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# Amazonian former gold mined soils as a source of methylmercury: Evidence from a small scale watershed in French Guiana

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ABSTRACT

Total mercury (HgT) and monomethylmercury (MMHg) were investigated in a tropical head watershed (1 $km^2$) of French Guiana. The watershed includes a pristine area on the hill slopes and a former gold mined flat in the bottomland. Concentrations of dissolved and particulate HgT and MMHg were measured in rain, throughfall, soil water and at three points along the stream. Samples were taken in-between and during 14 storm events at the beginning and middle of the 2005 and 2006 rainy seasons. Dissolved and particulate HgT concentrations in the stream slightly increased downstream, while dissolved and particulate MMHg concentrations were low at the pristine sub-watershed outlet (median = 0.006 ng $L^{-1}$ and 1.84 ng $g^{-1}$, respectively) and sharply increased at the gold mined flat outlet (median = 0.056 ng $L^{-1}$ and 6.80 ng $g^{-1}$, respectively). Oxisols, which are dominant in the pristine area act as a sink of HgT and MMHg from rain and throughfall inputs. Hydromorphic soils in the flat are strongly contaminated with Hg (including $Hg^0$ droplets) and their structure has been disturbed by former gold-mining processes, leading to multiple stagnant water areas where biogeochemical conditions are favorable for methylation. In the former gold mined flat high dissolved MMHg concentrations (up to 0.8 ng $L^{-1}$) were measured in puddles or suboxic soil pore waters, whereas high dissolved HgT concentrations were found in lower Eh conditions. Iron-reducing bacteria were suggested as the main methylators since highest concentrations for dissolved MMHg were associated with high dissolved ferrous iron concentrations. The connection between saturated areas and stagnant waters with the hydrographic network during rain events leads to the export of dissolved MMHg and HgT in stream waters, especially at the beginning of the rainy season. As both legal and illegal gold-mining continues to expand in French Guiana, an increase in dissolved and particulate MMHg emissions in the hydrographic network is expected. This will enhance MMHg bio-amplification and present a threat to local populations, whose diet relies mainly on fish.



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## 1. Introduction

Mercury (Hg) contamination of Amazonian ecosystems through the use of elemental Hg for gold amalgamation has been highlighted by many scientific studies (Dorea and Barbosa, 2007; Lechler et al., 2000; Malm, 1998; Pfeiffer et al., 1993; Roulet et al., 1999b; Wasserman et al., 2003).Toxicological concerns related to high monomethylmercury (MMHg) concentrations in Amazonian fish have been evidenced for Amerindian populations whose diet relies mainly on fish (Brabo et al., 2000; Durrieu et al., 2005; Frery et al., 2001; Harper and Harris, 2008; Porvari, 1995).

The main sources of MMHg have been identified in areas where oxygen content drops sharply, such as river and lake sediments, as well as in lake water columns at the oxyclines and in temperate flooded environments (Coquery et al., 2003; Hall et al., 2008). Amazonian ecosystems combine most of the surrounding geochemical conditions favorable for Hg methylation such as high temperature, high organic matter content, abundant electron acceptors (i.e., sulfate ions and ferric iron contents), and intensive microbial activities (Benoit et al., 2003; Ullrich et al., 2001). Nevertheless, most studies performed in Amazonian watersheds have focused on total Hg distribution in waters, river sediments and soils (Barbosa et al., 2003; Dorea and Barbosa, 2007; Marchand et al., 2006; Roulet et al., 1998b) and few data are available for MMHg. It is important to gain knowledge about Hg methylation in tropical watersheds since correlations found between total Hg and MMHg concentrations are commonly weak and related to external environmental factors, such as the chemical form of $Hg^{II}$, which have a strong influence on its bioavailability for methylation (Birkett and Lester, 2005; Lambertsson and Nilsson, 2006; Ullrich et al., 2001). The presence of elemental Hg is also an important factor which must be considered in gold-mining areas, since Dominique et al. (2007) have recently shown that, under experimental conditions, the presence of elemental Hg droplets can enhance MMHg production.

In this study, we examined if MMHg was produced in flooded soils of a former gold mined area and tested in the field the experimental findings of Dominique et al. (2007) regarding Hg methylation in the presence of $Hg^0$ droplets. We focussed on particulate and dissolved HgT and MMHg outputs from a small watershed covered by tropical-humid vegetation. This watershed was chosen (i) because it includes a pristine area and a Hg contaminated former gold mined flat, and (ii) because of its small scale (1 $km^2$), which enables an optimal understanding of Hg distribution in and between the different pedological and hydrological compartments. Finally, we attempted to analyze the influence of internal (i.e., geochemical, hydrological, geomorphological) and external (i.e., seasonality) determinants on Hg methylation and emissions to the watershed's hydrological network.

## 2. Site, material and methods

### 2.1. Environmental settings

#### 2.1.1. Location

The study site is the *Combat* Creek (CC) watershed, located in French Guiana, South America (52°23′W, 4°35′N) (Fig. 1), covered by tropical rain forest. Its surface area is approximately 1 $km^2$. The climate is tropical-humid with a mean annual rainfall of 4000 mm (Barret, 2004). Precipitation mainly occurs from December to July, with May and June as the wettest months.

#### 2.1.2. Bedrock

The CC watershed is located in the 'Amina series' of the Guiana Proterozoic shield consisting primarily of dark schist and thin sandstone (Milési et al., 1995). Vast gravel deposits from ancestral rivers within the valleys contain large quantities of placer gold, derived from the weathering of gold–quartz veins.

#### 2.1.3. Soil cover

Soil associations of the CC watershed have been described in detail in a previous publication (Guedron et al., 2009). Oxisols are developed on the hill tops and on the steep upper- and middle-slopes, ultisols occur mostly on the foot-slopes, and hydromorphic soils are found in the valley referred to as "flats". A large part of the watershed was considered to be pristine while in the lowland, ancient "Long Tom" sluices, gold-bearing gravel heaps and elemental Hg droplets attest to the former gold-mining activities dating from the early 1950s.

#### 2.1.4. Hydrology

The Combat Creek is a tributary of the *Boulanger* River (BR). The CC watershed outlet exhibits a permanent discharge, in contrast to intermittent flow in upstream channels. Water discharge response to rain is progressive and lasting, with a high amplitude at the outlet, contrary to upstream and midstream sections, where the response is rapid and short with low amplitude. Surface runoff is visible during heavy rainfalls on the steep hill slopes (often between 15 and 30%). In the former gold mined flat, due to the disorganized original topography, the flow is fractionated into a web of small creek tributaries and multiple stagnant water zones which are not always linked to each other or connected to the hydrographic network.

### 2.2. Sampling procedure

Four points were monitored along the streams (Fig. 1): PS (pristine spring) is a spring of the CC which drains a small subwatershed and only flows during the rainy season; MS (middlestream) and CO (contaminated flat outlet) are respectively in the upstream and downstream part of the former gold mined flat; BR is located on the Boulanger River, upstream the confluence with the CC (Fig. 1). Rain and stream waters were sampled during and between fourteen rain events at the beginning (08th, 09th and 13th December 2005; 08th, 09th and 12th December 2006) and in the middle of the rainy season (24th, 25th, 27th and 30th May 2005; 18th, 20th, 21st and 25th June 2006). In addition, several superficial stagnant water areas of the former gold mined flat were sampled, as well as the hydromorphic soil's pore waters. Metacrylate-lined rain gauges were set up close to each sampling point to measure rainfall under forest cover and to collect throughfall samples after each rain event. At the pristine spring, an additional rain