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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.

Highlights :

► Mercury and monomethylmercury were investigated in a tropical head watershed of French Guiana. ► The pristine area covered by oxisol acted as a sink for both species from rain and throughfall inputs. ► Hg contaminated soils of the former gold-mining flat were identified as a source of methylmercury. ► Monomethylmercury was mainly produced at the beginning of the rainy season and released latter on. ► As gold-mining continues to expand, an enhancement of methylmercury bio-amplification is expected.

Keywords : Mercury; Methylmercury; Tropical watershed; Gold placers; Stream water; Oxisols; Hydromorphic soils

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 et al., 2007, Lechler et al., 2000, Malm, 1998, Pfeiffer et al., 1993, Roulet et al., 1999b, Wasserman et al., 2003).Toxicological concerns related to high monomethyl-mercury (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 et al., 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 favourable 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 et al., 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 et al., 2005, Lambertsson et al., 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 goldmined flat, and (ii) because of its small scale (1 km²), which enables an optimal understanding of Hg distribution in and between the different pedological and hydrological compartments. Finally, we attempted to analyse 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

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 km². 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.

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.

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.

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 (S) of the CC which drains a small sub-watershed 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 12^{sd} 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 rain fall under forest cover and to collect throughfall samples after each rain event. At the pristine spring, an additional rain gauge was set up outside the forest cover to collect rain

samples. The creek flow was gauged using a C2 OTT® current meter set, a mobile decameter and vertical ladders, as described by Herschy (1995). Mercury specific fluxes were calculated using discharge and Hg concentration data obtained during and between rain events, and considered the surface area of upstream watersheds.

On the CC watershed, soil profiles next to PS, MS and CO were sampled systematically along toposequences (Fig. 1). The toposequences next to the MS and CO reached the gold-mined flats. Soil samples were collected, every 10 or 20 cm depths, down to 1 to 2 meters, using an auger. All soil samples were collected in sterile plastic bags.

Water sample collection and treatment were performed using ultra-clean techniques (Cossa et al., 2000). All materials in contact with samples were acid-washed (5 days in 20% HNO_3 v/v, then 3 days in HCl 10 % v/v) and rinsed several times with demineralized water (Milli-Q®) before use. Polyethylene gloves were used for handling operations. Clean Teflon® (FEP) bottles were stored in double polyethylene bags until use. Aliquots for total dissolved mercury ($(HgT)_D$) and dissolved methylmercury ($(MMHg)_D$) analysis were collected in FEP bottles and acidified (HCl 0.5 % v/v, Millipore Seastar) after filtration on 22-mm-filters (0.45 µm Sterivex®-HV) (Parker et al., 2005). Dissolved Organic Carbon (DOC) samples were stored in Pyrex® bottles (previously heated at 500°C) and acidified (HCl 1 % v/v, Millipore Seastar) after filtration (0.45 µm Sterivex®-HV). Total particulate mercury ($(HgT)_P$) and methylmercury ($(MMHg)_P$) samples were obtained by filtration on 47-mm-diameter filters (0.45 µm hydrophilic - LCR Teflon®) (Cossa et al., 1996). All samples for major elements were filtered (0.45 µm PVDF). Samples for cations analysis were acidified (HNO_3 2 % v/v, Seastar), and samples for anion analysis were stored in polyethylene bottles and frozen until analysis. Particulate Organic Carbon (POC) samples were obtained through filtration (0.7 µm GF/F®, Whatman).

Interstitial soil waters were sampled using Milli-Q® rinsed microporous polymer tube samplers (Rhizon® SMS, Rhizosphere Research Products). The samplers were placed on the CC bank between the stream sampling points. One interstitial soil water profile was sampled using dialysis membrane techniques (metacrylate peeper) with a 0.45 µm HAWP membrane. The peeper was first acid washed as described above, then filled with Milli-Q® water and degassed with Hg-free nitrogen during a 15-day period. The peeper was placed in a hydromorphic soil from the former gold mined flat for 15 days for osmotic equilibration. The Eh profile was monitored several centimeters away from the peeper on the last day of equilibration just before the removal of the peepers. The sulfide-accumulating zone (SAZ) was identified with sulfide-sensitive sellotape (fixed on the peeper), through the formation of a surface darkening Ti-S complex (Jezequel et al., 2007). Aliquots for $(MMHg)_D$, DOC, anions, sulfides and (Fe^{II}) analysis were sampled in peeper cells every 3 cm and stored as previously described.

2.3 Analytical measurements

Soil analysis: Soil samples were freeze-dried, sieved, and the fraction < 2 mm was crushed to grain size smaller than 63 µm for Hg analysis. Total Hg concentrations ([HgT]) were determined by atomic absorption spectrophotometry after dry mineralization and gold amalgamation with an automatic mercury analyser (Altec, Model AMA 254) with a relative precision of ± 10 % (Roos-Barraclough et al., 2002). Concentrations obtained for repeated analyses of certified reference materials (CRM) never exceeded the range of concentration given for standards CRM 7002 (0.09 ± 0.012 µg g^{-1} - Czech Metrological Institute) and MESS-3 (0.091 ± 0.008 µg g^{-1} - National Research Council of Canada). The analytical quality was assured by analyzing every sample twice. Typically, the measurement error is usually about 5% and always below 10%. The detection limit, defined as three times the standard deviation of the blank (SD_{blk}), was 0.005 µg g^{-1}.

