Accumulation and oxidation of elemental mercury in tropical soils

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HIGHLIGHTS

- Retention and oxidation of Hg^0 in tropical soils depends on soil properties.
- Those processes vary greatly both quantitatively and qualitatively with soil type.
- Organic matter is the main soil characteristic in Hg adsorption and oxidation.
- pH and CEC also appear to be important soil characteristics in Hg adsorption.
- Hg^0 oxidation occurred at the air/soil interface rather than only in the air.

ARTICLE INFO

ABSTRACT

The role of chemical and mineralogical soil properties in the retention and oxidation of atmospheric mercury in tropical soils is discussed based on thermal desorption analysis. The retention of gaseous mercury by tropical soils varied greatly both quantitatively and qualitatively with soil type. The average natural mercury content of soils was $0.08 \pm 0.06\ \mu g\ g^{-1}$ with a maximum of $0.215 \pm 0.009\ \mu g\ g^{-1}$. After gaseous Hg^0 incubation experiments, mercury content of investigated soils ranged from 0.6 ± 0.2 to $735 \pm 23\ \mu g\ g^{-1}$, with a mean value of $44 \pm 146\ \mu g\ g^{-1}$. Comparatively, A horizon of almost all soil types adsorbed more mercury than B horizon from the same soil, which demonstrates the key role of organic matter in mercury adsorption. In addition to organic matter, pH and CEC also appear to be important soil characteristics for the adsorption of mercury. All thermograms showed Hg^{2+} peaks, which were predominant in most of them, indicating that elemental mercury oxidized in tropical soils. After four months of incubation, the thermograms showed oxidation levels from 70% to 100%. As none of the samples presented only the Hg^0 peak, and the soils retained varying amounts of mercury despite exposure under the same incubation conditions, it became clear that oxidation occurred on soil surface. Organic matter seemed to play a key role in mercury oxidation through complexation/stabilization of the oxidized forms. The lower percentages of available mercury (extracted with KNO_3) in A horizons when compared to B horizons support this idea.

1. Introduction

Mercury and mercury-containing compounds are toxic to humans and the environment (Bernhoft, 2012). One significant aspect of the global biogeochemical cycling of mercury, which differs from those of other metals, is its volatility (Fergusson, 1990). Most mercury in the air is gaseous elemental mercury, which is deposited onto the ground and water in various ways and may be transformed into methylmercury through microbial action (UNEP, 2008). Since gaseous elemental mercury has a long atmospheric lifetime (6–18 months) and can be transported around the globe, it is characterized as a global pollutant (UNEP, 2008). The behavior of the mercury remaining in soil is initially governed by physical and chemical processes that redistribute it within the soil and allow some of it to enter the soil solution (Renneberg and Dudas, 2001).

Abiotic oxidation of elemental mercury to Hg^{2+} occurs in the atmosphere, in water and in soil, but because so far research has focused on atmospheric transformations, little is known about the oxidation mechanisms of elemental mercury in water and soil (Barkay et al., 2003).

Several studies have demonstrated that atmospheric deposition from nearby industries is the most likely source of mercury in soil (Wang et al., 2003; Hissler and Probst, 2006; Guédron et al., 2013; González-Fernández et al., 2014) and water (Hissler and Probst, 2006; González-Fernández et al., 2014). A comparison of vertical mercury profiles in soil from Grenoble, France, to those of other metals not emitted by the same plant suggested mercury enrichment in surface horizons due to atmospheric mercury input from the chlor-alkali plant (Guédron et al., 2013). A study conducted in Gijón, Spain (González-Fernández et al., 2014) showed that the recharge area of the springs exhibited mercury concentrations higher than the base level established for sandstone in the region and that the concentration of easily mobilized mercury was higher in the superficial soil horizon, suggesting mercury enrichment via atmospheric deposition. According to the authors, the source of mercury for atmospheric deposition on soil surface and its accumulation in soil was nearby industrial activity. The mining and roasting of Mercury-ore-containing rocks are also important sources of mercury release to the environment because of atmospheric mercury emissions (Li et al., 2009) and mercury leaching from contaminated soils to surface water and deeper into the soil (Tersic et al., 2014). Field investigation experiments showed a positive correlation between atmospheric mercury concentration and mercury content in a Cambisol (Wang et al., 2003). The same authors demonstrated in simulated experiments that a higher Hg^0 content in the air resulted in a higher mercury retention in a specific soil sample; however, they did not evaluate different soil classes.

In Brazil, gold mining is the major source of mercury in the atmosphere (UNEP, 2008). During the gold mining boom in the late 1980's, gold mining contributed about $110\,t\,yr^{-1}$ mercury to the environment, with nearly 65% to the atmosphere. The most recent mercury release estimates show that gold mining has been greatly reduced due to the exhaustion of easy mining deposits, but that it still contributes about $31\,t\,yr^{-1}$ of mercury, about $20\,t\,yr^{-1}$ is released into the atmosphere (Lacerda et al., 1999).

According to the annual report by the Brazilian National Department of Mineral Production (DNPM), Brazil has gold reserves of 2592 tons, 582 tons (22% of total) of which are in Minas Gerais (DNPM, 2010). The scarce data available on atmospheric deposition due to mining are estimated for the Amazon region, where this activity is concentrated (Lacerda et al., 1999). Recent studies have also shown the importance of burning processes in the remobilization of mercury in the Amazonian ecosystem (Perez et al., 2014).

Most studies have been conducted on Northern hemisphere soils in addition to a few studies focused mostly on the Amazon region in the Southern hemisphere. Thermal desorption has been used to determine the total content of mercury in cinnabar since 1904. In this technique, solid samples are heated to high temperature and the vaporized mercury is swept by a gas flow to an atomic absorption spectrometer cell for quantification (Henry et al., 1972). Subsequently, Goleb also used this technique to differentiate mercury from natural and anthropogenic sources. They obtained mercury release profiles as a function of temperature for different rocks (Goleb, 1971).

Many other studies have shown the potential of this technique for the speciation and/or determination of different mercury interactions in contaminated area soils (Windmöller et al., 1996; Biester and Scholz, 1997; Biester et al., 2000; Biester et al., 2002; Valle et al., 2005).

Recently, in a study of fifteen commercial mercury compounds, researchers analyzed their use as fingerprints and showed that the identification of mercury species by thermal desorption is possible (Rumayor et al., 2013). Thermal desorption has also been used

even in the development of an innovative technology for the remediation of contaminated soils (Navarro et al., 2009).

Therefore, in order to evaluate mercury retention and oxidation in tropical soils, we analyzed several types of tropical soils exposed to an atmosphere saturated with gaseous mercury using thermal desorption coupled to atomic absorption spectrometry (TDAAS), a technique that allows the qualitative speciation of mercury (Valle et al., 2005).

Studies have demonstrated that soil characteristics affect the mercury exchange flux between the soil and the atmosphere (Hissler and Probst, 2006; Liu et al., 2014).

In this work, the role of chemical and mineralogical soil properties in the retention and oxidation of atmospheric mercury in tropical soils is discussed based on laboratory experiments and thermal desorption analysis.

