Quantification of methylmercury and geochemistry of mercury in sediments from a contaminated area of Descoberto (MG), Brazil

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ABSTRACT

In 2002, metallic Hg was found buried in a rural area of Descoberto city, Brazil. The origin of the Hg was a gold mining explotation plant established nearly one century ago. Although a number of studies have been conducted in order to assess the contamination of the area, none of them investigated the presence of methylated Hg in the hydric system. In this work methylmercury (CH_3Hg^+) was determined using gas chromatography-pyrolysis-atomic fluorescence detection (CG-pyro-AFS) in material from rain sedimentation boxes and stream sediments near the contaminated area. Total Hg concentration (HgT) along with the chemical speciation by thermo-desorption were performed. HgT in material from the sedimentation boxes was found to be very high, up to 41,580 $\mu g\ kg^{-1}$, even in the rainy season, when in general HgT were much lower than in dry season. The samples from the Grama and Rico streams show a range of HgT from 5.8 to 266 $\mu g\ kg^{-1}$. The thermo-desorption analysis showed predominance of Hg^{2+}, possibly linked to organic sulfur, suggested by a good positive correlation between Hg^{2+}, HgT, organic mater (OM) and total S. The CH_3Hg^+ concentration in stream sediment samples ranged from <0.07 to 1.87 $\mu g\ kg^{-1}$ and in the samples of sedimentation boxes the concentrations were 1.33 and 8.0 $\mu g\ kg^{-1}$ during dry season. The sample with the highest percentage of HgT as Hg^{2+} (98%) presented also the highest percentage of CH_3Hg^+ (0.7%). These are high values, showing that care should be taken to avoid the transport of this material to the hydrological system. Further studies on the transfer through the food chain would be very important.

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1. Introduction

The most common forms of Hg found in the environment are: Hg^0, Hg^{2+} (inorganic) and organic mercury, mostly as methylmercury (CH_3Hg^+). It is well known that the latter form is easily bioaccumulated and biomagnified in the food chain (Jenne and Luoma, 1977; Lázaro et al., 2013) and this is why this species is relevant in the cycle of this metal. Understanding the biogeochemical cycling of Hg is an important contribution to diagnose the impact of this element to humans and biota. In the atmosphere Hg can be found primarily as Hg^0 (Amouroux et al., 1999) and small amounts of CH_3HgCH_3 which

are the most volatile species of this element. The Hg^0 can be photo-oxidized to Hg^{2+} in the presence of O_3 and the CH_3HgCH_3 can be converted to Hg^{2+} by the UV radiation (Barkay et al., 2003).

After deposition on the water and on the sediments, the Hg^{2+} undergoes methylation to CH_3Hg^+, which can be re-methylated to form CH_3HgCH_3 (Barkay et al., 2003; Leopold et al., 2010). Upon entering the aquatic ecosystems, Hg can further react with various compounds in water, and therefore a portion of it precipitates on the sediment where numerous organic and inorganic reactions occur (Green-Ruiz et al., 2005). It binds primarily to organic matter and to oxides and hydroxides of Fe and Mn present in sediments (Canário et al., 2003). In this compartment, Hg^{2+} can also undergo reactions leading to the formation of HgS, CH_3Hg^+ and $(CH_3)_2SHg$ (Leopold et al., 2010). Therefore, several species with varying degrees of toxicity of this element will be in equilibrium in the environment. It is noteworthy to point out that the methylation and demethylation reactions are mainly mediated by bacteria (Barkay

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et al., 2003; Gosnell et al., 2016; Mauro et al., 1999), but information on mercury methylators in many compartments are still uncertain (Achá et al., 2011). In the Amazon, for instance, the macrophyte banks are considered an important site of mercury methylation (Achá et al., 2011; Mauro et al., 1999).

The sediment in the water system is a major sink and source of Hg, and is considered a relevant production site of CH_3Hg^+ (Canário et al., 2003; Shi et al., 2005), mainly mediated by the sulfate reducing bacteria (Achá et al., 2011). The assessment of this environmental compartment is interesting, since it can act as a good indicator of Hg input and other elements in the environment.

Hyphenated techniques are commonly used to determine CH_3Hg^+ in soil and sediment samples (Carrasco and Vassileva, 2015). Generally, they are based on separation techniques coupled with selective detector for Hg, such as gas chromatography-pyrolysis-atomic fluorescence spectrometry (GC-pyro-AFS) (Beldowski et al., 2014; Carrasco and Vassileva, 2015; Nevado et al., 2011; Oh et al., 2010); gas chromatography-inductively coupled to plasma mass spectrometry (GC-ICP-MS) (Nevado et al., 2011; Pietilä et al., 2015); and high performance liquid chromatography-inductively coupled to plasma mass spectrometry (HPLC-ICP-MS). The detection by ICP-MS usually uses the isotopic dilution method, which makes possible the investigation of formation of artifacts during the extraction of the analyte (Avramescu et al., 2010; Carrasco and Vassileva, 2015; Jagtap and Maher, 2015; Rahman and Kingston, 2004; Santos et al., 2009).

The study area, in the countryside of the municipality of Descoberto - MG, Brazil, was heavily affected by the exploitation of gold in the nineteenth century. For unclear historical reasons Hg was buried by prospectors at that time. In December 2002, the owner of the area, performing soil relocation, noticed the presence of liquid Hg (Hg^0) (FEAM and CDTN, 2006). At the time of exploitation, the amalgamation procedure was widely used to improve the gold removal efficiency (patio procedure). Consequently, part of the Hg was lost to the atmosphere as gaseous Hg in the amalgam burning process, some was dumped in rivers and some eventually left and buried there.

Confirmation of the presence of Hg in the soil of the municipality was found by three governmental state agencies (FEAM - Minas Gerais State Environmental Agency, COPASA- Minas Gerais State Water Supply Company and IGAM – Minas Gerais State Water Mangemnet Agency) and CDTN (Brazilian Nuclear Technology Company), which carried out an on-site inspection and interdicted it. Since then, various studies have been conducted in the area in order to assess the degree of contamination of the environmental compartments by HgT (Alexandre, 2006; Durão Júnior, 2010; Durão Júnior et al., 2009; FEAM, 2005; Tinôco, 2008), which observed the presence of this metal above the recommended concentration limits, i.e., 12 mg kg^{-1} (CONAMA 420/2009), for land use for agricultural purposes. This area is a very important case to be studied even today, not only for an assessment of the current situation and possible impacts to the environment but also to be used as an example for other similar cases of contamination from gold mining in Brazil and world.

The main objective of this work was to evaluate the possibility of Hg methylation in sedimentation boxes and in sediment from hydrological system around the area, and search for parameters that could be influencing this processes, as HgT, seasonality, oxidation state of the metal and chemical characterization of the sediments.