Water analyses: Samples were analysed for [$(HgT)_D$] and [$(HgT)_P$], [$(MMHg)_D$] and [$(MMHg)_P$] by cold vapor atomic fluorescence spectrometry (CVAFS) after conversion of all mercury species into Hg^0 (Bloom et al., 1988) followed by detection using a Tekran® (Model 2500) mercury detector. The principles of the methods used originate from the Bloom and Fitzgerald (1988) gold amalgamation method for $(HgT)_D$, from the Liang et al. (1994) ethylation method for $(MMHg)_P$ and from the Tseng et al. (1998) hydruration method for $(MMHg)_D$ modified by Cossa et al. (2009). $(HgT)_P$ was performed after HCl/HNO_3 digestion (10h at 70°C) in PFA Teflon reactors (Coquery et al., 1997). The detailed procedures are described elsewhere (Cossa et al., 2003, Cossa et al., 2002). These quantifications were performed after checking for possible interference with the internal spikes (Coquery et al., 2003). The accuracy of analyses was checked using the CRM ORMS-3 (National Research Council of Canada) for $(HgT)_D$, CRM 7002 for $(HgT)_P$ and CRM ERM-AE670 (IRMM - European Commission) for $(MMHg)_D$ and $(MMHg)_P$. Analytical quality was assured by triplicating several samples, and the measurement error usually was approximately 10 % and always below 15% for [$(HgT)_D$], [$(HgT)_P$], and [$(MMHg)_D$] and always below 30 % for [$(MMHg)_P$]. The detection limits ($3SD_{blk}$) were 0.01 ng L^{-1} for $(HgT)_D$, 0.004 ng L^{-1} for $(MMHg)_D$, and 0.05 ng g^{-1} for $(MMHg)_P$. Dissolved chloride, sulfate and nitrate ([Cl^-], [SO_4^{2-}] and [NO_3^-]) were determined using ionic chromatography (Dionex, model CD20). Dissolved reduced iron ([Fe^{II}]) and sulfide ([S^{II}]) were measured in the field with a Hach® (model DR/850) spectrometer (methods 8146 and 8131 for [Fe^{II}] and [S^{II}], respectively). [DOC] was determined using a Non Dispersive Infra-Red CO_2 spectrometer (NDIR, Shimatzu®) after humid oxidation in a sodium persulfate solution at 100°C. [POC] was determined by dry combustion of GF/F filters, using a Fisons 1500 CHN autoanalyser. Detection limits ($3SD_{blk}$) were 0.06 and 0.05 mg L^{-1} for [SO_4^{2-}] and [NO_3^-], 0.01 mg L^{-1} for [Fe^{II}] and [S^{II}], and 0.2 mg L^{-1} for [DOC]). Eh, pH and conductivity were performed in situ using a Sentron Eh meter

(model, Argus with probe 67597), a WTW pH meter and a conductimeter (model 340i), respectively.

2.4 Use of chloride as hydrological index

Chloride (Cl^-) was used as a hydrological index to trace the proportion of mixing in the stream between recent water, generally surface runoff characterized by low [Cl^-] close to throughfall concentrations, and old water, corresponding to subsurface runoff or deep groundwater with typically higher [Cl^-] (Christophersen et al., 1990, Grimaldi et al., 2004, Peters et al., 1998, Soulsby et al., 2007). The [Cl^-] increase between both hydrological compartments is due to evapo-transpiration related to the residence time of water in the soil. Cl^- was thus used as a conservative element to compare the behaviour of the various Hg species.

2.5 Statistical treatment

Since most geochemical data were not normally distributed, we have listed in tables: the mean, the median and the standard error of the mean (SEM), and as suggested by Webster (2001), the 6 following parameters (supplementary data): the mean, the standard error of the mean (SEM), the median, 25^{th} percentiles (25^{th} perc.), 75^{th} percentiles (75^{th} perc.) and the number of observations (N). We also used non-parametric tests, the Mann-Whitney rank sum test (*U* test), or the Kruskal-Wallis one way analysis of variance on ranks (*H* test), to compare two, or more than two sets of data, respectively, and pairwise multiple comparison according to Dunn's method to isolate the set or sets that differed from the others. Correlation coefficients (R) and P values (P) are reported. All statistical analyses were performed using Sigmastat®.

3. Results

3.1 Total Hg in soils

On the slopes of the pristine part of the watershed, soil [HgT] globally decreased from oxisols to ultisols (Tab. 1), but the difference was statistically significant (*t* test, P <0.001) only for the deeper layers (> 0.5m), because [HgT] rapidly decreased with depth in the ultisols. Soil surface layer [HgT] significantly increased (*U* Test, P=0.006) from the pristine to the former gold mine flat soils (by a factor between 2 and 4 for the median values), up to a [HgT] maxima of 5.47 $\mu g\ g^{-1}$. [HgT] were highly variable over short distances and with depth in the former gold mined flat.

3.2 Total Hg in stream and rain waters

A global increase in total Hg concentrations (Tab. 2) in the CC stream waters was observed between the pristine spring (PS) and the contaminated flat outlet (CO). $[(HgT)_P]$ and $[(HgT)_D]$ significantly increased downstream (*H* test, P< 0.001) from PS to CO. On the contrary $[(HgT)_P]$ and $[(HgT)_D]$ were not significantly different between CO and BR. $[(HgT)_D]$ were higher in both throughfall and rain waters than in stream waters at PS and MS (*U* test, P<0.001), and were in the range of $[(HgT)_D]$ measured at (Tab. 2 and 3 and Fig. 2). Conversely, $[Cl^-]$ were higher in stream waters at PS than in throughfall and rain waters (*H* test, P< 0.001) due to the residence time in soil. Downstream, $[Cl^-]$ increased at CO, fed by older waters than the outlet of the pristine sub-catchment.

Most of the total Hg measured in the stream was bound to suspended particles with log partitioning coefficients ($\log K_D = \log[(HgT)_P] - \log[(HgT)_D]$) ranging from 3.8 to 8.3, with a median value of 5.9. HgT was not specifically associated with suspended organic particles since no correlation was observed between $[(HgT)_P]$ and [POC].

Seasonal variations for total Hg concentrations were noticeable at MS and CO. At PS, the absence of discharge at the beginning of the rainy season precluded water sampling and seasonal comparison. $[(HgT)_P]$ at CO were lower during the rain events at the beginning of

the rainy season than those in the middle (*U* test, P< 0.05; respective medians of 1.01 and 0.77 µg g^{-1}). $[(HgT)_D]$ at MS and CO were higher at the beginning of the rainy season than later in the season (*U* test, P<0.05) (Fig. 2). At the same time, $[Cl^-]$ decreased between the beginning and the middle of the rainy season (U test, P<0.05) due to the progressive renewal of soil waters and/or to the increase of surface water runoff in relation with intense rain events and to soil water saturation.