Therefore, this study goes beyond the simulation of soil contamination by gaseous mercury to distinguish possible processes of gaseous mercury retention and oxidation in tropical soils and in two of their horizons (A and B) as well.

2. Material and methods

2.1. Sampling area and geological setting

One of the study areas is located in Southeast Brazil and covers most of Minas Gerais state and the other, Itaperuna town, is in Rio de Janeiro state. The soil sampling points, sample horizon and identification, geographical location, soil classification and chemical and textural characteristics are given in Table 1.

Minas Gerais is a large state, with an area of $586,522.122\,km^2$, comparable to the size of Ukraine. It has a great geological variability, with two outstanding regions: Triângulo Mineiro, a region of volcanism, with mafic rocks, and the Quadrilátero Ferrífero, with geochemical anomalies and mineral deposits (Mello and Abrahão, 2013). Most samples were collected in and around the Quadrilátero Ferrífero. Quadrilátero Ferrífero is the greatest Brazilian iron mining region. It also presents deposits of manganese, gold, bauxite and gems like topaz and emerald (Roeser and Roeser, 2010). Two of the most important hydrographic basins are located in Minas Gerais state, the Doce River basin and the Velhas River basin.

2.2. Soil sampling

Samples of typical tropical soils (ultisol, oxisols, inceptisols, alfisols and entisol) were collected at three points at two depths (horizons A and B) from areas not affected either by agricultural or industrial activities. The samples were disaggregated, sieved with a 2-mm sieve and air dried (air-dried fine earth). These samples were submitted to textural analysis. For chemical analysis, the samples were also ground and sieved with a mesh 80 (0.177 mm) sieve.

2.3. Characterization

The following soil parameters were determined: pH, cation exchange capacity (CEC) and carbon, clay, silt, sand and iron and aluminum oxide contents were determined. pH, CEC and granulometry values were determined following EMBRAPA (1997). Crystalline iron oxides were extracted using a dithionite-citrate-bicarbonate (DCB) and amorphous iron oxides were extracted using ammonium oxalate, following Mehra and Jackson (1960) and McKeague (1966), respectively. Iron and aluminum analysis was performed in a Perkin Elmer atomic absorption spectrometer,

Table 1
Identification, classification, geographical location, chemical and physical (textural analysis) characteristics of soils[a].

Soil	Soil classification[b]	Coordinates	Horizon	pH		CEC (cmol$_c$ kg^{-1})	Clay (g kg^{-1})	Silt (g kg^{-1})	Sand (g kg^{-1})	Texture	%C	Fe$_2$O$_3$ (g kg^{-1})		Al$_2$O$_3$ (g kg^{-1})	
				H$_2$O	KCl							DCB	oxalate	DCB	oxalate
PVA	Typic Hapludult	S 20°45′14″	A	5.10(5)	4.39(4)	4.5(2)	436.3	211.7	342.0	Clayey	1.62(5)	116.1(2)	3.01(7)	3.24(1)	2.75(1)
		W 42°52′55″													
LVd	Rhodic Hapludox	S 20°39′37″	A	4.98(3)	4.20(3)	3.1(3)	454.5	127.2	418.3	Clayey	3.02(7)	182.9(5)	2.51(2)	17.2(2)	10.4(2)
		W 43°47′10″	B	5.10(6)	5.42(1)	2.4(3)	633.3	239.4	127.3	Clayey	1.83(8)	155.8(4)	2.54(2)	31.5(4)	3.83(1)
LVAd$_1$	Humic Xanthic Hapludox	S 21°13′33″	A	5.24(2)	4.55(3)	2.2(7)	551.8	208.7	239.5	Clayey	2.4(2)	31.6(3)	2.7(3)	6.93(1)	7.68(8)
		W 43°46′25″	B	6.22(1)	5.48(2)	4.2(1)	484.5	174.6	340.9	Clayey	0.4(1)	33.04(1)	0.71(5)	<LQ	1.62(1)
LVj	Humic Rhodic Acrudox	S 19°59′08″	A	5.31(4)	4.83(3)	4.8(2)	216.0	414.2	369.8	Medium	3.5(4)	428.8(7)	7.8(9)	102.6(3)	7.8(2)
		W 43°50′48″	B	5.81(1)	5.67(2)	6.4(7)	250.3	431.5	318.2	Medium	2.49(7)	454.9(6)	8.2(6)	123.0(6)	3.27(4)
NVef	Typic Rhodudalf	S 21°00′28″	A	6.17(1)	5.12(2)	8.0(2)	413.9	217.6	368.4	Clayey	1.5(3)	90.2(1)	2.65(2)	11.11(4)	2.76(7)
		W 42°43′04″	B	5.44(2)	4.41(4)	9.6(1)	542.4	404.7	53.0	Clayey	0.37(1)	181.1(6)	5.70(1)	19.94(8)	2.55(8)
TCp	Typic Haplustalf	S 19°37′05″	A	6.13(1)	5.32(1)	6.3(4)	418.1	244.3	337.6	Clayey	3(3)	72.12(5)	1.10(1)	5.18(2)	1.34(2)
		W 44°02′35″	B	6.10(2)	5.65(3)	5.8(2)	619.5	199.2	181.3	Clayey	0.60(2)	79.8(2)	1.14(1)	7.06(5)	1.03(4)
CXbe	Oxic Eutric Haplustept	S 19°37′05″	A	7.52(1)	6.85(3)	12.2(2)	524.4	380.6	95.0	Clayey	3.220(0)	68.6(3)	1.73(5)	13.43(3)	13.1(2)
		W 44°02′35″	B	6.91(1)	6.29(3)	5.5(2)	703.5	209.4	87.1	Clayey	0.93(4)	64.1(7)	1.08(1)	10.11(7)	2.49(2)
FFcd$_1$	Petroferric Acrustox	S 17°04′53″	A	5.45(2)	4.32(2)	6.6(2)	114.2	318.2	567.7	Medium	2.5(7)	23.15(6)	1.48(2)	3.73(2)	0.96(5)
		W 46°00′16″	B	4.88(3)	3.85(6)	2.4(1)	221.7	315.3	463.1	Medium	0.74(6)	23.05(1)	0.47(3)	<LQ	0.91(5)
FFcd$_2$	Petroferric Acrustox	S 17°05′16″	A	5.61(3)	4.48(2)	3.36(2)	147.1	521.1	331.8	Medium	1.9(1)	18.1(2)	1.04(4)	3.65(3)	0.89(1)
		W 45°59′12″	B	4.30(4)	3.73(1)	2.3(3)	193.2	297.7	509.1	Medium	0.700(0)	24.6(5)	0.36(1)	<LQ	0.73(1)
CXd	Typic Dystrudept	S 17°04′59″	A	5.66(3)	4.47(5)	7.2(1)	193.4	315.8	490.1	Medium	4(1)	55.1(1)	2.09(5)	6.20(5)	1.66(1)
		W 46°00′05″	B	5.05(2)	3.91(2)	2.9(1)	285.6	225.2	410.8	Medium	0.66(1)	36.8(6)	1.10(5)	<LQ	1.38(7)
RQo	Quartzipsamment	S 17°25′48″	A	4.49(3)	3.68(4)	1.30(8)	110.1	36.9	853.0	Sandy	0.55(1)	2.73(2)	0.20(1)	0.92(2)	0.73(3)
		W 46°04′36″	B	4.71(1)	3.91(1)	1.1(5)	148.5	29.8	821.8	Sandy	0.5(2)	2.17(3)	0.18(1)	0.71(1)	0.48(3)
LVAd$_2$	Xanthic Hapludox	S 17°47′50″	A	5.40(5)	3.97(3)	7.6(4)	338.1	107.5	554.4	Medium	2.8(6)	48.3(3)	1.5(2)	17.07(9)	6.50(5)
		W 46°08′05″	B	4.61(2)	4.10(2)	7.7(4)	472.7	78.5	454.6	Clayey	0.73(9)	62.3(5)	0.75(1)	18.05(7)	1.13(9)

