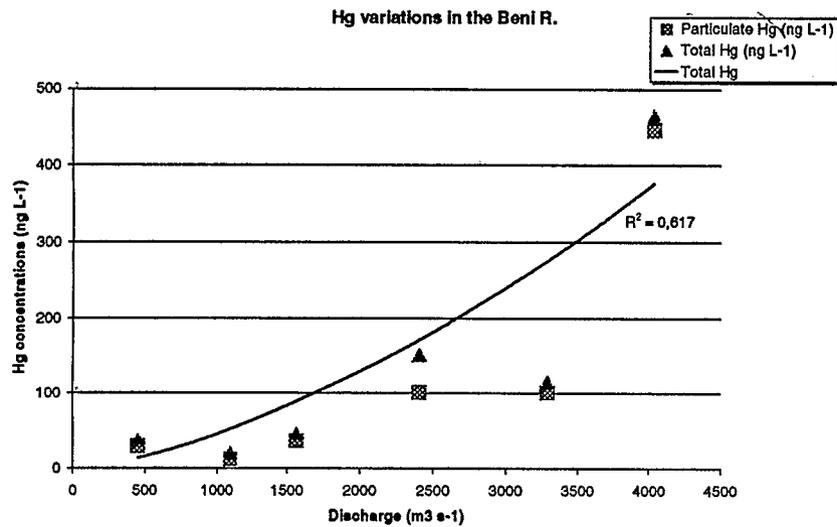


Figure 3. Temporal variability and hydrological control of the total and particulate mercury in the Beni River, edge of the subAndes.