3.3 Methylmercury in stream and rain waters

The mean [MMHg]/[HgT] ratios in stream waters equalled 2 % and 1 %, for the particulate and dissolved phases, respectively. For total Hg, a large downstream increase was observed for MMHg concentrations between the pristine sub-watershed and the contaminated flat (Tab. 2). $[(MMHg)_P]$ were similar at PS, MS and BR but higher at CO (*H* test, P<0.001), with a 3 times median increase between PS and CO. $[(MMHg)_D]$ measured at PS and MS were very low, often under the detection limit (<0.004 ng L^{-1}), but significantly increased at CO (*H* test, P< 0.001), with a high variability. $[(MMHg)_D]$ at BR ranged between the concentrations measured at PS, MS, and CO. In rain samples, $[(MMHg)_D]$ were not significantly different than those in throughfalls, however, both were a slightly larger than the concentrations measured in PS stream waters (Tab. 3).

MMHg had a strong affinity for particulate organic matter since log partitioning coefficients ($logK_D=log[(MMHg)_P]-log[(MMHg)_D]$) were high (between 7.4 and 9.5), and $[(MMHg)_P]$ measured at CO were correlated with [POC] (R = 0.457, P< 0.05, N=24). $[(MMHg)_P]$ monitored at CO were lower at the beginning than in the middle of the rainy season (*U* test, P< 0.001; respective medians of 12.26 and 5.59 ng g^{-1}), as opposed to $[(MMHg)_D]$ which was highly variable but globally higher (*U* test, P< 0.001) at the beginning of the rainy season than in the middle.

3.4 Dissolved total and methyl mercury in soil waters of the gold mined flat

$[(MMHg)_D]$ measured in various locations of the former gold mined flat area largely exceeded those measured in the pristine area for both overlying and subsurface soil pore waters (Tab. 3, Fig. 3). The highest $[(MMHg)_D]$ were related to slightly negative or positive Eh values and high $[Fe^{II}]$. They also were associated with pH values between 5 and 6, while pH values measured in stream waters ranged from 4 to 5. High $[(HgT)_D]$ also were found in these soil waters, especially with low Eh conditions and high $[Fe^{II}]$ (Fig. 3); however, no relation was observed between $[(HgT)_D]$ and $[(MMHg)_D]$.

Figure 4 illustrates a complete vertical profile of $[(MMHg)_D]$ for both overlying and pore waters of a disorganized hydromorphic soil of the flat, sampled near an ancient sluice at the beginning of the rainy season. In this profile, $[(MMHg)_D]$ were low in the pore water and sharply increased in the overlying water. High $[(MMHg)_D]$ were found in the upper part of the SAZ where the Eh increased, and above the SAZ where $[Fe^{II}]$ sharply increased.

Both median $[(MMHg)_D]$ and $[(HgT)_D]$ in overlying soil and pore waters were higher at the beginning of the rainy season (0.27 ng L^{-1} and 4.27 ng L^{-1}, for $(MMHg)_D$ and $(HgT)_D$, respectively) than in the middle of the rainy season (0.11 ng L^{-1} and 1.60 ng L^{-1}, for $(MMHg)_D$ and $(HgT)_D$, respectively - *H* test, $P<0.01$).

4. Discussion

4.1 Oxisols as a sink of total mercury and methylmercury in the pristine area

In the pristine area of the CC watershed, the decreasing $[(HgT)_D]$ with increasing $[Cl^-]$ found between rain or throughfall waters and the stream (Fig. 2) is due to the adsorption of Hg on oxisol components during water percolation. The strong adsorption capacity of oxisols

300 already was observed in another study on the Hg distribution in oxisols at the same site
301 (Guedron et al., 2009).
302 The comparison of our data with those of other studies showed that in rain and throughfall
303 waters, $[(HgT)_D]$ were within the range of reported concentrations for 83 rain events (2.34 ±
304 0.27 ng L^{-1}) monitored in French Guiana (Muresan et al., 2007b) and that $[(MMHg)_D]$ were
305 within the range of concentrations published for temperate regions (Lawson et al., 2001) and
306 for 50 rain events (0.03 ± 0.09 ng L^{-1}) monitored in French Guiana (Muresan et al., 2007b). In
307 spring waters, $[(HgT)_D]$ were similar to concentrations reported for larger Amazonian rivers
308 (0.4 to 2.8 ng L^{-1} in Lechler et al., 2000, Roulet et al., 1998a) and $[(MMHg)_D]$ were within the
309 range of concentrations reported by several authors (Bisinoti et al., 2007, Roulet et al., 1999a)
310 for large Amazonian rivers (0.02 to 0.24 ng L^{-1}) and for large French Guiana rivers (0.06-0.10
311 ng L^{-1} according to Muresan, 2006, Roulet et al., 1999a). These comparisons confirm that
312 tropical soils act as a sink for Hg and regulate Hg fluxes towards small as well as large
313 hydrosystems (Roulet et al., 2001).
314

315 **4.2 Evidence of soil total mercury contamination in the former gold mined flat**

316 The [HgT] reaching up to 100 times the values reported from pristine hydromorphic soils in
317 French Guiana (Guedron et al., 2006) demonstrates the large contamination of the former
318 gold mined flat by mercury. This large Hg contamination of the flat explains the downstream
319 increase of $[(HgT)_P]$ along the stream (Tab. 2), which carries an increased proportion of
320 contaminated particles from the pristine spring to the flat outlet. $[(HgT)_P]$ in suspended
321 particles are higher than in the soil surface (Tab. 1 and 2), since suspended particles consist of
322 the soil's finest granulometric fraction, which are enriched in Hg (Grimaldi et al., 2008). In
323 contrast, $[(HgT)_P]$ monitored at the outlet of the pristine sub-catchment are within a similar

range of reported data from larger Amazonian rivers (0.11 to 0.36 µg g^{-1} in Lechler et al., 2000, Roulet et al., 1998a).

