



Geochemistry of mercury in tropical swamps impacted by gold mining



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HIGHLIGHTS

- Methylation is higher in the dry season in tropical swamps sediments with lesser T-Hg.
- Mercury is mainly associated (33–43%) to the organic fraction in both marshes.
- The organic Hg is higher during the dry, whereas elemental Hg is during flooding.
- Elemental Hg is related with anthropogenic activities in upstream gold mining sites.
- High amount (>15%) of labile Hg species poses a potential risk to biota and humans.

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ABSTRACT

Artisanal and small-scale gold mining (ASGM) poses a serious threat to the local environment. Colombia has very active ASGM activities, where mercury (Hg) ends in piles of mining waste, soils, and waterways. In this study, we assessed Hg speciation and bioavailability in sediments of two tropical swamps, impacted by ASGM. In Ayapel swamp, total Hg (T-Hg) concentrations in sediments ranged between 145 and 313 ng g⁻¹ dry weight (dw) (mean: 235 ± 49 ng g⁻¹ dw), whereas Grande Achi swamp levels are 3-fold higher (range: 543–1021 ng g⁻¹ dw; mean: 722 ± 145 ng g⁻¹ dw). Even though lower levels of Hg were found in Ayapel, methylation was found to be significantly higher than in Grande Achi, and it is significantly higher in the dry than in the rainy season for both swamps. This increased methylation is linked to the statistically significant correlation between T-Hg, MeHg and organic matter in the Ayapel swamp. In fact, Hg content in both swamps is mainly associated to the organic fraction (Hg-o), with a higher statistically significant difference in Ayapel (43 ± 5%) compared to Grande Achi (33 ± 5%). On the other hand, a significant percentage (30 ± 6%) of elemental Hg fraction (Hg-e) was found in Grande Achi, directly related with Hg released during the gold recovery process from upstream ASGM sites. The percentage of the bioavailable fraction (Hg-w and Hg-h) is elevated (up to 15%), indicating a potential risk to the aquatic environment and human health because these labile Hg species could enter the water column and bioaccumulate in biota.

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1. Introduction

The mercury (Hg) dynamics within the aquatic environment and especially in sediments are complex; it depends mainly on the physical, chemical and biological conditions of the environment (Bacon and Davidson, 2008). It is well established that bioaccumulation and toxicity of Hg are not related to total concentrations, but rather to the concentration of specific chemical species. Then, Hg speciation analysis in water and sediments has

been considered almost as a mandatory method to understand its mobility in the environment. Different diagrams of Hg extraction for speciation in sediments of different contaminated sites around the world have been reported (Bloom et al., 2003; Issaro et al., 2009; Yuan et al., 2010; Subirés-Muñoz et al., 2011; Coufalik et al., 2011). In tropical ecosystems, mercury contamination has been fully documented in the Amazon river basin (Beras et al., 2010), but very few works have been undertaken in other tropical areas where gold mining activities are abundant and information about the real impacts of Hg pollution is scarce. Northern Colombia is a particular case, where the Cauca and Magdalena rivers form a vast complex of marsh rich in biodiversity but highly threatened by the extensive activities of artisanal and

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small-scale gold mining (ASGM). In Colombia, gold mining is the major contributor to the Hg pollution (Güiza and Aristizábal, 2013) and the Mojana region is one of the ecosystems most impacted (Marrugo et al., 2008a,b; Pinedo-Hernández et al., 2014). Among the most important natural bodies of water in Colombia are the Grande Achi and Ayapel marshes, both located in the Mojana region. These ecosystems are strategic because they control flood events and regulate the water currents from the rivers, and possess a great diversity of wildlife, many of them for pivot for the survival of nearby communities. Unfortunately, these water bodies receive gold-mining residues from the Caribona and Cauca rivers, where extensive ASGM is taking place. In its watershed, gold is recovered mostly from alluvial deposits where sedimentary deposits are subjected to particle size selection and then treated with elemental Hg for gold amalgamation. Since the gold-rich amalgam is burned near the riverbanks in open air to obtain the precious metal, Hg reaches easily the aquatic environment. In sediment, Hg is present in different forms that can be bound to various matrix phases, such as methylmercury (MeHg) that is considered the most toxic specie due to its high mobility, bioavailability and bioaccumulation in biota (Diez, 2009; Carrasco et al., 2011). Although the amount of MeHg in sediments often represents less than 10% of THg, this harmful Hg-species readily remobilizes from the stable and less reactive sediments into the overlying water. Information on mercury chemical forms in sediment is, therefore, required in order to assess efficient abatement strategies and to predict the effect of future changes in the environment. In this sense, sequential extraction, a widely used method for Hg speciation, can provide useful information related to environmental behaviour of Hg in sediment, such as solubility, mobility, and bioavailability (Biester et al., 2000; Davidson et al., 2006; Pinedo-Hernández, 2014). Therefore, in order to understand Hg dynamics and its behaviour in tropical ecosystems, the main aim of this study was to establish Hg levels in surface sediments in two important water bodies, its geochemical fractionation and methylation, to assess changes in Hg distribution at different sampling sites during the dry and the rainy seasons of three consecutive years (i.e. 2010, 2011, 2012).