[a] LQ = Limit of Quantification. Numbers in brackets represent the error in the last significant digit, estimated as the standard deviations from the mean of three replications.
[b] According to Soil Taxonomy (approximately).

model Analyst 200, by direct aspiration of aqueous samples using acetylene/air and acetylene/nitrous oxide flame, respectively.

2.4. Quantification of total natural mercury in soil

Air-dried fine earth samples were ground in an agate mortar and about 0.1000 g of each sample was submitted to mercury quantification in a *Milestone Direct Milestone Analyzer* (DMA-80). Accuracy was verified with the standards Montana Soil Nist-2711 ($6.25 \pm 0.19 \, \mu g \, g^{-1}$) and River Sediment GBW–GBW 08301 RCV 8221 ($0.220 \pm 0.040 \, \mu g \, g^{-1}$).

2.5. Soil incubation experiment

2.5.1. Incubation
About 2.00000 g of each soil sample were plated onto 50-mm id Millipore plastic plates, which were randomly placed into five identical 160-mm desiccators. The samples were randomly placed in the desiccators, but for each soil class A and B horizon samples were place in the same desiccator for proper comparison. A 50-mm Petri dish with 100 g of metallic mercury and two 5-mL beakers filled with ultrapure water were also placed in each desiccator (Fig. 1). The desiccators were then closed under reduced pressure.

After two weeks the beakers containing water were removed and the desiccators were then left open for 48 h for excess condensed water evaporation and closed again for another four months, the first three months under reduced pressure and the fourth month under room pressure.

After this time, the samples were exposed to air for 24 h at room temperature for removal non-adsorbed mercury before being submitted to thermal desorption analysis. The samples that presented characteristic peaks for the release less oxidized mercury (Hg^0 and Hg_2^{2+}) after incubation were analyzed again to check for changes in the thermal desorption profiles one week after air drying.

2.5.2. Thermal desorption analysis
Mercury speciation was determined using an atomic absorption spectrometer (CG Analytical model GBC 932 AA) coupled to a thermal desorption oven (TDAAS). This technique is based on heating the sample from room temperature to approximately 600 °C at a constant rate ($33 °C \, min^{-1}$). Thermograms of vapor released by the samples were obtained in an atomic absorption detector cell using nitrogen flow ($200 \, mL \, min^{-1}$) as a carrier gas.

Thermograms, which are records of the absorbance per gram as a function of temperature, were then obtained. The differentiation between Hg^0/Hg_2^{2+} and Hg^{2+} present in the samples was determined by comparing the obtained thermal desorption profiles with standard mercury profiles from previous studies (Valle et al., 2005, 2006). The thermograms were obtained with a sample mass between 10 and 100 mg and mathematically treated to normalize the absorbance for mass; unresolved peaks were deconvoluted using Microcal Origin 8.0 software.

2.5.3. Extraction and quantification of total retained mercury
The total mercury content retained in the soils was quantified by cold vapor atomic absorption spectrometry - CVAAS (USEPA SW-846, Method: 7470A/1994) after extraction with 10.00 mL of a 7 M HNO_3 solution added to 0.1000 g of each soil sample in a Falcon tube.

The suspensions were stirred for 1 h on a horizontal table with the tubes set in vertical position and allowed to stand for 16 h. After this, the soil solutions were filtered through qualitative filter paper, washed with ultrapure water and the collected supernatant was transferred to 50.00 mL volumetric flasks, which were completed with ultrapure water. The supernatant was analyzed to determine the mercury content.

The background was obtained by subjecting each non-incubated soil sample to the same extraction procedure. Extraction and quantification were performed in duplicate for both non-incubated and incubated soil samples.

2.5.4. Extraction and quantification of available mercury
The available mercury content in incubated soils was quantified after extraction with KNO_3 solution. To 1.0000 g of each soil sample, in a Falcon tube, 20.00 mL of 0.1 M KNO_3 solution was added. The suspensions were stirred for 12 h on a horizontal shaker and were centrifuged at 2493 g (RCF) (3500 rpm – SIGMA Lab Centrifuge 6–15) for ten minutes. The supernatants were analyzed for mercury content in a Milestone Direct Milestone Analyzer (DMA-80). The background was obtained by subjecting each non-incubated soil sample to the same extraction procedure. Extraction and quantification were performed in duplicate for both non-incubated and incubated soil samples.

3. Results and discussion

The main objective of this study was not to simulate natural contamination of soil by elemental mercury, but to differentiate the retention processes in action in horizons (A and B) of different tropical soils upon sample contact with gaseous mercury. The samples were exposed to a large quantity of gaseous mercury for a long period. The amounts of mercury retained by each soil sample under long exposure to high mercury concentrations can be said to be the maximum mercury retention capacity of the soils under
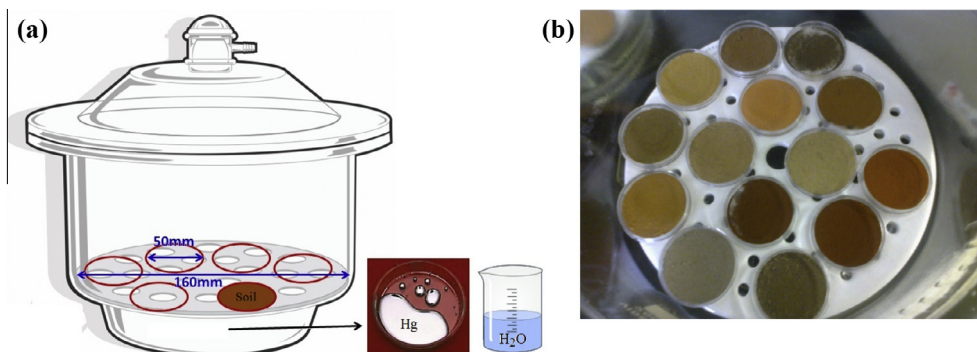

Fig. 1. Incubation soil scheme with mercury vapor: (a) arrangement of the samples, mercury and water in the desiccator. (b) Soil samples randomly placed into desiccator view.

the study conditions (contact with elemental mercury, pH, moisture, microorganisms, etc.).

Table 1 gives the soil sample characterization results. Soil classification is according to Soil Taxonomy (Soil Survey Staff, 2010) and sample identification code of the sample is in agreement with the Brazilian soil classification (Santos et al., 2006), followed by capital letters A or B, corresponding to A or B soil horizon, as for example: NVef-A is a A horizon Eutrophic Red Nitosol sample.