2. Methodology

2.1. Sampling and sample preparation

Fig. 1 shows the location of the Municipality of Descoberto (MG)

as well as the sampling stations. Considering that the contaminated area is located on a declivity in the direction of the Rico stream, Brazilian authorities interdicted it and built channels and sedimentation boxes in the lower part of the area in order to retain the rain water and to avoid, as far as possible, the transport of particulated material from the contaminated area into the Rico stream. In the rainy season the pluviometric precipitation is so high that part of the water of these boxes overflows and reaches the stream. Samples were taken from the two sedimentation boxes (A1 and A2) and in 6 points at the Rico stream (A5 to A10) chosen in order to assess the possible impact of the Hg transport from the sedimentation boxes which are, as stated above, in a higher topographic level. Sample A3 is located outside the interdicted area, after the junction of Rico and Grama streams (downstream). Sample A4 was taken as control, because it does not receive waters from the Rico stream.

The collection of samples was performed in August 2014 (dry season) and in December 2015 (rainy season) in order to assess the methylation in different climate conditions. A total of 18 sediment samples were collected; 14 in the streams (8 in the dry season and 6 in the rainy season) and 4 (2 in each season) were taken from the two sedimentation boxes. Collection of samples A9 and A10 in the rainy season was not carried out because of difficulties to access these stations in the rainy season 2015.

Samples were collected using an auger steel and a plastic scoop, then sieved through 2 mm sieve to discard the gravel upper size fractions and then transferred to amber glass flasks which were stored in boxes containing ice until arrival at the laboratory where they were stored at - 20 °C. In the laboratory, part of the samples were lyophilized and sent for HgT determination, Hg speciation using thermo-desorption and determination CH_3Hg^+. For chemical analysis (CHN, Total S and X-ray fluorescence), the samples were air dried.

2.2. Chemical characterization of the samples

The sediment samples were ground and sent for CHN analysis, total S and XRF. Determination of organic carbon to obtain the organic matter content in the samples was carried out in the elemental analyzer CHNS/O, Perkin Elmer, PE2400, Series II. It is noteworthy to mention that the data obtained from CHN were converted into OM and ratio of C/N (Radojević and Bashkin, 1999). The total S analysis was performed on the instrument Leco SC632. Certified standards were used for instrument calibration: Standard 502-309/1006 Soil; standard 502-318/1009 Ore Tailings Material Calibration; standard 502-319/1014 Ore Tailings Material Calibration; and standard KZK Acid Base Accounting Material CANMET.

The quantification of the concentration of metals was performed with an X-ray fluorescence spectrometer, Philips - PANalytical, Magix model PW 2540 autosampler equiped withRh 2.4 kW tube.

2.3. HgT determination and speciation by thermo-desorption/ atomic absorption

The determination of HgT and its speciation by thermo-desorption were performed in a direct mercury analyzer (DMA-80, brand Milestone, Italy). The DMA-80 uses the principle of thermal decomposition, amalgamation, amalgam thermo-desorption and determination of Hg by atomic absorption at a wavelength of 253.65 nm. The analytical curve was set up with injections of different volumes of solutions of 10 and 100 μg L^{-1} prepared from a standard solution of 1000 mg L^{-1} HgCl$_2$. The absolute Hg concentration ranged from 0 to 100 ng. The certified reference material GBW 08301 river sediment, with an HgT value of (220 ± 40) μg kg^{-1} was used to assess the accuracy of the method.
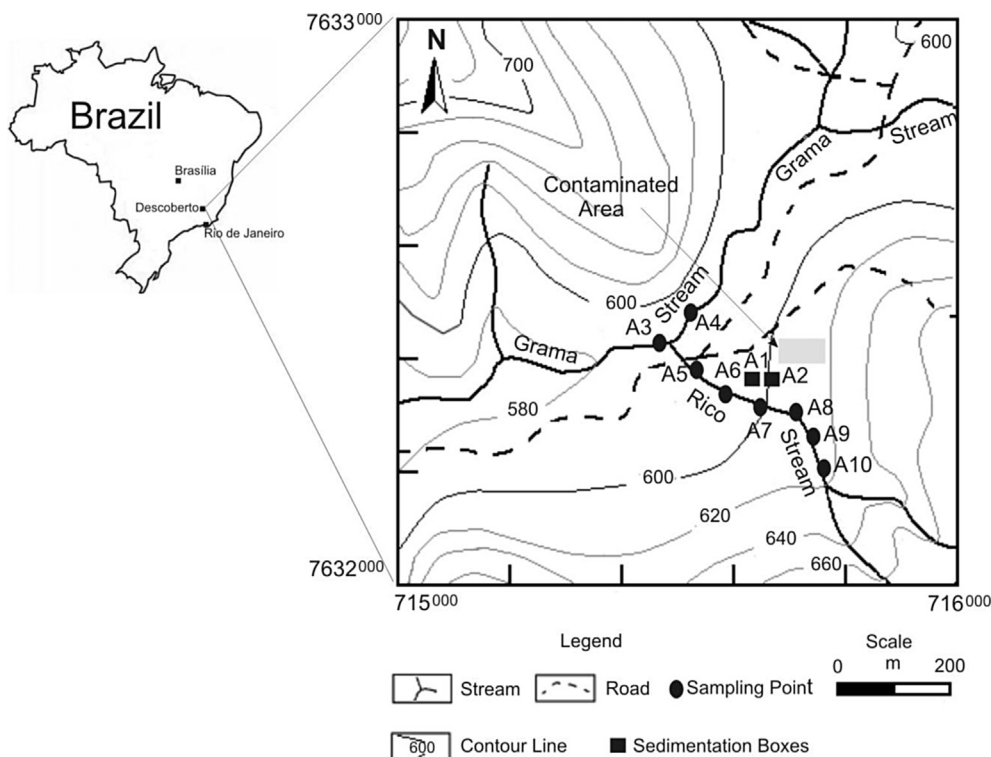
Fig. 1. Location of the Municipality of Descoberto − MG/Brazil (left). Location of the sampling stations at Grama and Rico streams (right). Coordinates are given in UTM, grid zone 23 K, datum WGS 84. Contour lines are given in meters above the sea level.

The HgT found in the certified reference material, analyzed by DMA, was (227 ± 10) µg kg^{-1}. This value corresponds to 103% recovery, showing therefore a good accuracy of the method. The detection limit (LOD) and quantitation limit (LOQ) for this technique were 0.97 and 1.07 µg kg^{-1} (for sample weight 0.3000 g), respectively.

Speciation by thermo-desorption is based on the principle that different species of Hg are released from a solid matrix by the action of heat at different temperature ranges (Windmöller, 1996). Approximately 0.3000 g of sample was weighed and subjected to different temperature levels: 50, 100, 150, 200, 250, 300, 400, 500, 600 and 700 °C for 3 min heating at each level. The results were compared with patterns of Hg species analyzed under the same conditions of the samples, such as Hg^0, HgCl$_2$, Hg$_2$Cl$_2$, HgSO$_4$ and HgS. These standards were prepared and analyzed by Windmöller et al. 2013, using solid dilution (Windmöller et al., 2013). As there is no reference material registering mercury contents in different oxidation states, we decided to make analysis of the same reference material used to validate the total Hg determination, i. e., GBW 08301 (river sediment) and compared the sum of the results of all quantification steps (from 50 to 700 °C) with the certified value for total Hg. The obtained result (224 ± 19) µg kg^{-1} was in good agreement compared to the reference value (220 ± 40) µg kg^{-1}.