2. Materials and methods

2.1. Study area

The samples used in the present study were collected in swamps in the Mojana region (Fig. 1). This is located in northwestern part of Colombia with an area of approximately 5500 km², surrounded by three main rivers (Magdalena, Cauca and San Jorge) and crossed by many channels that drains the area in flooding times, which occurs mainly in the western part of San Jorge river basin, which is one of the most important swampy complexes in the country. This receives loads contaminated with Hg from Cauca and Caribona rivers during the rainy season, due to that these rivers transport waste from the largest mining gold area in Colombia (i.e. South of Bolivar and Northeast of Antioquia). The Ayapel swamp is located in the southwestern part of the Mojana (8°17′–8°24′N and 75°4′–75°9′O) with an approximate area of 120 km², in which several streams and creeks converge, and communicates with San Jorge river by the northern part through Caño Grande. The Grande Achi swamp is located in the southeastern part of the Mojana (8°19′–8°22′N and 74°29′–74°32′O) on the basin of Cauca river, receives waters from Caribona river and communicates with Cauca river by a stream in the western part (DANE, 1999).

2.2. Sample collection

Sampling was conducted at 3 and 11 sampling stations in Grande Achi and Ayapel swamps, respectively, from 2010 to

2012, covering both the dry and rainy seasons (Fig. 1). At each station four subsamples were collected at all cardinal points, within a radius of 3 m from a reference point, and a representative composite sample per station was generated by mixing the samples. Sediments samples were taken in the first 5 cm of surface layer with a Van Veen dredge launched from a boat, and only the central part of the sediment sample was collected, to avoid possible sample contamination with the walls of the dredge. Samples were placed in plastic bags, labeled, packed in ice, transported to the laboratory, and dried in an oven at 40 °C for 48 h (Canário et al., 2007).

2.3. Sample analysis

T-Hg concentrations were determined following US EPA recommendations. First, sediment samples (0.5 g) were digested with mercury-free H₂SO₄/HNO₃ 7:3 v/v and 5% w/v KMnO₄ at 100 °C for 1 h (Sadiq et al., 1991). A five-step sequential extraction scheme (Bloom et al., 2003) was used to study the fractionation of mercury in the sediments as previously described elsewhere (Pinedo-Hernández et al., 2015). Therefore, water soluble (Hg-w), human stomach acid soluble (Hg-h), organo-chelated (Hg-o), elemental mercury (Hg-e) and mercuric sulfide (Hg-s) fractions were extracted in this order and determined. T-Hg analysis was performed by cold-vapor atomic absorption spectroscopy (CVAAS) using a Thermo Elemental Solaar S4. MeHg was determined using a method described by Caricchia et al. (1997) and modified by us. An aliquot of dry sediment (2.0 g) was weighed and extracted with 5 mL KOH/CH₃OH (25%) in ultrasonic bath (45 min). After cooling, 5 mL of H₂SO₄ (4 M, saturated with CuSO₄), 5 mL of 4 M KBr and 4 mL of toluene were carefully added and the sample was manually shaken for about 3 min. After centrifugation (2200 rpm for 10 min), the supernatant organic phase was collected. The solvent extraction was repeated three times by 2 mL of toluene. The collected organic extract (10 mL) was subjected twice to a back-extraction by 1.0 mL of a cysteine solution (1.0%). The two cysteine extracts (1 + 1 mL) were collected in the same vial and extracted by a mixture of toluene (0.5 mL), CuSO₄ saturated solution (0.5 mL), and 4 M KBr (1.0 mL). After manual shaking, the organic phase was separated from the aqueous phase and 2.0 μL were injected into GC-ECD system Perkin Elmer, Autosystem XL. The organic matter (OM) was determined as percentage loss on ignition of 2.0 g of sediment in an oven at 450 °C for 4 h (Coquery and Welbourn, 1995). The pH and potential redox was determined in situ sediment with a combination glass electrode pH meter and electrode redox coupled to a computer (WTW, 330i).

2.4. Quality assurance

The method was validated with a certified reference material (IAEA-405, T-Hg 810 ng g⁻¹ and MeHg 5.49 ng g⁻¹). The percentage of recovery was 98.0 ± 0.2 for T-Hg and 97.2 ± 0.5 for MeHg. The limit of detection, defined as the mean background noise in a procedural blank triplicate plus three times the standard deviation of the background, was 14 ng g⁻¹ and 2.5 ng g⁻¹ dry weight (dw), for T-Hg and MeHg, respectively. The sequential extraction method showed no statistically significant differences (*p* < 0.05) between ∑Hg of the learned fractions and the T-Hg concentrations determined by digestion of the sediments, showing that the method used presented good precision (<2.5%) and accuracy (<5.0%).

2.5. Statistical analysis

Results for each sample were calculated as the mean ± SD (standard deviation from triplicate determinations). A Student's *t*-test was used to evaluate if there were significant differences between

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