The analyzed samples presented a maximum natural mercury content of $0.215 \pm 0.009\ \mu g\ g^{-1}$ and a mean value of $0.08 \pm 0.06\ \mu g\ g^{-1}$, which are below the prevention level of $0.500\ \mu g\ g^{-1}$ (Fig. 2a) set forth for soils by Brazilian environmental regulations (CONAMA, 2009), and also below the thermal desorption detection limit, for which reason pre-incubation thermograms are not shown. The mercury content of incubated samples ranged from 0.6 ± 0.2 to $735 \pm 9\ \mu g\ g^{-1}$ (Fig. 2b) with a mean value of $44 \pm 146\ \mu g\ g^{-1}$. This result gives evidence that mercury retention depends on soil characteristics, because, although all the samples had been submitted to the same incubation conditions (mercury atmosphere, moisture, etc.), the retained mercury contents varied greatly.

Table 2 shows the mercury contents of the samples before and after incubation with elemental mercury. It also gives the normalized absorbance values (ratio of the area under the curve to the analyzed sample mass) and the mercury retention factors (ratio of the mercury contents before and after incubation) for each soil. These results will be discussed in detail further ahead.

The mercury retention factors ranged from 4 to 4539 (Table 2). Out of the 23 investigated samples, only LVAd$_1$-B had a retention factor lower than 10; 5 samples had factors between 14 and 53 (TCp-B, RQo-B, LVd-A, LVAd$_1$-A, and NVef-B) and 8 had retention factors between 74 and 227 (LVAd$_2$-B, LVj-B, FFcd$_1$-B, PVA-A, LVj-A, NVef-A, CXd-B, RQo-A and LVd-B). The other samples had retention factors higher than 335, with the highest values for samples FFcd$_2$-A, 1208, and CXbe-A, 4539.

The results in Table 2 demonstrate that mercury retention depends on the soil characteristics and horizon as well. Comparison of same soil A and B horizons (Fig. 2b) showed that in almost all soils, A horizon adsorbed a greater amount of mercury than B horizon. The retention factors (Table 2) of A horizon samples were about 1.4–46 times higher than those of B horizon samples, with the highest value for TCp-A.

Considering that the main difference between A and B horizons in these soils is the organic matter content, we can infer that organic matter plays a major role in mercury retention by soil, even though the retained mercury content did not correlate significantly with the organic matter content. Ravichandran (2004) investigated mercury retention in aquatic systems and proposed that the lack of correlation between these two parameters does not mean that their interaction is weak or little significant, since the binding of mercury to organic matter depends on a small number of molecules that present sulfur functional groups.

CXBe-A had the highest mercury retention capacity according to both after the nitric acid extraction method and detection by CVAAS and the normalized absorbance result, after TDAAS analysis. This soil sample also had the greatest pH (7.52) and CEC values and one of the greatest clay and organic matter contents (Table 1). The synergy of these factors is responsible for the great adsorption capacity of this soil, since it presents specific and non-specific mercury adsorption sites. Clay has a large specific surface area, which allows physical sorption to occur, and it contains minerals that provide specific adsorption sites, such as iron oxides, present in a high content in this sample. Organic matter also presents specific adsorption sites, such as hydroxyl and -SH functional groups, the latter being the main group responsible for mercury chemical binding. According to Fergusson (1990), mercury in soil probably occurs mainly chelated to S-containing amino acids, proteins and humic acid-like substances. Since this is a eutrophic soil with a high organic matter content and near-neutral pH, conditions that are favorable to great microbial activity, it may have greatly affected the oxidation of elemental mercury (Smith et al., 1998; Colombo et al., 2013; Colombo et al., 2014) and its retention through different mechanisms by specific and non-specific adsorption sites and even precipitation after oxidation.

For the soil with the lowest retention capacity, the two employed methods, TDAAS and CVAAS, disagreed to a degree for adsorption capacity order, but agreed that the lowest adsorption capacity soils were RQo-B and LVAd$_1$-B (Table 2). The low retention capacity of RQo-B is explained by the simultaneous occurrence of low CEC, pH, and organic matter, clay and iron oxide contents.

To determine which soil characteristics are the most important for mercury retention, they were correlated with their retained mercury contents and the significance of the obtained correlation coefficients was validated with t-test at 95% confidence.

The mercury contents obtained by CVAAS, after nitric acid extraction and normalized absorbance (by TDAAS) showed high and significant correlation ($r = 0.90^*$, 95% *t-test* confidence), that is, the two methods agreed in the comparison of mercury retention in the investigated soils. Both the extracted mercury contents and the normalized absorbance values correlated significantly with pH
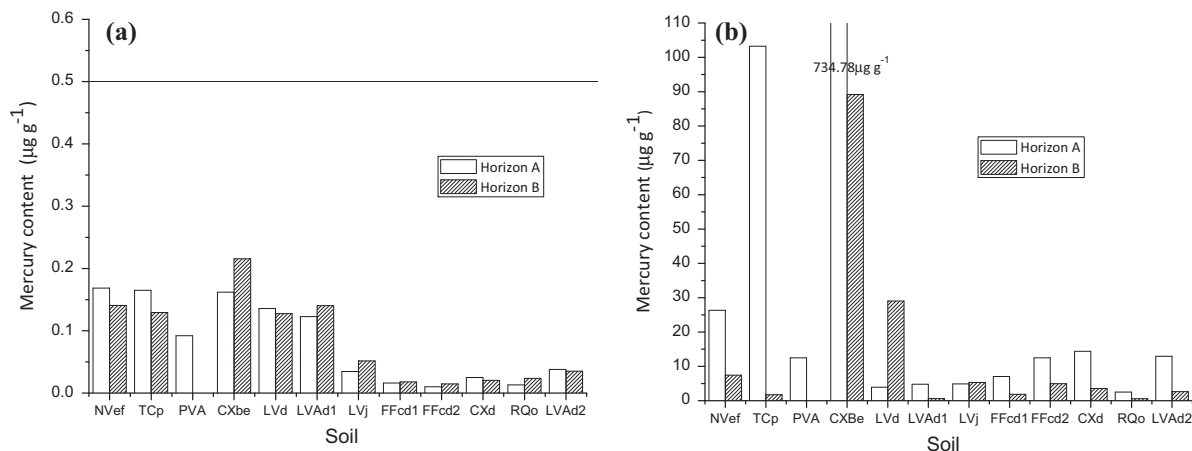

Fig. 2. Mercury content in soils: (a) before incubation. Line plotted parallel to the *X* axis with *y* = 0.5000 μg g^{-1}, prevention level set forth for soils by Brazilian environmental regulations (CONAMA, 2009). (b) After incubation.

Table 2
Corrected thermogram areas after incubation, mercury contents before (natural content) and after (extracted content) incubation, accumulation factor (Af) of each soil (ratio between mercury contents before and after incubation) and ratio between the accumulation factors of A horizons (Af_{HzA}) and B horizons (Af_{HzB}).