2.4. Determination of CH$_3$Hg$^+$

The determination of (CH$_3$Hg$^+$) was performed on a gas chromatographer coupled to a pyrolysis system with an atomic fluorescence detection system (CG-pyro-AFS), MERX, Mark Brooks Rand Labs, USA. The analytical curve for absolute concentration from 0 to 500 pg was prepared from CH$_3$HgCl standard solution of 1000 µg L^{-1}, Brooks Rand Labs, USA. The sediment samples were subjected to a distillation system (Brooks Rand Labs) modified Horvat et al. (1993). Samples of 0.1000−0.5000 g were weighed in a teflon tube to which 30 mL of ultrapure water was added together with 500 µL H$_2$SO$_4$ 8 mol L^{-1} and 200 µL KCl 20% w v^{-1}. Teflon tubes for collection of the distillate containing 5 mL of ultrapure water were placed in an ice bath. The samples were distilled at 125 °C under a nitrogen flow of 61 mL min^{-1} during approximately 3 h after which 75% of the distillate had been collected. Then, the distillate was diluted to 50 mL and transferred to a glass jar derivatization system. To this system it was added 300 µL of sodium acetate buffer and 50 µL of sodium tetraethylborate solution (NaBEt$_4$). The set was left to stand for 17 min for the contact of the reactants (reaction time), and then purged with nitrogen gas at 91 mL min^{-1} for 25 min. Traps were dried with nitrogen gas for 6 min and analyzed individually by the thermo-desorption system coupled to a chromatographic column filled with OV-3. The GC temperature was maintained at 35 °C. Argon gas was used as mobile phase and flow rate used was 17 mL min^{-1}.

It is noteworthy to point out that the parameters of the chromatographic column (temperature GC and mobile phase flow rate) and derivatization (flow of the bubbler, trapping time, volume of sodium tetraethylborate, trap drying time, reaction time) were optimized preliminarily to analysis. For quality assurance of CH$_3$Hg$^+$ analysis in sediments, certified reference material ERM$^®$-CC580 (estuary sediment) was used, whose concentration of CH$_3$Hg$^+$ is (75 ± 4) µg kg^{-1}. The CH$_3$Hg$^+$ concentration determined in the CC580-ERM$^®$ CRM reference material was (71.1 ± 2.1) µg kg^{-1}. This value corresponds to 95% recovery and it is within the certified range. The calculated LOD and LOQ for the method for samples with mass weight of 0.5000 g were 0.11 µg kg^{-1} and 0.33 µg kg^{-1}, respectively.

Table 1
Location of the samples and results of HgT, CH_3Hg^+, percentage of CH_3Hg^+, OM, C/N, total S, XRF and percentage of species of Hg obtained from the analysis of records by thermo-desorption with temperature levels in sediment samples collected at Descoberto (MG).

	Samples	Location Grid zone 23 K	*HgT ($\mu g\ kg^{-1}$)	*CH_3Hg^+ ($\mu g\ kg^{-1}$)	CH_3Hg^+ (%)	*OM (%)	*C/N	*Total S (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	$(Hg^0 + Hg_2^{2+})$ (Up to 150° C) (%)	Hg^{2+} (labile) (200–300 °C) (%)	Hg^{2+} (>300 °C) (%)
Dry season	A1 SB	7632360/ 715634	41580 ± 5	8.0 ± 0.9	0.02	6.4 ± 0.4	8.4 ± 1.1	0.034 ± 0.007	8.25	4.32	0.036	6.1	84.4	9.4
	A2 SB	7632360/ 715669	3835 ± 7	1.33 ± 0.07	0.04	8.1 ± 0.2	8.4 ± 0.8	0.047 ± 0.002	8.47	4.38	0.059	2.2	97.6	0.2
	A3 GS	7632425/ 715472	45 ± 10	<0.11	0.19	0.61 ± 0.01	1.42 ± 0.16	0.011 ± 0.004	9.54	10.04	0.071	4.5	50.3	45.2
	A4 GS	7632488/ 715524	44 ± 5	0.21 ± 0.04	0.48	0.61 ± 0.01	1.54 ± 0.38	<0.01	8.55	9.96	0.063	7.5	43.1	49.4
	A5 RS	7632374/ 715535	44 ± 2	0.139 ± 0.009	0.32	1.16 ± 0.04	1.55 ± 0.14	<0.01	8.16	7.30	0.095	3.7	38.6	57.7
	A6 RS	7632331/ 715594	266 ± 2	1.87 ± 0.33	0.70	7.7 ± 0.2	7.3 ± 1.0	0.039 ± 0.004	19.34	14.67	0.125	2.2	92	5.8
	A7 RS	7632315/ 715640	74 ± 3	0.29 ± 0.01	0.39	1.5 ± 0.1	2.09 ± 0.67	0.0107 ± 0.0008	10.12	7.52	0.094	4.4	52.4	43.2
	A8 RS	7632299/ 715717	74 ± 1	0.23 ± 0.06	0.31	1.56 ± 0.06	2.21 ± 0.32	0.0121 ± 0.0003	12.43	9.81	0.141	1.7	30.9	67.4
	A9 RS	7632256/ 715742	175 ± 1	0.63 ± 0.09	0.36	3.8 ± 0.2	3.48 ± 0.23	0.025 ± 0.002	16.86	12.45	0.136	1.4	60.1	38.5
Rainy season	A10 RS	7632205/ 715764	141 ± 5	0.51 ± 0.11	0.36	3.7 ± 0.1	3.38 ± 0.13	0.020 ± 0.004	16.53	11.50	0.131	2.1	55.0	42.9
	A1 SB	7632360/ 715634	3581 ± 235	0.77 ± 0.12	0.02	11.7 ± 0.2	6.8 ± 1.1	0.096 ± 0.021	16.8	5.7	0.10	0.2	99.5	0.3
	A2 SB	7632360/ 715669	2312 ± 87	1.01 ± 0.13	0.04	4.31 ± 0.04	2.5 ± 0.4	<0.01	27.7	7.2	0.022	0.3	85.2	14.5
	A3 GS	7632425/ 715472	73 ± 3	<0.11	–	0.44 ± 0.01	0.25 ± 0.07	<0.01	15.1	12.6	0,093	9.7	28.3	62.0
	A4 GS	7632488/ 715524	41 ± 4	<0.11	–	0.60 ± 0.05	0.35 ± 0.09	<0.01	18.0	10.6	0.041	3.4	62.8	33.9
	A5 RS	7632374/ 715535	183 ± 5	0.35 ± 0.03	0.19	6.8 ± 0.5	4 ± 1	0.066 ± 0.0006	33.0	9.8	0.25	2.3	82.5	15.2
	A6 RS	7632331/ 715594	36 ± 1	<0.11	–	0.8 ± 0.2	0.48 ± 0.09	<0.01	18.5	7.7	0.18	11	30	59
	A7 RS	7632315/ 715640	26 ± 1	<0.11	–	0.53 ± 0.02	0.31 ± 0.07	<0.01	26.5	8.8	0.10	9.9	20.8	69.3
	A8 RS	7632299/ 715717	5.8 ± 0.9	<0.11	–	0.43 ± 0.02	0.25 ± 0.01	<0.01	17.5	8.0	0.20	16.2	25.2	58.5

SB: sedimentation boxes; GS: stream Grama; RS: stream Rico.
*mean concentration ± standard deviation (n = 3).