4.3 Hydromorphic soils as a source of methyl mercury for the stream

While the downstream increase in $[(HgT)_P]$ and $[(HgT)_D]$ is gradual until reaching the watershed outlet, the sharp increase in $[(MMHg)_P]$ and $[(MMHg)_D]$ between MS and CO suggests a particularly strong MMHg input from the contaminated flat. Both $[(MMHg)_P]$ and $[(MMHg)_D]$ monitored at the outlet of the watershed exceeded the range of concentrations given in the literature cited above for large Amazonian and French Guiana rivers, including the Boulanger river (Muresan, 2006, Roulet et al., 1999a). Puddles and pore waters of hydromorphic soils are the most probable MMHg sources in the flat.

The numerous locally isolated water puddles in the flat are attributed to former mining activities which have strongly disturbed the flat's topography. The former "Long Tom" mining process and stream tapping, which was shifted laterally by miners along the flat, have led to a web of small creek tributaries and to multiple stagnant water areas which are not always connected to the hydrographical network. The intense disturbance of soil structure leads to local drainage deficiency reflected by the presence of quasi-permanently flooded soils. Because the ancient gold-mining activities, such as gold amalgamation and burning of amalgams, were performed on site, Hg contamination in the flat is due both to the loss of Hg^0 droplets, and to the rapid deposition of atmospheric Hg in the local environment. This explains the high variability of [HgT] in soils. In addition, Hg was observed to be present mainly in its elemental form in these contaminated soils (Guedron et al., 2009). The high $[(MMHg)_D)]$ monitored in various locations of the flat corroborates the laboratory simulation of gold-mining activities (Dominique et al., 2007), which indicated that the presence of Hg^0 can enhance Hg methylation in the Amazonian environment. The local soil disturbance

favours the existence of high methylation areas. In hydromorphic soils and isolated puddles, water residence time can be long, which induces anoxic conditions and high concentrations of dissolved elements. Low Eh, pH between 5 and 6, iron oxides, high concentrations of DOC, SO_4^{2-} and $(HgT)_D$ are favorable for methylation (Benoit et al., 1999, Benoit et al., 2003, Bisogni et al., 1975, Mason et al., 1995). Under these conditions iron-reducing as well as sulfate-reducing bacteria (IRB and SRB, respectively) are reported to be the main mercury methylators (Barkay et al., 1997, Fleming et al., 2006). The increase of $[(MMHg)_D]$ within the 10 first centimetres of overlying waters with high dissolved $[Fe^{II}]$, and to a lesser extent in the upper SAZ in soil pore waters (Fig. 4) reinforces the hypothesis of a contribution of IRB and SRB in the methylation, as supported by archetypal chemical changes where microorganisms shift from FeOOH(s) to SO_4^{2-} as an electron acceptor. The occurrence of high $[(MMHg)_D]$ with high $[Fe^{II}]$ suggests a greater availability of $(HgT)_D$ for IRB than for SRB in the SAZ, since in absence of sulfides, the adsorption and co-precipitation of Hg(II) onto FeS(s) is restricted (Fink, 2002, Mehrotra et al., 2003, Mehrotra et al., 2005). The striking feature of high $[(MMHg)_D]$, associated with slightly negative or slightly positive Eh values measured in various overlying and soil pore waters of the flat (Fig. 3 and 4), corresponds well with the observations made in lake sediment/water interfaces (Birkett et al., 2005, Muresan et al., 2007a, Muresan et al., 2007b, Ullrich et al., 2001).

4.4 Seasonal influence on MMHg emissions to the stream.

The favourable geochemical conditions for mercury methylation can occur during the dry season when they are favoured by a long residence time of water in puddles and soils of the gold mined flat. At the beginning of the rainy season $(MMHg)_D$ is discharged by pulses during rain events which leads to high concentrations in the stream. In the middle of the rainy season the decrease of $[(MMHg)_D]$ is due both to unfavourable methylation conditions and

374 global dilution, as indicated by [Cl^-] decrease at the same time. Similarly, the gold mined flat
375 puddles and soil pore waters are more concentrated in Cl^- at the beginning of the rainy season
376 than later (*U* test, $P< 0.05$). As for Cl^-, the renewal of stagnant overlying and pore waters of
377 the contaminated flat leads to the dilution of $(MMHg)_D$ and $(HgT)_D$, as well as other dissolved
378 elements such as DOC and SO_4^{2}. The dissolution of particulate OM and minerals, as well as
379 methylation reactions are slow reactions (Bisogni et al., 1975, Langley, 1973). Therefore,
380 since DOC is the most important complexing ligand in surface waters in the absence of
381 sulphide the bio-availability of Hg for methylating bacteria may decrease in the middle of the
382 rainy season (Benoit et al., 2003, Ullrich et al., 2001). The change in geochemical conditions
383 such as the decrease of pH and conductivity and the increase in Eh from the beginning to the
384 middle of the rainy season, also limits bacterial activity and Hg availability, which can lead to
385 the decrease of methylation rates (Birkett et al., 2005, Ullrich et al., 2001).
386
387 **4.5 Hg and MMHg export from the CC watershed to the stream**
388 The comparison of (HgT) and (MMHg) specific fluxes between the outlet of the pristine
389 oxisol sub-watershed (PS) and the entire watershed (CO) indicates that the contribution of the
390 contaminated flat is especially substantial for (MMHg). Additionally, calculated specific
391 fluxes for both dissolved and particulate MMHg were increased by factors of 6 and 4 between
392 PS and CO, respectively (*U* tests, $P\leq0.001$ - Tab. 4), while those for $(HgT)_D$ and $(HgT)_P$ were
393 within the same range and doubled (*U* test, $P=0.043$) between PS and CO, respectively. The
394 estimation of annual specific fluxes from the CC watershed highlights its large contamination,
395 all the more since the flat's contribution is diluted by the fluxes originating from the pristine
396 soils which cover the majority of the watershed and act as a sink for Hg and MMHg .
397 The comparison of our data with calculated fluxes in other Amazonian locations corroborates
398 this point. For example, the annual $(HgT)_P$ export at the outlet of the CC watershed (mean =