Soil	Horizon	Corrected area after incubation	Mercury content ($\mu g\ g^{-1}$)		Accumulation factor (Af)	Af_{HzA}/Af_{HzB}
			Before incubation	After incubation		
PVA	A	11648	0.092(2)	12(1)	136	–
LVd	A	4521	0.128(7)	3.9(4)	29	0.13
	B	23823	0.123(5)	29(9)	227	
LVAd$_1$	A	7195	0.140(14)	4.8(4)	39	9
	B	629	0.035(2)	0.6(2)	4	
LVj	A	8577	0.052(8)	4.9(9)	142	1.38
	B	5959	0.168(7)	5.3(3)	103	
NVef	A	85924	0.141(7)	26(6)	157	3.0
	B	5561	0.130(8)	7.4(8)	53	
TCp	A	49811	0.129(14)	103(2)	798	57
	B	11668	0.162(1)	1.8(3)	14	
CXbe	A	179795	0.215(9)	735(23)	4539	11.0
	B	45190	0.158(4)	89(4)	414	
FFcd$_1$	A	11962	0.016(2)	7.05(4)	436	4.13
	B	2862	0.018(2)	1.88(6)	106	
FFcd$_2$	A	9475	0.0103(4)	12(2)	1208	3.61
	B	3105	0.015(2)	5.0(1)	335	
CXd	A	20722	0.025(2)	14(1)	575	3.30
	B	2159	0.020(2)	3.6(8)	174	
RQo	A	4687	0.013(2)	2.5(6)	194	8.4
	B	954	0.024(3)	0.6(4)	23	
LVAd$_2$	A	34734	0.038(7)	12.9(3)	341	4.6
	B	1528	0.035(3)	3(1)	74	
Average		21789	0.08(6)	44(146)	415	

Numbers in brackets represent the error in the last significant digit, estimated as the standard deviations from the mean of three replications to mercury content before incubation and two replications to mercury content after incubation.

($r = 0.65^*$ and $r = 0.74^*$, respectively), CEC ($r = 0.57^*$ and $r = 0.66^*$, respectively) and amorphous iron oxide contents isomorphically substituted with aluminum, Al_{ox} ($r = 0.55^*$ and $r = 0.60^*$, respectively). One can see that the thermal desorption results had higher coefficients, which may indicate a greater sensitivity to variations in mercury content or that some data may have been lost during the nitric acid extraction. Pearson correlation also shows that the A horizon samples showed a greater correlation for extracted mercury content and normalized absorbance values with pH and CEC probably due to the influence of organic matter. Again, thermal desorption was more sensitive, with the exception of pH in B horizon samples, which had practically the same values from CVAAS and TDAAS. The separate investigation of the two horizons showed the major role that organic matter seems to play. The correlation of retained mercury with pH in A horizon samples was 26.5% higher on average than for whole soil values. In contrast, the effect of pH on mercury retention in B horizon samples was much smaller. The high correlation values of pH and mercury retention may have been due to the extreme importance of pH in soil sorption processes. For example, increasing the pH may increase the quantity of negative charges in soil and the CEC of the organic and mineral fractions in variable charge soils (McBride, 1994; Zhang and Zhang, 1997). pH influences specific adsorption (Yu et al., 1997) and non-specific adsorption (Ji and Li, 1997) of metals, as well as the formation of precipitates and redox processes (McBride, 1994).

Another important characteristic of soils with near-neutral pH, good availability of mineral nutrients and organic matter is a greater microbial activity, to which the oxidation of Hg^0 in contact with soil may be attributed, as will be discussed later on. Bacteria may oxidize elemental mercury to ionic mercury (Smith et al., 1998; Colombo et al., 2013; Colombo et al., 2014), which can be adsorbed by the soil.

After oxidization to Hg^{2+}, the main mercury retention factors in soil are: inorganic and organic CEC and iron oxide and organic matter contents. The former promotes electrostatic adsorption and the latter also contribute to specific adsorption with the formation of strongly covalent bonds (Yu et al., 1997). Since the CEC of highly weathered soils is strongly dependent on organic matter negative charges (McBride, 1994; Zhang and Zhang, 1997; Ji and Li, 1997), its effect on the surface horizon seems to be more important ($r = 0.85^*$ and $r = 0.72^*$ with TDAAS or CVAAS, respectively). This was corroborated by the lack of correlation of CEC with the retained mercury contents in B horizon soil samples. In contrast to what was observed for A horizon samples, extremely low correlations were observed for B horizon samples, and CEC and retained mercury content did not correlate significantly either with TDAAS or CVAAS results after nitric acid extraction, which had correlation coefficients of 0.08 and 0.17, respectively.

3.1. Available mercury

Table 3 shows the available mercury content in soils after Hg^0 incubation and its percentage related to the total retained mercury.

The available mercury is expected to include soluble and exchangeable Hg_2^{2+} and Hg^{2+} species. Considering all the mercury present in the form of Hg^0, its solubility in water ($5.6 \times 10^{-5}\ g\ L^{-1}$ according to the Committee on the Toxicological Effects of Methylmercury, 2000), according to the method used, a recovery of $1.12\ \mu g\ g^{-1}$ mercury might be achieved from all samples, except LVAd$_1$-B and RQo-B, which exhibited a total mercury content lower than $1\ \mu g\ g^{-1}$. However, that was not observed. The available mercury content of soils after Hg^0 incubation ranged from 0.001 to $7.74\ \mu g\ g^{-1}$, with an average of $0.67\ \mu g\ g^{-1}$ (Table 3). The available mercury content ranged from 1120 times lower to 6.9 times higher than the Hg^0 solubility itself could produce. This behavior was expected since Hg^{2+} originated on the soil surface may be weakly adsorbed on a negatively charged soil matrix and may form stronger inner sphere complexes with OM, Fe and Al oxides, besides precipitates that the KNO_3 solution cannot extract. The average percentage of available mercury in soils after Hg^0 incubation was 2.97%, with a maximum of 13.38% (Table 3). Furthermore, the available mercury content was correlated with CEC and pH ($r = 0.61^*$ and 0.68^*, respectively), which supports the hypothesis on Hg^0 oxidation to Hg^{2+} in soils.

Table 3
Available mercury content (AM) in soils after Hg^0 incubation.

Soil	Horizon	AM[a] ($\mu g\ g^{-1}$)	AM[b] (%)
PVA	A	0.58	4.64
LVd	A	0.001	0.02
	B	0.39	1.33
LVAd$_1$	A	0.10	2.11
	B	0.01	1.79
LVj	A	0.21	4.21
	B	0.12	2.29
NVef	A	0.87	3.29
	B	0.83	11.16
TCp	A	2.03	1.97
	B	0.08	4.54
CXbe	A	7.74	1.05
	B	1.24	1.39
FFcd$_1$	A	0.09	1.31
	B	0.21	11.17
FFcd$_2$	A	0.06	0.46
	B	0.05	0.97
CXd	A	0.29	2.04
	B	0.10	2.76
RQo	A	0.11	4.46
	B	0.01	1.85
LVAd$_2$	A	0.18	1.38
	B	0.06	2.14

[a] Extracted with 0.1 M KNO_3 solution.
[b] Ratio between mercury concentration on KNO_3 extract and total mercury concentration, extracted with 7 M HNO_3.