3. Results and discussion

3.1. HgT concentrations

Table 1 shows location of the samples and the results of HgT, CH_3Hg^+, percentage of CH_3Hg^+, organic matter (OM), C/N, total S, XRF and percentage of species of Hg obtained from the analysis of records by thermo-desorption with temperature levels for all samples collected in Grama and Rico streams, along with the ones from sedimentation boxes, in dry and rainy seasons.

The HgT in sediment samples ranged from 44 to 266 µg kg^{-1} during the dry season, and from 5.8 to 183 µg kg^{-1} during the rainy season, in samples collected along the Rico and Grama streams, showing clearly a decrease in the concentrations in the rainy season. It is worth mentioning that the rainfall difference between the two stations is quite large. The sediment samples taken from local sedimentation box, A1 and A2, presented discrepant concentrations compared to other samples in the Rico and Grama streams. The A1 box presented HgT of 41,580 µg kg^{-1} during the dry season and 3581 µg kg^{-1} during the rainy season. In the sedimentation box of the A2 sediment sample, the Hg concentrations during the dry season and during the rainy season were 3835 µg kg^{-1} and 2312 µg kg^{-1}, respectively.

It is presumed, therefore, that in the dry season Hg-containing particulate material is l retained in sedimentation tanks for a longer time, as also noted by Durão Júnior et al. (2009). During the rainy season, this material is somewhat drawn to the stream and the finer particles of the sediment there spreads and dilutes the Hg into the hydric environment.

Although only the information of HgT is not enough to predict possible biological effects of Hg in sediments the results were compared with the guide values established by the Canadian Council of Ministers of the Environment (CCME, 2001) called TEL (Threshold Effects Level) and PEL (Probable Effects Level) that are the same for the Brazilian legislation, CONAMA 454. The concentrations below the TEL value represent low probability of adverse effects to biota and concentrations above the PEL value represent a likely adverse effect on biota. Between the PEL values and TEL it is not possible to speculate about the likelihood of an effect. The TEL and PEL values for Hg in the sediment are 170 and 490 µg kg^{-1}, respectively. Fig. 2 shows the HgT in sediment samples and their corresponding TEL value, except for A1 and A2 samples that have very different values.

It is observed that 11 of 14 samples collected in the Rico and Grama streams, in both seasons, showed concentrations below the TEL val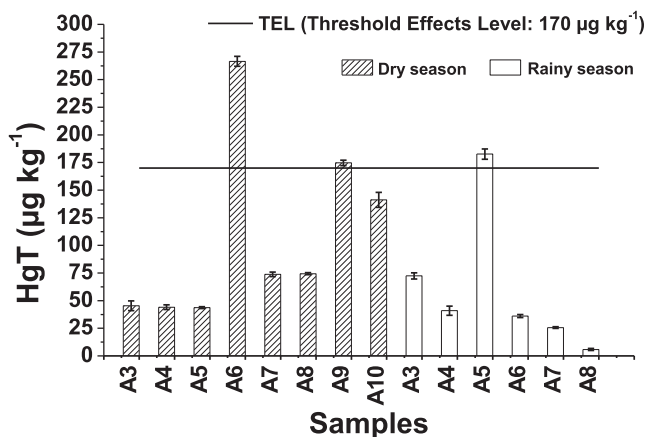ues. The A6, A9 (both in the dry season) and A5 (rainy season) samples showed Hg concentrations between TEL and PEL values, 266; 175 and 183 µg kg^{-1}, respectively, indicating the possibility of occasional occurrence of adverse effects to biota.

Samples of the sedimentation boxes (A1 and A2) showed HgT of about 85 and 8 times higher than PEL during dry season, respectively. This points to a serious problem, given that values above the PEL represent a potential adverse effect on the biota and the material of these samples may possibly be carried to Rico stream during the rainy season.

It is interesting to observe in Fig. 2 that sample A5 showed higher HgT content in the rainy season compared with the content in the dry season. This suggests that the rain water can be really overflowing the sedimentation box and transporting the finer particulate matter present in the contaminated area from the point A8 in the direction of the point A5 and being accumulated there. It is also observed that Hg reached the point A3 (Grama stream), since the HgT content is also larger in the rainy season. There is a significant difference at the level of 95% between the HgT for sample A3 collected in different seasons, showing that mercury is being transported from the contaminated area and reaching the water system. This poses hazard to the local population, considering that the Grama stream supplies water to the community of the city of Descoberto.

FEAM found, in 2005, HgT at Rico stream in the range of 20–750 µg kg^{-1} and in the Grama stream in the range of 20–61 µg kg^{-1}. Concentrations found in this work along the Rico stream ranged from 5.8 to 266 µg kg^{-1} (Table 1) and the four samples from the Grama stream show a range of Hg concentration from 41 to 73 µg kg^{-1}. Although the results obtained 13 years after the report of FEAM are similar, this shows that Hg is still present on the site, in concentrations above the allowed for quality standards for samples A6, A9 and A5, as shown in Fig. 2. Tinôco (2008) found a range of HgT in sediments from the same area of this work slightly higher, between 130 and 610 µg kg^{-1}.

It is interesting to compare the levels of Hg in sediments from Descoberto with those observed in areas where the gold exploitation activity is still widespread like in the Iron Quadrangle (MG) close to Ouro Preto (MG) and Mariana (MG) municipalities. It is observed that the HgT found in the sediment of Rico stream (5.8–266 µg kg^{-1}) is lower than that observed by Rhodes (2010) and Windmöller et al. (2007), who found concentrations ranging 40–530 µg kg^{-1} and 40–1100 µg kg^{-1}, respectively. This can be explained by the fact that in these areas, gold prospecting is still carried out, although illegal, which is not the case of Descoberto where these activities have been closed for nearly one century.

Studies in other countries affected by gold mining using mercury amalgamation still nowadays show, in general, HgT content in sediments larger than found in this work. Pinedo-Hernández et al. (2015), for example, found HgT in the range of 196–1187 µg kg^{-1} in sediment samples impacted by gold mining in Colombia. According to these authors, the region of study, Mojana, receives most of the waste from the largest gold mining of the country through flooding processes occurring during the rainy season. Güiza and Aristizábal (2013) claim that the increase in HgT levels in Mojana region in the last decade should be related to the gold mining proliferation in Colombia. According to these authors, the number of mines in that country raised from 2000 to 4000 between the years 2002–2011. The study Reichelt-Brushett et al. (2016) in Buru Island Indonesia showed HgT ranging from 4.23 to 82 mg kg^{-1} in sediments from several locations downstream of a small-scale artisanal gold mining. It must be pointed out that in these studies gold mining activities are recent, which is not the case of Descoberto.

The similarity between Descoberto mercury contamination case and the ancient cases in other contaminated sites, for example, west of United States (Carson River Drainage Basin, Nevada)

Fig. 2. HgT in sediment samples collected along the Rico and Grama streams.