399 93 ± 37 µg m^{-2} yr^{-1}) is much larger than the fluxes (2.6 - 8.5 µg m^{-2} yr^{-1}) calculated for a small
400 forested Amazonian area (1.6 km^2), located far from gold-mining activities (Fostier et al.,
401 2000), and for fluxes (30 to 35 µg m^{-2} yr^{-1}) measured for the large Cururai floodplain system
402 (Maia et al., 2009) where the large size of the basin (3800 km²) may dilute the fluxes
403 originating from gold mined areas significantly. Our data also exceed the range of fluxes
404 found for the Seine river (Coquery et al., 1997) and for urban-type watersheds (0.2 - 20 µg m^{-2}
405 yr^{-1}) according to the Wisconsin's US system of rivers classification (Hurley et al., 1995).
406 No MMHg fluxes are available for Amazonian watersheds. However, a comparison with
407 boreal and temperate environments shows that the $(MMHg)_P$ exported from the CC watershed
408 (mean fluxes = 0.68 ± 0.12 µg m^{-2} yr^{-1}) is larger compared to fluxes (0.02 to 0.183 µg m^{-2} yr^{-1}) measured for a selection of sixteen US streams (Balogh et al., 2005, Brigham et al., 2009).
409
410

411 **5. Conclusions**

412 This study shows that, even 60 years after exploitation, former gold-mining activities largely
413 contribute to the in-stream load of MMHg, whereas their contribution for total mercury
414 remains moderated. Hydromorphic soils, disturbed and strongly Hg contaminated (including
415 Hg^0 droplets) by former gold-mining, were identified as the main sources of MMHg.
416 Methylation was suggested to be induced mainly by IRB during the dry season when the
417 surface and pore waters are stagnant, whereas emissions of MMHg occurred during rainy
418 season events when these waters are discharged into the stream.
419 Such former goldmines can still contribute to MMHg inputs in larger hydrological systems.
420 Numerous former and current artisanal or semi-industrial goldmines exist in French Guiana
421 and elsewhere in Amazonia, but these areas are rarely mapped or referenced. Thus, the
422 evaluation of the real contribution of these former activities is sorely quantifiable and
423 suggests that it is an important contributor of MMHg emissions in Amazonian hydrosystems.

The continuous expansion of legal and illegal gold-mining in French Guiana implies an increase in dissolved and particulate MMHg emissions in the hydrographic network, with an enhancement of MMHg contamination of aquatic ecosystems and the consequent increase in the toxicological threat for local human populations whose diet relies mainly on fish.

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List of tables:

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Table 3. Rain, throughfalls, stagnant (overlying) waters and pore hydromorphic soil waters. Total dissolved mercury $(HgT)_D$ and dissolved monomethylmercury $(MMHg)_D$ median and mean concentrations, and SEM; presented as median / mean (SEM). Subscript 1 relates to single location of the gold mined flat between 1 and 10 cm for stagnant waters and 0 to 15 cm for pore waters, and subscript 2 relates to various locations in the gold mined flat.

Table 4. Stream waters at the outlet of the pristine oxisol sub-watershed and the entire watershed. Total dissolved mercury $(HgT)_D$, particulate mercury $(HgT)_P$, dissolved monomethylmercury $(MMHg)_D$, and particulate monomethylmercury $(MMHg)_P$ median and mean specific fluxes, and SEM; presented as median / mean (SEM).

650

Soil type	Soil depth (cm)	HgT ($\mu g\ g^{-1}$)
Oxisol (pristine slopes)	0-50	0.35 / 0.37 (0.04)
	> 50	0.42 / 0.38 (0.03)
Ultisol (pristine slopes)	0-50	0.20 / 0.25 (0.07)
	> 50	0.07 / 0.10 (0.04)
Hydromorphic soil (contaminated flat)	0-50	0.82 / 1.31 (0.35)
	> 50	0.75 / 1.01 (0.26)

651

652 Table 1. Soil total mercury (HgT) median and mean concentrations, and standard error of the
653 mean (SEM) for different soil types; presented as median / mean (SEM).

654

Sampling location:	$(HgT)_D$ (ng L^{-1})	$(HgT)_P$ (µg g^{-1})	$(MMHg)_D$ (ng L^{-1})	$(MMHg)_P$ (ng g^{-1})
PS	0.94 / 0.98 (0.13)	0.25 / 0.53 (0.13)	0.006 / 0.016 (0.004)	1.84 / 1.86 (0.37)
MS	1.34 / 2.77 (0.75)	0.61 / 0.82 (0.17)	0.009 / 0.048 (0.033)	0.75 / 0.75 (0.67)
CO	1.57 / 4.78 (1.46)	0.88 / 1.99 (0.94)	0.056 / 0.062 (0.005)	6.80 / 9.59 (1.28)
BR	1.67 / 4.94 (3.43)	1.51 / 1.42 (0.33)	0.024 / 0.025 (0.004)	1.69 / 2.67 (1.33)

Table 2. Stream water total dissolved mercury $(HgT)_D$, particulate mercury $(HgT)_P$, dissolved monomethylmercury $(MMHg)_D$, and particulate monomethylmercury $(MMHg)_P$ median and mean concentrations, and SEM; presented as median / mean (SEM).

Sampling location:	$(HgT)_D$ (ng L^{-1})	$(HgT)_P$ (µg g^{-1})	$(MMHg)_D$ (ng L^{-1})	$(MMHg)_P$ (ng g^{-1})
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Table 2. Stream water total dissolved mercury $(HgT)_D$, particulate mercury $(HgT)_P$, dissolved monomethylmercury $(MMHg)_D$, and particulate monomethylmercury $(MMHg)_P$ median and mean concentrations, and SEM; presented as median / mean (SEM).