The available mercury content also correlated with the total mercury content ($r = 0.99$). This high correlation coefficient is obvious since the source of soil mercury was gaseous Hg^0 and the more mercury is transferred to the soil and oxidized, the greater the amount that may be available (exchangeable and soluble).

3.2. Role of organic matter

Hissler and Probst (2006) demonstrated the relevance of organic matter in mercury retention. They proposed that most atmospheric mercury is retained by organic matter in soil and stream sediments. Rennerberg and Duda (2001) showed that decades after the contamination of soil with metallic mercury, over 85% of mercury was associated to the soil organic matter. Guedron and colleagues (2013) investigated the mechanisms of incorporation of mercury into soil near a chlor-alkali industry and concluded that it was strongly bound to organic matter. The relation between organic matter and Hg^0 oxidation was also observed by Valle and colleagues (2006) studying Amazon soils. They observed a range of 28–68% of Hg^0 oxidation, and kinetic studies concluded that the oxidation processes are predominant over the reduction processes. The efficiency of retention/stabilization by organic matter explain the high these findings and the background values found in these soils.

Fig. 3 shows the thermograms of some incubated samples. The areas under the thermogram replicates show a coefficient of variation from 2% to 31%, with an average of 14%, demonstrating the good precision of the thermal desorption analysis.

The thermograms of 15 of the 23 samples had only one peak around 300 °C (Fig. 3c), the region characteristic of Hg^{2+} release, which shows that mercury was oxidized during incubation under the investigation conditions. Another three types of thermograms were also observed: thermograms with a peak in the typical Hg^{2+} region with a shoulder around 100 °C (Fig. 3a), characteristic of thermal desorption of less oxidized forms of mercury (Hg^0/Hg_2^{2+}); thermograms with two distinct peaks, one between 100 and 200 °C (Hg^0/Hg_2^{2+} peak) and another around 300 °C (Hg^{2+} peak)

(Fig. 3d) and a rather broad thermogram with various peaks starting around 100 °C, which occurred with only one sample (Fig. 3b).

From these 15 samples with only one peak around 300 °C, 10 were from A horizon. Considering that the main difference between A and B horizons from the same soil is the organic matter content, we deduced that organic matter influenced mercury oxidation either through biotic via (Smith et al., 1998; Colombo et al., 2013; Colombo et al., 2014) or abiotic via (Yamamoto, 1995).

Abiotic mercury oxidation occurs because the organic matter has -SH groups, which have a high affinity to mercury ions, and as already demonstrated (Yamamoto, 1995), mercury oxidation is favored by the presence of compounds with high affinity to the mercury ion.

The microbial contribution to mercury oxidation was first proposed by Smith and colleagues (1998), who demonstrated that typical soil bacteria (*Bacillus* and *Streptomyces*) can oxidize elemental mercury to Hg^{2+} through enzymatic paths. Recent studies have shown that mercury can also be oxidized by anaerobic bacteria (Colombo et al., 2013; Colombo et al., 2014).

Oxidation probably occurs on the soil surface at the moment of or after the adsorption of elemental mercury. A rarefied and saturated gaseous mercury atmosphere in the desiccator ensured the presence of elemental mercury. If mercury were oxidized in the air and then deposited, the thermal desorption profiles of the samples from the same desiccator would not be much different either qualitatively or quantitatively, in contrast to the current observations (Fig. 2b). This behavior demonstrates that the characteristics soil play an essential role in the retention and speciation of adsorbed mercury. In the atmosphere, where 95% of the total mercury is in elemental form, Hg^0 is slowly oxidized to Hg^{2+}, with ozone as its main oxidant (Morel et al., 1998). Considering the ozone concentration inside the desiccator is nearly null, a probable abiotic oxidation path is the oxidation of elemental mercury in the air–soil interface by the oxygen in contact with the soil. Once in the Hg^{2+} form, mercury binds to the organic matter. According to Yamamoto (1995), the conversion of Hg^0 into Hg^{2+} is fast due to the change in the equilibrium of these forms caused by the formation of the stable $RS-Hg^{2+}$ complex. The lower percentages of available mercury in A horizons when compared to B horizons (Table 3) support this idea.

Correlation analysis of these 15 samples revealed a positive and significant correlation between the extracted retained mercury content and the pH and CEC values ($r = 0.73^*$ and $r = 0.67^*$, respectively). The positive correlation with CEC corroborates the hypothesis of microbial oxidation, since a greater CEC may result in greater soil nutrient availability, which also corroborates the fact that in soils with near-neutral pH, greater amounts of mercury are retained. One can see that at and below pH 5 (Tables 1 and 2), mercury retention was very low, even for LVd-A, which had a high organic matter content, and that the soil samples with very low mercury retention and pH higher than 5 were all from B horizon samples (TCp-B and LVAd$_1$-B).