(Bonzongo et al., 1996) and north of Georgia (Leigh, 1997), is that the gold explotation employing mercury uses hydraulic mining, in which the high density of mercury allowed gold and gold-mercury amalgam to sink, while sand and gravel passed over the mercury and through a sluice using water as a way to drag the solid materials. Large volumes of water flowing through the sluice caused many of the finer gold and mercury particles to wash through and out of the sluice before they could settle in the mercury-laden riffles. In this way mercury can be transported and spilled all over a large area. In the case of Descoberto there is little historical information about what exactly happened in the past, i.e., in the 19th century. As stated before, for unclear historical reasons Hg was buried by prospectors at that time. The consequence is that Hg is not spread over a large area what makes possible the mitigation of this contamination.

The few data about Hg in fish and human biological matrices from the contaminated area of Descoberto did not show Hg contamination. According FEAM (2005), the HgT in fish samples were below the values established by the National Health Surveillance Agency (ANVISA) Ordinance No. 685/1998 ANVISA. (FEAM, 2005). In 2008, Palmieri et al. (2009) collected 70 specimens of fish and only 3 samples showed concentrations exceeding the permitted value, but they concluded that there was no indication of Hg contamination. The Hg concentration in biological materials (hair, urine, blood) were considered normal in 47 people living near the site of upwelling (FEAM, 2005).

3.2. Hg speciation by thermo-desorption and chemical characterization

Fig. 3 shows records obtained by Windmöller et al. (2013) for the analysis of standard Hg compounds (prepared by solid dilution of the Hg compounds in an inert matrix), using a DMA heating program by temperature levels, identical to the conditions used in this work. The release of Hg^0 occurs mainly at 50 °C and Hg_2^{2+} at 100 and 150 °C. Therefore, the temperaure range of 50—150 °C corresponds to the release of reduced species (Hg^0 and Hg_2^{2+}). Oxidized species (Hg^{2+}) are released above 200 °C, and above 300 °C are the ones which interact more strongly with the matrix.

Fig. 4 and Fig. 5 display the records obtained for the analyses of the samples of this study and Table 1 shows the percentages for each Hg species, considering the sum of Hg concentrations corresponding to reduced species (up to 150 °C) and oxidized species (temperatures above 200 °C). The percentages of oxidized species were separated in two temperature ranges, from 200 to 300 °C and above 300 °C, in order to emphasize the percentage of more labil Hg^{2+} (from 200 to 300 °C) and the Hg^{2+} with stronger interaction with the matrix (above 300 °C).

It is observed from Table 1 and Figs. 4 and 5 in all samples the predominance of Hg^{2+}, i.e., Hg released in temperatures above 200 °C. The percentages of reduced Hg were low, ranged from 1.4 to 7.5 in dry season and 0.2 a 16.2 in rainy season (Table 1). The source of contamination of these samples is Hg^0 and it is known that the oxidation occurs in soil from this area (Durão Júnior et al., 2009; Windmöller et al., 2015). Durão Júnior et al (2009) also analyzed samples from the retention tanks and a sample from the Hg hotspot, observing the presence of Hg^0 only in the samples with very high HgT. These authors showed that the sample from the hotspot (analyzed without homogenization) shows sections with Hg^0, sections with a mixture of the three oxidation states (Hg^0, Hg_2^{2+} and Hg^{2+}) and sections with Hg totally oxidized (Durão Júnior et al., 2009). Therefore, it is not surprising that a mixture of Hg^0 and Hg_2^{2+} is present as reduced species in samples from the sedimentation boxes in the present study. Hg_2^{2+} is a less stable species compared to Hg^{2+} and, because of this, it is not considered in the majority of the speciation analysis. Nevertheless, it is well accepted that the species can be found in soils and/or sediments, as it is discussed mainly in articles about mercury oxidation and reduction processes, using thermo-desorption analysis where the transition of Hg^0 to Hg^{2+} and from Hg^{2+} to Hg^0 showed a well shaped peak between the peaks os Hg^0 and Hg^{2+} that were attributed to Hg_2^{2+} (Soares et al., 2015; Valle et al., 2006; Windmöller et al., 2015; Windmöller et al., 1996). The oxidizing environment may be contributing to the Hg oxidation and its adsorption on fine particles and therefore increasing their mobility.

Similar behavior was observed by Windmöller et al. (2007), working with sediment samples from the Iron Quadrangle (MG). This work also showed the predominance of oxidized Hg, the contents of this element and Mn were grouped by cluster analysis, indicating correlation between these parameters. The OM and clay minerals act stabilizing the Hg^{2+} formed and facilitate the balance toward the oxidation of Hg. The oxidation mediated by bacteria is also considered an important route (Barkay et al., 2003; Smith et al., 1998).

The comparison of the several graphics of Fig. 4 evidences that samples A2 and A6 are the ones that did not show Hg peaks at higher temperatures in spite of presenting higher HgT contents. This suggests that part of the Hg from the contamination is probably released from the sample by solubilization and/or volatilization and the amount that remains forms stronger interations with the matrix. This is confirmed by data of Table 1, according to which the percentage of species Hg^{2+} released above 300 °C is more prevalent in the samples A4, A5 and A8, with 49.4; 57.7 and 67.4% respectively. These samples are the ones with low HgT. For comparison, Fig. 5 displays the thermo-desorption graphics for selected samples (A1, A5 and A7) collected both in dry and rainy seasons. Sample A1, from one of the boxes, shows that the majority of Hg^{2+} is released up to 300 °C; sample A5 and A7 graphics show clearly that the season with lower HgT displays higher peaks at very high temperatures (600 °C and 700 °C), which means that Hg species are stronger bound in these samples.

Sample A8 shows an atypical behavior, i.e., it is the only sample that presented the highest Hg concentration at the temperature of 600 °C, indicating the presence of a highly stable Hg compound (Fig. 4). The graphic of this sample is similar to the $HgSO_4$ standard (Fig. 3), suggesting a possible presence of this species.

All samples from the sedimentation boxes (dry and rainy seasons) show Hg mainly as labile Hg^{2+}, 84.4—99.5% (Table 1, sample A1) and Fig. 5.

The predominance of oxidation processes over the Hg reduction in soils has been observed in other works, e. g., in soils of the Amazon and Minas Gerais (Brazil) (Valle, 2005; Valle et al., 2006). Windmöller et al. (2015) investigated the redox process of Hg in soil samples from the same contaminated area of this study. The results showed that the oxidation kinetics occurs to a greater extent and more quickly in relation to the Hg reduction process. This means that the composition of the soils from this area favors the oxidation of mercury in place. According to the authors, the oxidation facilitates the metal interaction with the fine particles of soil that can be lixiviated by the rain. The oxidized form makes possible their methylation (Windmöller et al., 2015).

The Pearson statistics analysis showed good correlations of Hg^{2+} with OM (r = 0.850, p < 0.05), C/N (r = 0.827, p < 0.05) and total S (r = 0.789, p < 0.05). The correlation of OM with S is an indicative of S present in OM. The strong interaction of Hg^{2+} with S (inorganic and organic compounds) is already well known, which justifies the observed correlations.