Sampling location	$(HgT)_D$ (ng L^{-1})	$(MMHg)_D$ (ng L^{-1})
Rain (PS)	4.83 / 4.63 (0.74)	0.010 / 0.011 (0.003)
Throughfall (PS)	3.98 / 3.93 (0.68)	0.017 / 0.026 (0.008)
Soil overlying water (Pristine subwatershed)	1.70 / 3.11 (1.25)	0.005 / 0.007 (0.002)
Soil overlying water[1] (Contaminated flat)	-	0.615 / 0.670 (0.080)
Soil overlying water[2] (Contaminated flat)	2.01 / 2.01 (0.40)	0.082 / 0.243 (0.098)
Soil pore water[1] (Contaminated flat)	-	0.136 / 0.113 (0.034)
Soil pore water[2] (Contaminated flat)	2.34 / 5.49 (1.65)	0.161 / 0.231 (0.047)

Table 3. Rain, throughfalls, stagnant (overlying) waters and pore hydromorphic soil waters. Total dissolved mercury $(HgT)_D$ and dissolved monomethylmercury $(MMHg)_D$ median and mean concentrations, and SEM; presented as median / mean (SEM). Subscript 1 relates to single location of the gold mined flat between 1 and 10 cm for stagnant waters and 0 to 15 cm for pore waters, and subscript 2 relates to various locations in the gold mined flat.

Specific fluxes	PS (surface 0.12 km²)	CO (surface 1.27 km²)
$(HgT)_D$ (ng s^{-1} km^{-2})	113 / 147 (32)	117 / 628 (276)
$(HgT)_P$ (ng s^{-1} km^{-2})	517 / 1458 (521)	1104 / 2951 (1158)
$(MMHg)_D$ (ng s^{-1} km^{-2})	0.67 / 0.97 (0.30)	4.20 / 4.17 (0.51)
$(MMHg)_P$ (ng s^{-1} km^{-2})	3.5 / 4.2 (0.96)	14.0 / 21.6 (3.80)

Table 4. Stream waters at the outlet of the pristine oxisol sub-watershed and the entire watershed. Total dissolved mercury $(HgT)_D$, particulate mercury $(HgT)_P$, dissolved monomethylmercury $(MMHg)_D$, and particulate monomethylmercury $(MMHg)_P$ median and mean specific fluxes, and SEM; presented as median / mean (SEM).

Figure captions

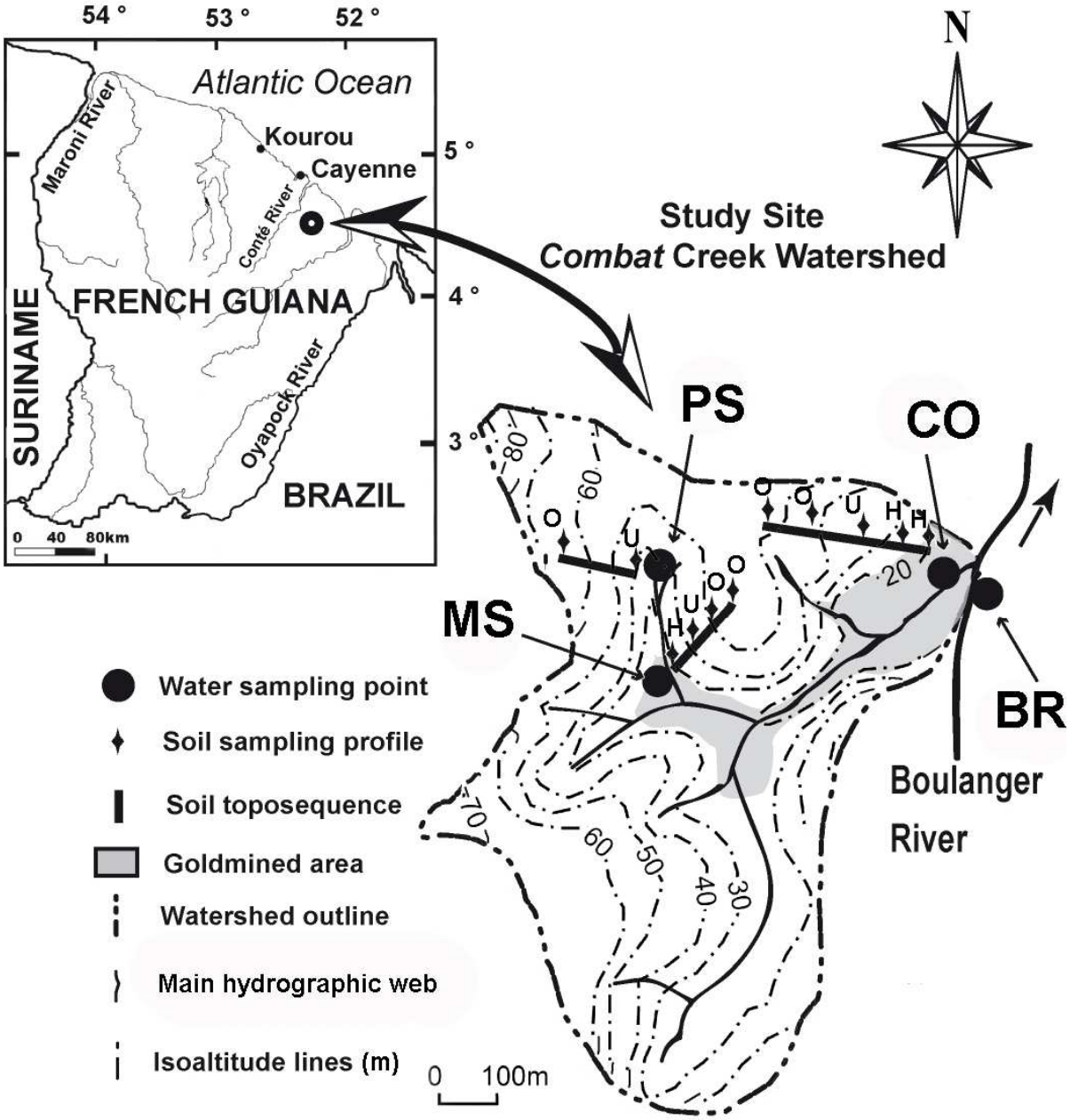
Figure 1. The watershed study site with water sampling (PS – pristine spring, MS – middlestream and CO - contaminated flat outlet, in the Combat Creek and BR-Boulanger River), soil sampling locations and soil types (O: oxisol, U: ultisol and H: hydromorphic soil).