The characteristics of soils TCp and LVAd$_1$ (Table 1) clearly show that organic matter is the most important factor among the factors considered important for mercury retention (pH, CEC and organic matter). The pH and CEC values of TCp sample A and B horizons did not differ much. The organic matter content of A horizon (2.92%) was 4.9 times higher than that of B horizon (0.595%) This different organic matter content was probably responsible for the retention of 46 times more mercury in A horizon than in B horizon in this soil (Table 2). This means that despite the high pH, the similar CEC values of A and B horizons and the high clay content of B horizon, the near non-existence of organic matter in B horizon prevented the retention of large amounts of mercury in sample TCp-B. The thermograms in Fig. 3a show that A horizon of TCp soil (TCp-A) retained mercury through the partial oxidization of Hg^0 to Hg^{2+}
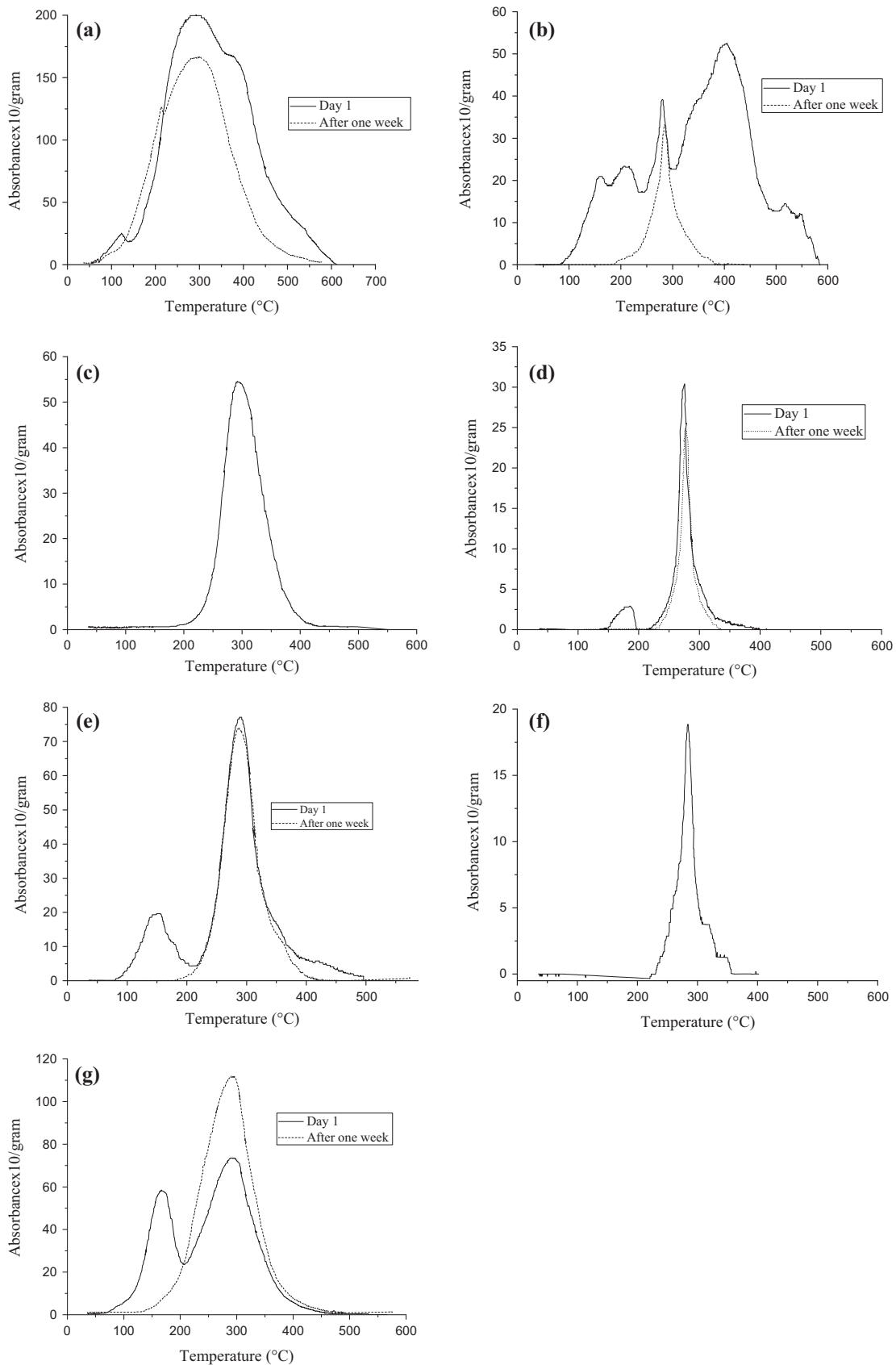
Fig. 3. Corrected thermograms (absorbance/gram) of soils (a) and (b) TCp A and B horizons, respectively, day 1 and one week after incubation; (c) RQo, A horizon, day 1 and (d) RQo, B horizon, day 1 and one week after incubation; (e) LVAd$_1$, A horizon day 1 and one week after incubation; (f) LVAd$_1$, B horizon day 1 and (g) PVA, A horizon, day 1 and one week after incubation.

and the desorption of excess elemental mercury. The initial thermogram (day 1) had a broad band with a small shoulder with an area of 1.23% of the total area (Fig. 4a) in the 100 °C temperature range. This shoulder, characteristic of Hg^0, disappeared after one week of exposure to the air. Comparatively, the final thermogram had an area reduction of 29% that cannot be justified only by the loss of the mercury corresponding to the shoulder in the initial thermogram. The deconvolution of the initial curve suggests a band with a peak around 250 °C that certainly corresponds to Hg^{2+}. Additionally, the one-week thermogram started at a lower temperature, which indicates the presence of Hg^0 in addition to Hg^{2+}. Therefore, it is possible that for this soil there was adsorption of a great excess of elemental mercury that was partially oxidized but that after one week was not completely desorbed.

The thermogram of sample TCp-B obtained 24 h after interruption of the incubation presented a characteristic Hg^{2+} peak at 280 °C with an area of only 9.0% (Fig. 4b) and other peaks at lower temperatures, which may mean that this sample adsorbed elemental mercury only on the surface through weak bonds that were broken after one week of exposure to the air. The fact that the peak at 280 °C did not increase after one week (Fig. 3b) leads to the conclusion that the initially adsorbed elemental mercury was neither oxidized nor remained in the soil and therefore was completely desorbed. The bands observed at very high temperatures in the initial thermogram (Fig. 4b) may have been due to elemental mercury trapped in micropores that had been released upon heating and not

by oxidized forms, as proposed by Biester and colleagues (2002). In contrast to A horizon, B horizon desorbed excess elemental mercury after one week, which shows that even though the retention of elemental mercury took place through physisorption, the interaction with mercury in A horizon was stronger than in B horizon.

The greater importance of the role of organic matter in the retention of mercury was also evident in sample $LVAd_1$, which had an organic matter content 5.59 times greater in A horizon (2.41%) than in B horizon (0.43%). Despite the organic matter content slightly higher than those of TCp soil, the mercury content retained in A horizon was 9.13 times greater than in B horizon, in contrast to the value 46 times greater of TCp (Table 2). This smaller concentration factor may have been set off by the greater pH of B horizon (6.22) in comparison to A horizon (5.24) and the greater CEC of B horizon (4.17 $cmol_c$ kg^{-1}) in relation to A horizon (2.16 $cmol_c$ kg^{-1}). Despite these compensatory effects, the mercury retention ratios of $LVAd_1$ horizons were the third highest, being lower only than TCp and CXbe, which corroborates the role of organic matter. One must bear in mind that besides the organic matter content, its quality directly influences the chemical and biological phenomena involved in mercury retention, which makes the comparison of different soil types very difficult, but which is feasible for same soil horizons. In contrast to that observed for TCp, $LVAd_1$ B horizon did not present a characteristic Hg^0 peak (Fig. 3f).