The degree of humification of OM in soil and sediments can be assessed by the C/N ratio. According to Jordão et al. (2000) the values of the C/N below 20 indicate the total decomposition of the
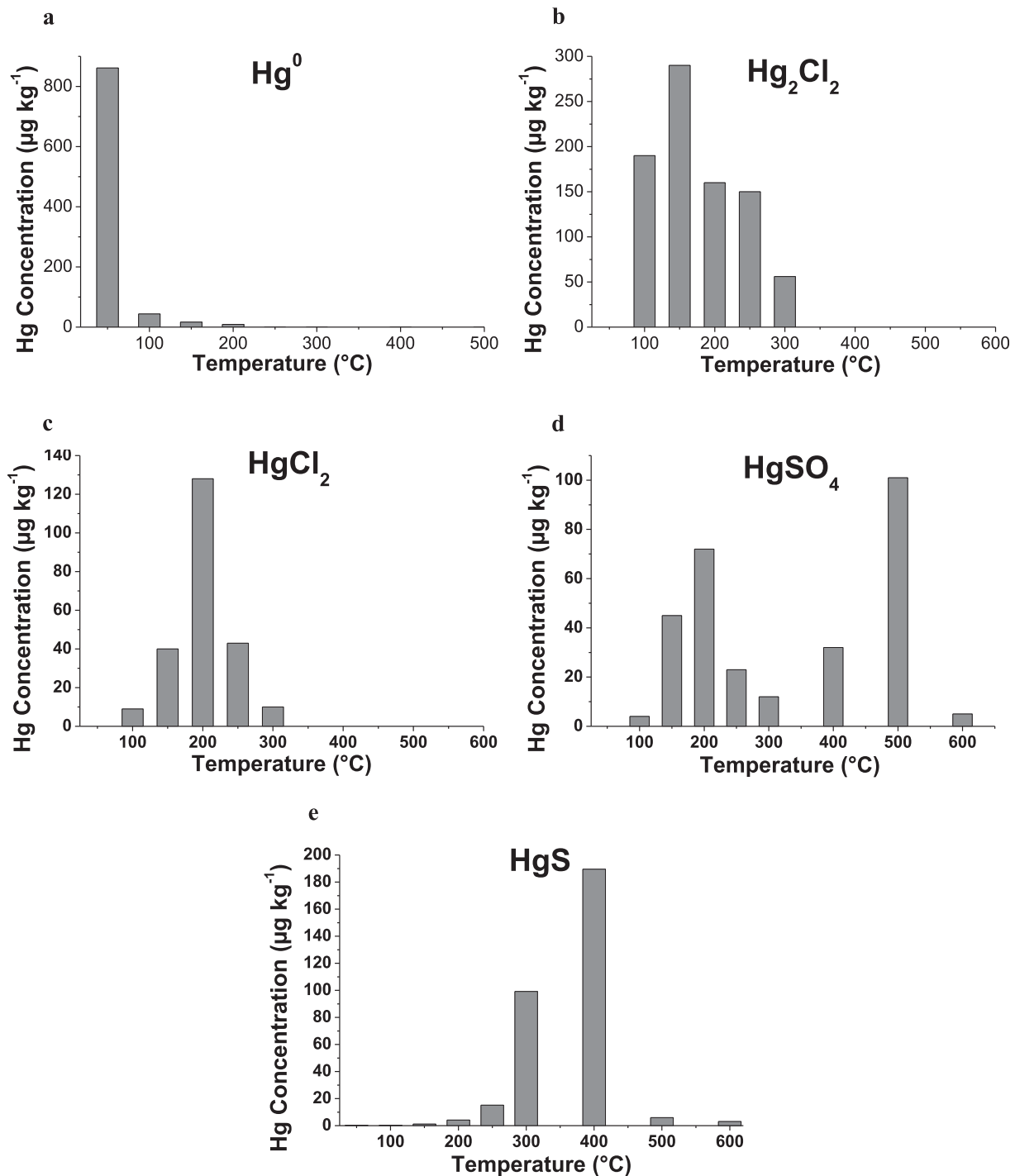
Fig. 3. Thermo-desorption graphics of Hg standards (modified from Windmöller et al., 2013).

OM in the environment and above 30 the decomposition is too low. All sediment samples showed C/N values below 20 (Table 1) suggesting that there is a high degree of decomposition of organic matter in the sample collection site, a condition which, among others, could favor the transport of Hg^{2+} and eventualy the methylation of Hg.