Figure 2. Dissolved [$(HgT)_D$] and [$(MMHg)_D$] versus [Cl^-], for rain, throughfall and stream waters at each sampling location; PS, MS and CO respectively, sampled during and out of rain events at the 3 sampling points (PS, MS and CO) and at the beginning and the middle of the rainy season, respectively.

Figure 3. [$(MMHg)_D$] and [$(HgT)_D$] versus Eh and [Fe^{II}] in soil waters. Soil pore waters and overlying waters were sampled near the PS and in the former gold mined area between MS and CO, in the beginning and middle of the rainy season. Regression lines are plotted if significant ($p < 0.05$).

Figure 4. [$(MMHg)_D$] (ng L^{-1}), [Fe^{II}] (mg L^{-1}), and Eh (mV) vertical profiles and sulfide-accumulating zone (SAZ - gray color area) of the overlying (10 cm thick water puddle) and pore water of a flooded hydromorphic soil in the former gold mined area between MS and CO, at the beginning of the rainy season. Soil-water interface (0cm) is plotted as a horizontal line.

707 Figure 1.



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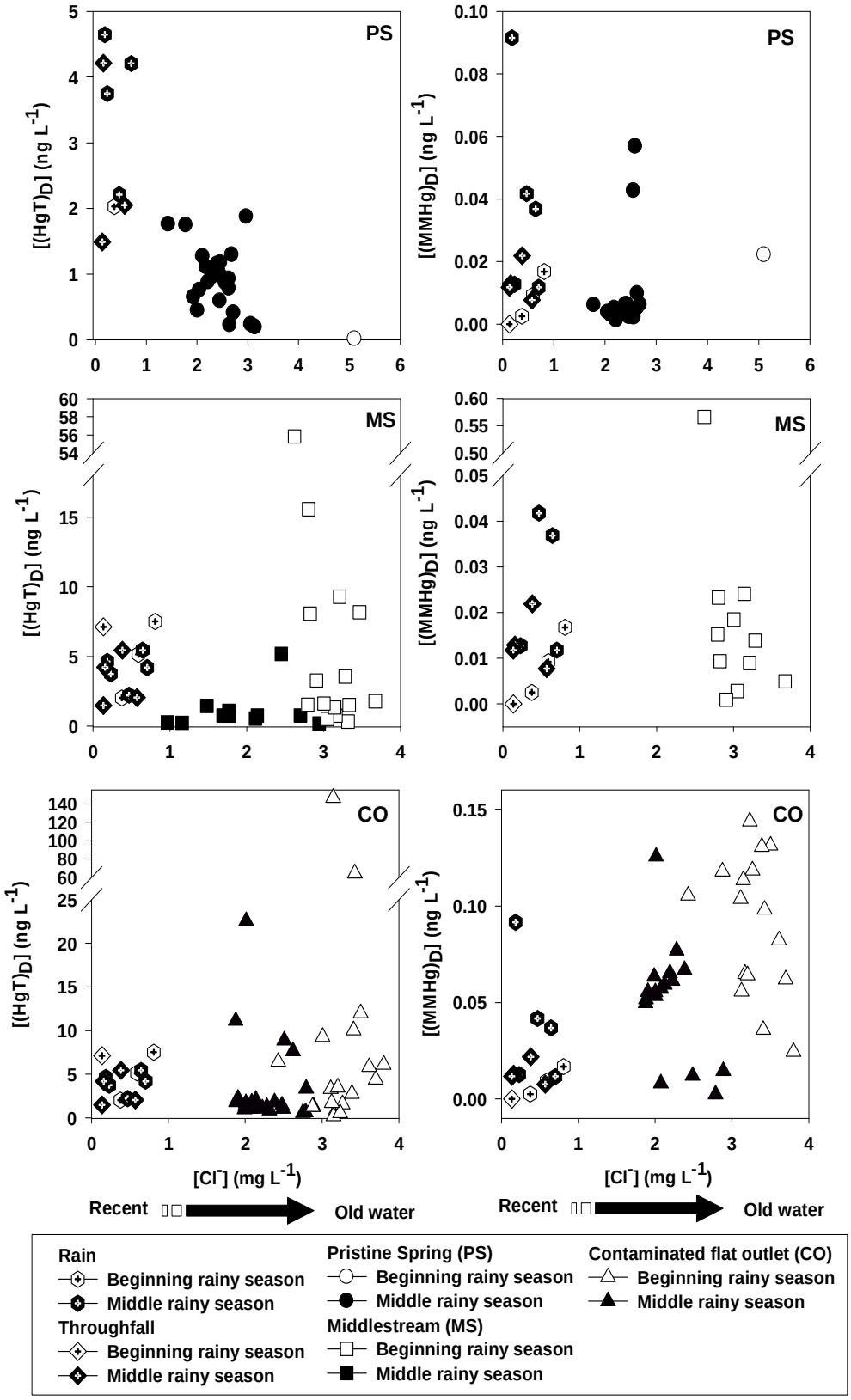
710 Figure 2.



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713 Figure 3.