A horizon of $LVAd_1$ soil presented an Hg^0 peak that disappeared after 1 week of exposure to the air without the appearance of any
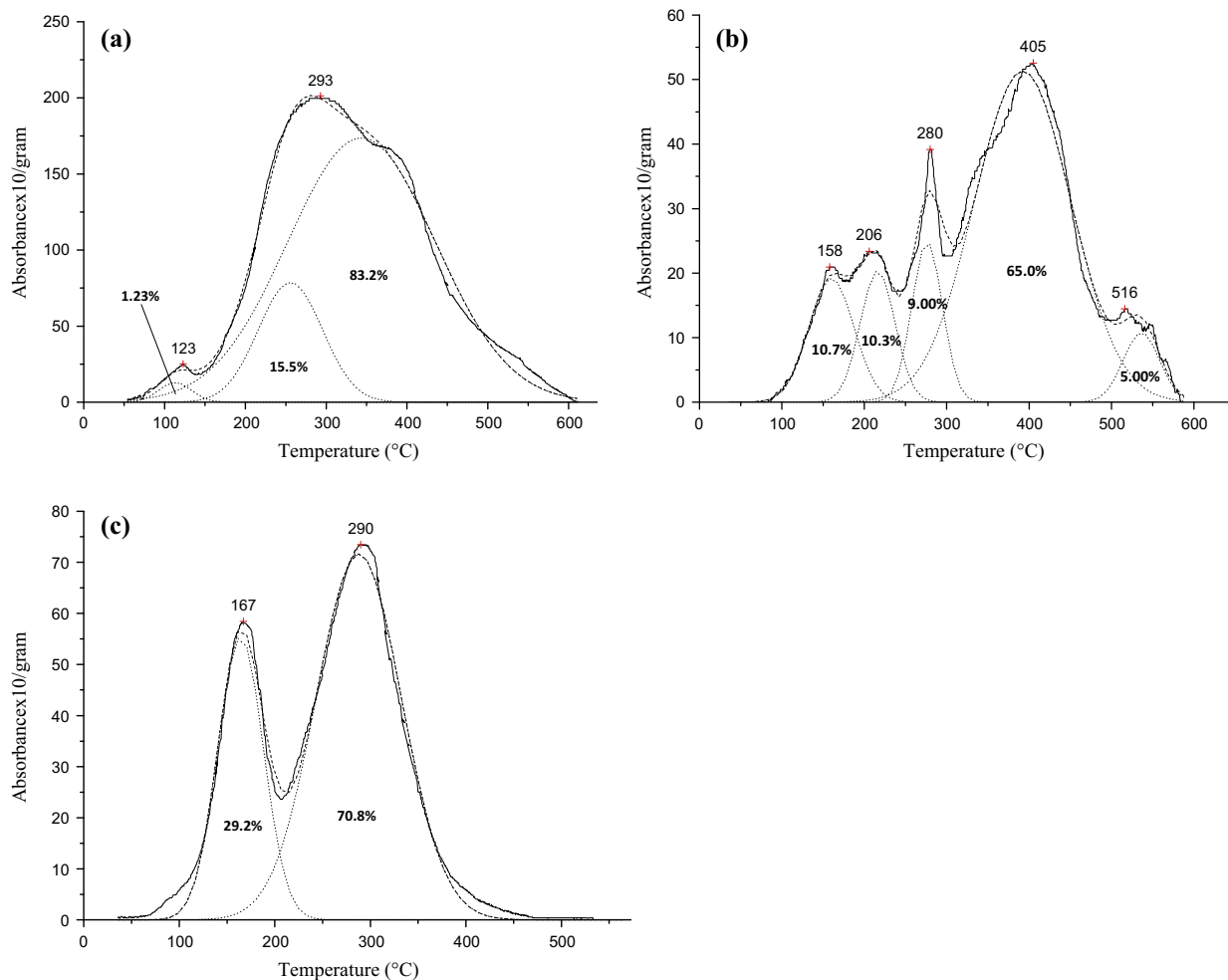

Fig. 4. Deconvolution of the thermograms of soils (a) TCp-A, (b) TCp-B, (c) PVA-A obtained 24 h after incubation (day 1). The thermograms show the temperature peaks and the percent contribution of the area of each band to the total area under the curve.

Hg^{2+}-related peak (Fig. 3e). In most cases of physical adsorption, Hg^0 was not further oxidized upon air exposure and followed by an increase in the Hg^{2+} peak, with the exception of PVA A horizon (Fig. 3g). Initially the area under the peak associated with Hg^0 was 29.2% of the total area (Fig. 4c). After 1 week, this peak disappeared and the Hg^{2+} peak increased, while the total area under the curve remained the same, suggesting that the Hg^0 in the soil had been completely oxidized at the air–soil interface and remained adsorbed in the soil. Once more, this behavior shows that various mechanisms determined by soil physical, chemical, microbiological and possibly mineralogical characteristics may act in the retention and transformation of elemental mercury in contact with soil.

When two different soils are compared, the soil with a greater organic matter content does not necessarily adsorb a greater quantity of mercury because beside differences in the organic matter characteristics other soil characteristics may influence the soil mercury retention capacity. However, same soil A and B horizons are more similar to each other both chemically and mineralogically and because both probably present much more qualitatively similar organic matters than soils from different regions. Nevertheless, care must be taken since organic matter composition may vary with profile depth because of preferential migration of more soluble organic compounds, such as fulvic acid, in addition to a possible constant input of organic matter not decomposed in the surface horizon (Stevenson, 1994). Nevertheless, the comparison of same soil A and B horizons still is the best way to compare soils with similar organic matters with only quantitative differences.

Comparison of the ratios between the HNO_3-extracted mercury content, normalized TDAAS absorbance and the carbon content from A and B horizons shows that these parameters are greater in A horizon than in B horizon in all the soils for most of the samples.

The behavior of the amounts of mercury retained in A and B horizons of soil LVd was atypical with a greater retention in B horizon than in A horizon, despite the greater organic matter content of A horizon. B horizon (Table 1) presented more aluminum-substituted iron oxides than A horizon, as shown by the aluminum extraction values by DCB and A horizon had greater amounts of exchangeable aluminum, as shown by the lower pH in KCl in relation to the pH in water and greater aluminum content by oxalate extraction. The greater exchangeable aluminum content of A horizon may have hindered the complexation of mercury at the organic matter complexation sites, since Al^{3+} has great affinity for the same sites (Stevenson, 1994). On the other hand, more isomorphically aluminum-substituted iron oxides have a greater specific surface area (Cornell and Schwertmann 1996), which may have favored a greater adsorption of mercury in B horizon.

4. Conclusions

The retention of gaseous mercury by tropical soils varied quantitatively and qualitatively as a function of soil type and soil horizon.

The different soil samples exposed to high concentrations of Hg^0 presented different mercury oxidation and adsorption capacities. The maximum adsorption capacity ranged from 0.6 ± 0.2 to $735 \pm 23\ \mu g\ g^{-1}$, with a mean value of $44 \pm 146\ \mu g\ g^{-1}$ of retained mercury.

For samples from the same soil, A horizon retained more mercury than B horizon, with one exception, which demonstrated the essential role of organic matter in this process.

The thermograms of all samples presented characteristic Hg^{2+} peaks, corroborating that elemental mercury had been oxidized not in the air, but in the air/soil interface, since the Hg^{2+} contents of the samples varied greatly.

No significant correlation was found between mercury retention capacity and organic matter content for any of the soil samples, which demonstrates that quantitative comparison of distinct organic matter may be unviable.

Among the soil characteristics responsible for the retention of elemental mercury, organic matter content, and soil pH and CEC stand out.

Soils with pH below 5.0 retained low amounts of mercury, even soil with high organic matter contents. The greatest mercury retention occurred in more eutrophic soils with near-neutral pH and with larger organic matter contents, which may suggest that the retention of mercury from the atmosphere was mediated by microorganisms.

Some thermograms presented characteristic adsorbed Hg^0 peaks that disappeared one-week after incubation. With the exception of Ultisol (PVA sample) which presented oxidation after incubation, the Hg^0 peak of the thermograms of the other samples disappeared after 1 week of exposure to the air without the corresponding increase in the Hg^{2+} peak.

The available mercury content after Hg^0 incubation ranged from 0.001 to 7.74 $\mu g\ g^{-1}$, with an average of 0.67 $\mu g\ g^{-1}$ and correlated with the total mercury content, CEC and soil pH.

The soils that retained more mercury, due mainly to organic matter, were those that presented the lowest exchangeable fraction recovery percentages. This strong retention of mercury by organic matter may make the remediation of these soils more difficult.

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