3.3. CH_3Hg^+ concentration

The concentration of CH_3Hg^+ in sediment samples collected over

Rico and Grama streams ranged from <0.11 to 1.87 μg kg^{-1} during the dry season (Table 1). In the rainy season only one samples showed CH_3Hg^+ concentration above the detection limit, sample A5, with 0.35 μg kg^{-1} of CH_3Hg^+. It is worthy mentioning that this sample was the only one with significative higher HgT in the rainy season. For samples A1 and A2, collected from sedimentation boxes, the concentration of CH_3Hg^+ was higher during dry season, 8.0 and 1.33 μg kg^{-1}, respectively. In the rainy season the concentration of CH_3Hg^+ in these samples was 0.7 μg kg^{-1} and 1.01 μg kg^{-1}, respectively.
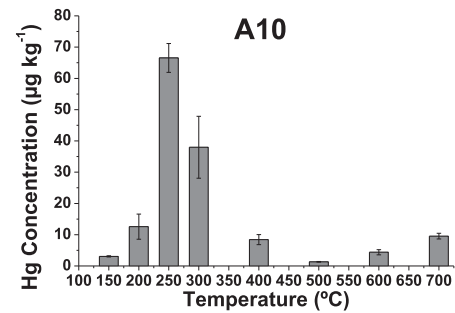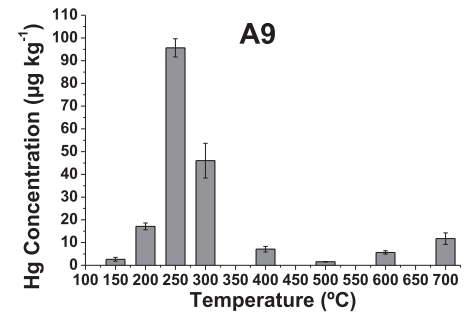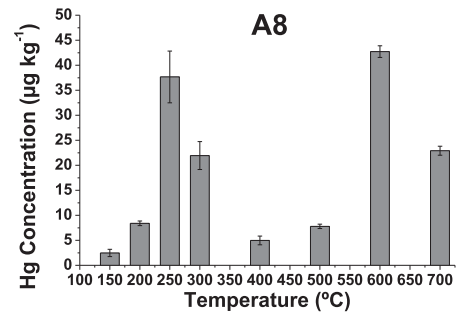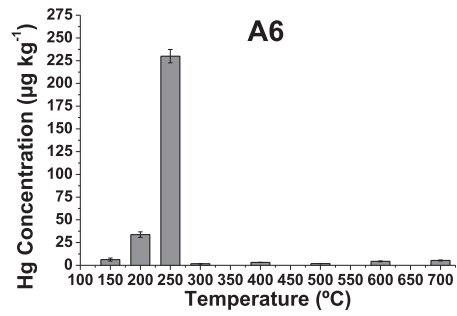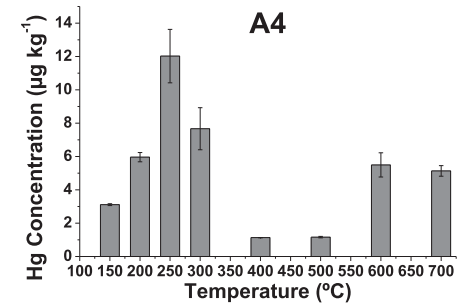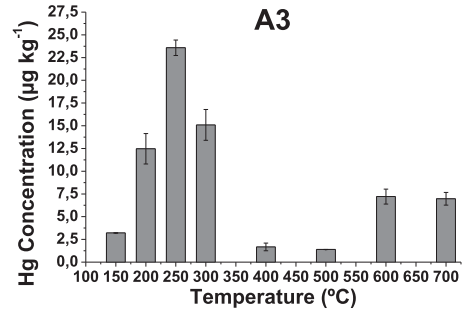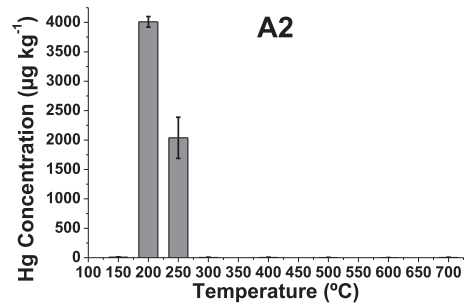
Fig. 4. Thermo-desorption graphics of Hg in sediment samples collected in Descoberto-MG in the dry season.
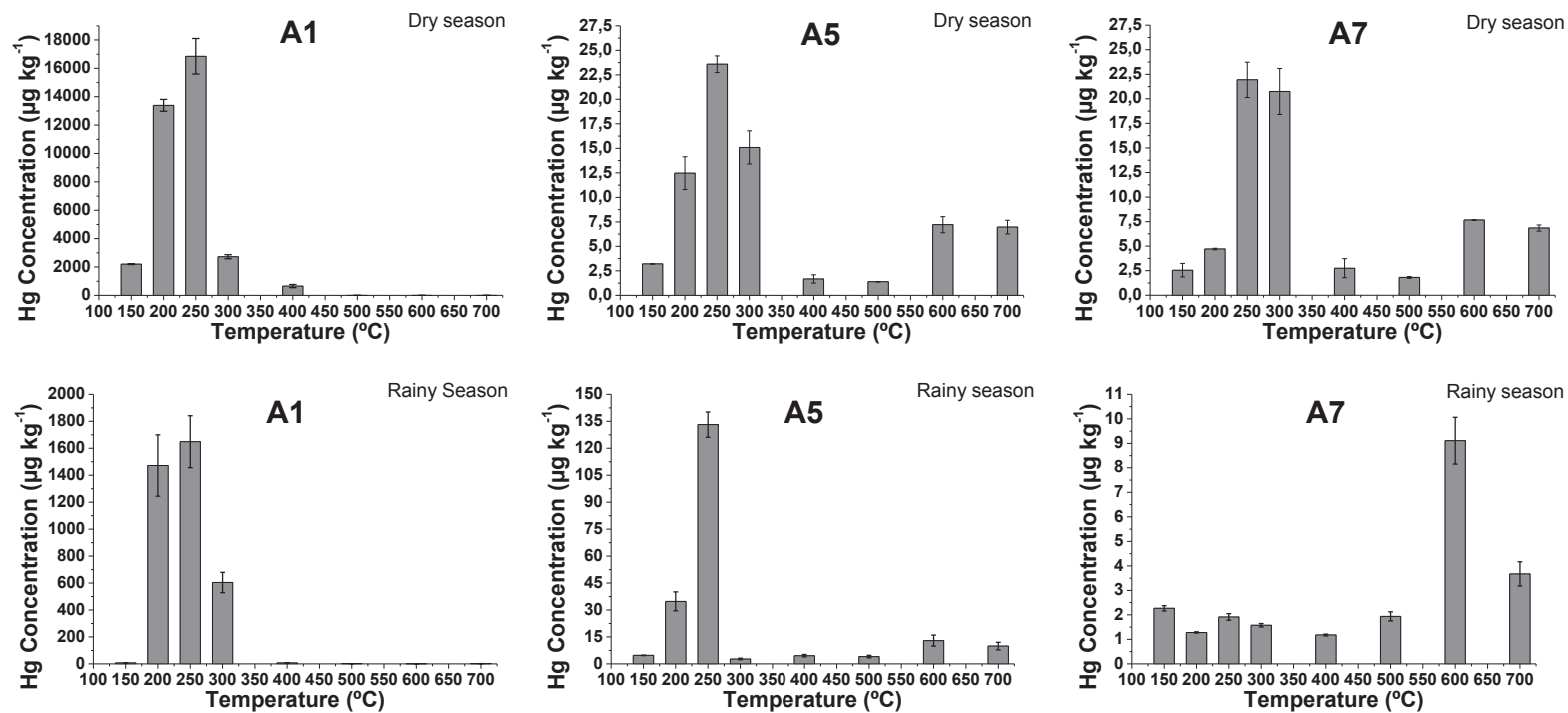
Fig. 5. Thermo-desorption graphics of Hg in sediment samples collected in Descoberto-MG in the dry and rainy season.

Table 2
Concentrations of CH_3Hg^+ and percentages in relation to HgT found in sediment in this study and other papers.

CH_3Hg^+	[a]Present study	[b]Pinedo-Hernández et al. (2015)	[c]Marrugo-Negrete et al. (2015)	[d]Beldowski et al. (2014)	[d]Carrasco and Vassileva (2015)	[e]Pietilä et al. (2015)
$(\mu g\ kg^{-1})$	<0.11–8.0	4.1–43.4	8–68	0,061–0.94	~0.89–~7.5	0.8–18
(%)	0.02–0.7	1.5–3.7	3–11	0.12–1.05	<0.4	1.2–12

[a] River Sediment/Sedimentation boxes.
[b] River Sediment.
[c] Swamp Sediment.
[d] Sediment marine.
[e] Peat Soil.

The percentages of CH_3Hg^+ ranged from 0.02 to 0.7% in which the lowest value corresponds to the sample with highest HgT (sample from one of the boxes) and the highest value corresponds to the sample from the stream with the highest HgT (A6). Marrugo-Negrete et al. (2015) studying sediment samples from tropical swamps in Colombia (Great Achi and Ayapel) impacted by gold mining, found the lowest percentage of CH_3Hg^+ in the sample with the highest concentration of the HgT. The HgT from Great Achi sediments ranged from 543 to 1021 $\mu g\ kg^{-1}$ and the percentage of CH_3Hg^+ ranged between 3 and 7%, whereas for samples from Ayapel HgT contents ranged from 145 to 313 $\mu g\ kg^{-1}$ and the percentage of CH_3Hg^+ ranged from 5 to 11%. These are, in general, higher percentages compared to this work. This diference is expected because the conditions of swamps in terms of higher organic matter contents and lower water flow rates favors the Hg methylation. Other research study of the same group, Pinedo-Hernández et al. (2015), studying surface sediments affected by artisanal and small-scale gold mining in the Mojana region of Colombia found HgT between 196.2 and 1187.6 $\mu g\ kg^{-1}$ and CH_3Hg^+ concentrations significantly correlated with the HgT and organic matter (OM) and represent between 1.7% and 3.6% of the HgT, i.e., also higher than the results obtained here. According to the authors the temperature was the parameter that favored the methylation due to increased biological activity in higher temperature in the dry season. The Pearson correlation between HgT and CH_3Hg^+ found in this work, excluding the samples from the box, was positive and very high (r = 0.878, p < 0.05). This information pointed out that the methylation increases with the increase of HgT, but there should be an Hg concentration from which the methylation is inhibited. The CH_3Hg^+ concentrations also correlated positively with OM (r = 0,824, p < 0.05), C/N (r = 0,931, p < 0.05), Hg^{2+} labile (r = 0,727, p < 0.05) and Fe_2O_3 (r = 0,693, p < 0.05).