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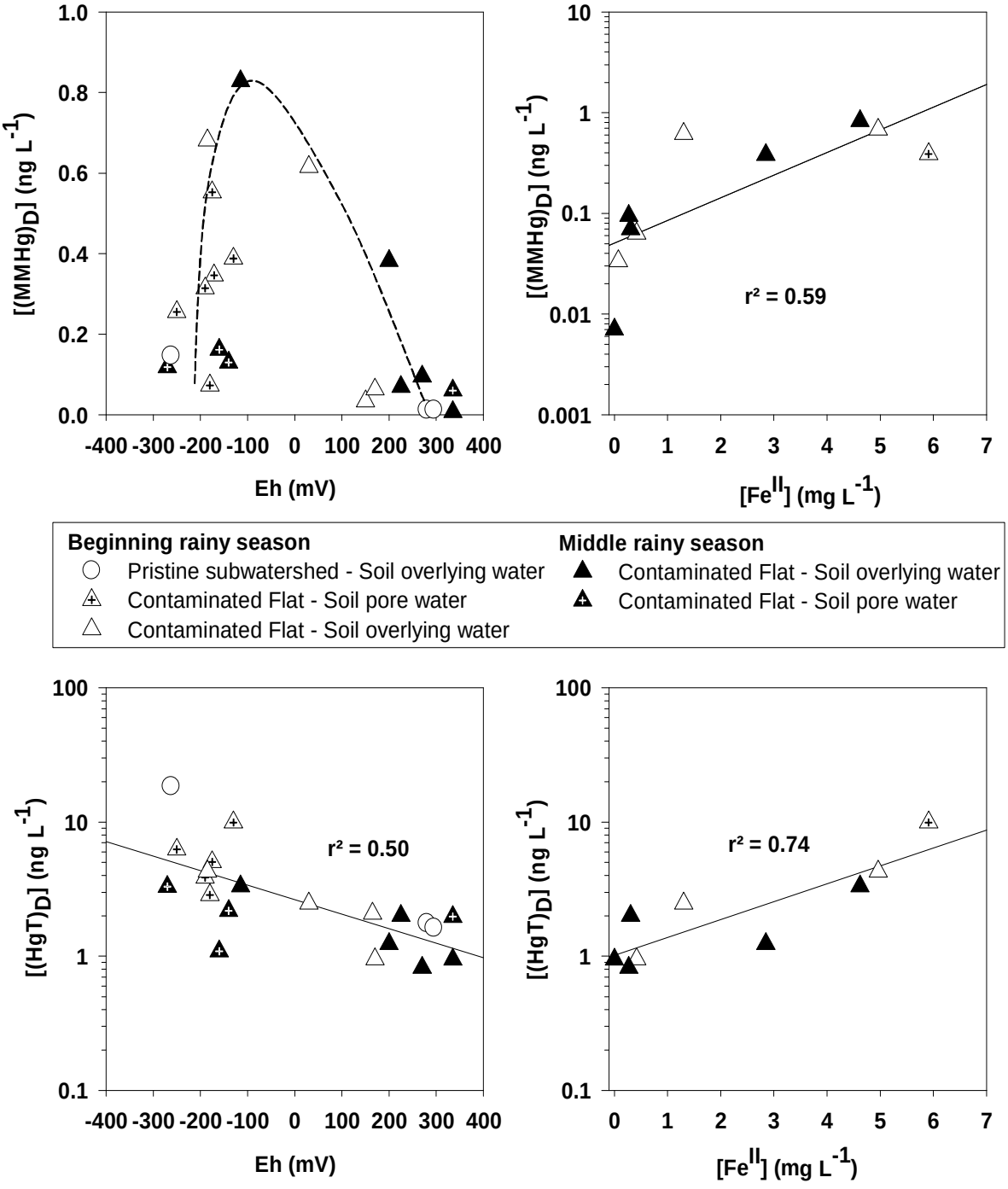

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717 Figure 4.

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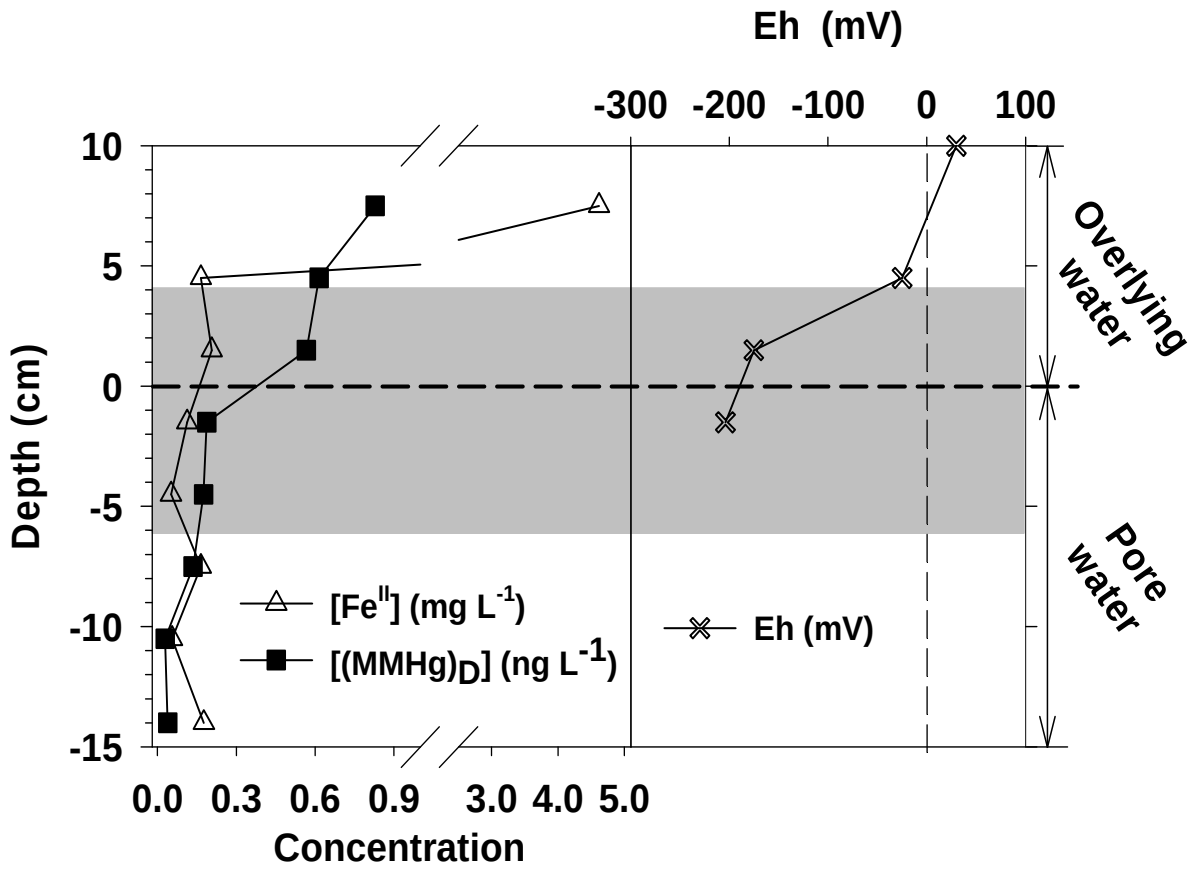

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