Although the percentages of CH_3Hg^+ are low during dry season (0,02 and 0,04%, respectively), the results showed that the concentrations of this toxic pollutant can be extremely high (up to 8.0 $\mu g\ kg^{-1}$). It is showed that the CH_3Hg^+ concentrations in the boxes can reach 8 times the values found in the streams and therefore the results point out that care should be taken to avoid the transport of this material to the streams.

Sample A1 in the dry station, showed only 6.1% of the HgT is in the forms Hg^0 and Hg_2^{2+} and it presented the lowest percentage of CH_3Hg^+ (0.02%, Table 1) compared with the other samples. On the other hand, the percentage of Hg^{2+} labile, correlated strongly with CH_3Hg^+ concentration (r = 0.727, p < 0.05), both data suggesting that oxidized Hg favors the methylation of the metal.

The study by Feng et al. (2011) showed that the redox conditions are very important for the methylation of Hg and that this decreases with water depth and sediment, i.e., from oxic to anoxic conditions. Study by Eckley et al. (2015), in sediments of Cottage Grove Reservoir, west of Oregon, USA, showed that in the sediments of wetlands, CH_3Hg^+ concentrations of the more superficial layers 0–2 cm are clearly higher when compared to deeper layers (up to approximately 2.8 $\mu g\ kg^{-1}$ which corresponds to up to 0.9% of

CH_3Hg^+). The authors also observed increased concentrations and percentages of CH_3Hg^+ in flood water sediment when compared to permanently flooded areas, i.e., an oxidizing redox potential favors the metal methylation. These layers also had organic carbon concentrations and higher sulfate.

Table 2 shows the comparison of the results of CH_3Hg^+ concentrations obtained in of this study with other works. They are comparable to the concentrations of some marine sediments as studied by Beldoswisk et al. (2014) and Carrasco and Vassileva (2015) but the values are lower than river sediments studied by Pinedo-Hernández et al. (2015), swamp sediments studied by Marrugo-Negrete et al. (2015) and by peat soil by Pietilä et al. (2015). Although these results show a lower range, the results showed that the concentration can be as high as 8.0 $\mu g\ kg^{-1}$, which is means that the possibility of bioccumulation and biomagnifications is not negligible.

In the investigated site, methylation occurs primarily by an aerobic process, as the samples collected are surface sediment. The microscope observation of the water collected from the sedimentation box where the CH_3Hg^+ concentration was highest (8.0 $\mu g\ kg^{-1}$), it was found the presence of microalgae and cyanobacteria. This observation brings the hypothesis that the methylation box sedimentation can be occurring due to the presence of these microorganisms, or biotic methylation.

The biological process mediated by micro-organisms and fungi can occur via transmethylation reaction. Methylcobalamin, also known as vitamin B12, coenzyme is produced by the aerobic and anaerobic bacteria. The synthesis of CH_3Hg^+ in the environment via this compound is due to the transfer of a methyl group to Hg in oxidized form, ie Hg^{2+} (Barkay et al., 2003; Bisinoti and Jardim, 2004). It is noteworthy that methylcobalamin is widely distributed in the environment (Bisinoti and Jardim, 2004), and possibly this coenzyme is also produced in the investigated site. It is known that other parameters such as pH, temperature, OM concentration, concentration of sulfide, redox conditions also influence the methylation process (Achá et al., 2011), working in together or separately (Bisinoti and Jardim, 2004) as each contributes differently to form CH_3Hg^+. The characteristics of the medium are defining the process (Bisinoti and Jardim, 2004). Abiotic methylation can not be discarded and systematic stydies would be necessary to a better understanding of the ways that this important reaction is occurring.

Jonsson et al. (2012) studied methylation ratios in sediments of the estuary of the River Ore, the Bothnian Bay, Sweden. The results of this study showed that the combination of thermodynamic and kinetic effects of dissolution and desorption of Hg^{2+} from the solid phase influence and result in large differences in the observed methylation rates ranging up to two orders of magnitude. Our results show the difference between the samples in terms of Hg thermo-desorption profiles from the solid phase, thus indicating differences in Hg^{2+} interaction with the matrix and the importance of studying how these differences affects the kinetics and thermodynamics of metal methylation.

4. Conclusions

After 13 years of coming to light Hg contamination in a rural area of Descoberto, Brazil, the present results showed the presence of Hg in sediments near the area at concentrations that exceed the value of quality set by the Canadian Council of Environment (170 $\mu g\ kg^{-1}$ and 490 $\mu g\ kg^{-1}$). The samples from the Grama and Rico streams show a range of HgT from 5.8 to 266 $\mu g\ kg^{-1}$. HgT in material from the sedimentation boxes was found to be very high, up to 41,580 $\mu g\ kg^{-1}$, even in the rainy season, when in general HgT were much lower than in dry season. One of the collection points from the streams shows higher HgT in the rainy season, indication a transport and the possibility of Hg accumulation depending on particulate matter transport fenomena.

The thermo-desorption analysis showed predominance of Hg^{2+}, possibly linked to organic sulfur, suggested by a good positive correlation between Hg^{2+} (labile), HgT ($r = 0.886$, $p < 0.05$) organic mater (OM) ($r = 0.850$, $p < 0.05$) and the total S ($r = 0.789$, $p < 0.05$). The analysis also showed that in the rainy season, that the HgT are in general lower than in dry season, the Hg release at higher temperatures, which means, the Hg that remains in the sediment is stronger bound to this matrix.

The Hg contamination source in the study area is Hg^0. The oxidation of Hg, observed in thermo-desorption studies, is an essential step prior to methylation and the results of this study support other author results that showed the facility of Hg oxidation in tropical soils.

The CH_3Hg^+ concentration in streams sediment samples ranged from <0.07 to 1.87 $\mu g\ kg^{-1}$ and in the samples of sedimentation boxes the concentrations were 1.33 and 8.0 $\mu g\ kg^{-1}$ during dry season. CH_3Hg^+ concentration showed good Pearson correlation coefficients with HgT ($r = 0.878$, $p < 0.05$), Hg^{2+} (labile) ($r = 0.727$, $p < 0.05$), OM ($r = 0.824$, $p < 0.05$), C/N ($r = 0.931$, $p < 0.05$) and Fe_2O_3 ($r = 0.693$, $p < 0.05$). The sample with the highest percentage of HgT as Hg^{2+} (98%) presented also the highest percentage of CH_3Hg^+ (0.7%) which corroborates the thesis that where the oxidation is happening, methylation is favored.

These values are very preoccupying, showing that care should be taken to avoid the transport of this material to the streams and further studies on the transfer through the food chain would be very important.

Acknowledgments

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