Quantification and speciation of mercury in soils from the Tripuí Ecological Station, Minas Gerais, Brazil

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Abstract

Contents of total mercury, organic carbon, total sulfur, iron, aluminum and grain size and clay mineralogy were used along with Pearson's correlation and Hg thermal desorption technique to investigate the presence, distribution and binding behavior of Hg in soils from three depths from the Tripuí Ecological Station, located near Ouro Preto, Minas Gerais State, Brazil. The soils studied had predominantly medium and fine sand texture (0.59–0.062 mm), acid character and Hg contents ranging from 0.09 to 1.23 μg/g. The granulometric distribution revealed that Hg is associated with coarse sand (2–0.59 mm) and silt and clay (<0.062 mm) and presents similar Hg concentrations in both fractions. Mercury distribution in soil profiles showed that Hg was homogeneously distributed throughout the depths at most sites. Hg thermal desorption curves show that mercury occurs not only as Hg^{2+} predominantly bound to organic components in most of the samples, but also in the form of cinnabar in some. Pearson's correlation confirmed that mercury is associated with organic matter and sulfur and possibly with sulfur-bearing organic matter in most samples.
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1. Introduction

For decades, the Tripuí Ecological Station (TES) has been the object of interest of many studies due to its historical, ecological, and environmental importance. It was turned into an ecological station in 1981 due to the discovery of the invertebrate, *Peripatus acacioi*, a prob-able ancestor of annelids and arthropods (Guimarães Neto, 1999) in 1954. It lies in Quadrilátero Ferrífero, a region of rudimentary gold mining in the late 17th century (Eschewge, 1979; Guimarães Neto, 1999). Even though there is no evidence that gold miners might have used Au–Hg amalgamation in the TES area (Busher, 1992), mercury was found in sediments and some plant species as reported by Cruz (2002), Busher (1992) and Palmieri et al. (2003).

Mercury occurs on Earth's crust as more than 20 minerals. Cinnabar (HgS) and the free mercury (Hg^0) are the main natural mercury sources found in soils and aquatic environments (Salomons et al., 1995). Due to

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the extremely low solubility of HgS (10^{-54} mol dm^{-3}), it has fundamental importance in the immobilization of Hg under low oxygenation and in slightly oxidant-to-reducing environmental conditions. However, under altered conditions, it may become soluble (Moore and Ramamoorthy, 1984).

Depending on redox conditions, inorganic Hg may occur in three different states, Hg_2^{2+}, Hg^0, and Hg^{2+}. The last two are normally found in soil. pH and Cl^{-1} concentration are also key parameters in determining the speciation and the chemical transformations of mercury in soil solution. Due to the large susceptibility of Hg^{2+} to form complexes, only a minute fraction of this ion occurs in soil solution. The major fraction is either bound to soil minerals or adsorbed onto solid inorganic and organic surfaces (Steinnes, 1995).

Anderson (1979) demonstrated a close correlation between Hg and organic matter in acid soils, whereas in slightly acid and neutral soils (pH>6), the co-variation between Hg and Fe was stronger than that between Hg and organic matter. The formation of organic Hg complexes is largely due to the affinity of Hg^{2+} and its inorganic compounds for sulfur-containing functional groups (Shuster, 1991; Xia et al., 1999).

Due to the high affinity of Hg for organic matter and minerals, soil Hg leaching rates are very low and are mostly associated with dissolved organic matter (Anderson, 1979; Shuster, 1991; Mierle and Ingram, 1991).

The determination of Hg by thermal desorption/ atomic absorption technique was initially applied in geochemical prospection (Azzaria and Webber, 1969), and in recent years, it has proved to be useful to distinguish different Hg-binding forms (Hg phases) by their thermal release characteristics (Windmöller et al., 1996; Biester et al., 2000; Higueras et al., 2003).

The aim of this work was to investigate the presence, distribution and binding behavior of Hg in soil samples collected at three depths on the banks of the main streams and near a pond in TES. Total Hg was determined by cold vapor atomic absorption spectrometry (CVAAS) and Hg phases were determined by thermal desorption atomic absorption spectrometry (TDAAS). Factors that govern the mobility of mercury such as organic carbon, pH, total sulfur, iron and aluminum contents and clay mineralogy were also examined.

2. Study area

The area studied lies between UTM coordinates "23 K; 648000/653000 E and 7743500/7747500 N" and comprises an area of approximately 7 km^2. The Tripuí Ecological Station (TES) (Fig. 1) has an area of 3.37 km^2 and is located in the Tripuí Stream valley, about 3
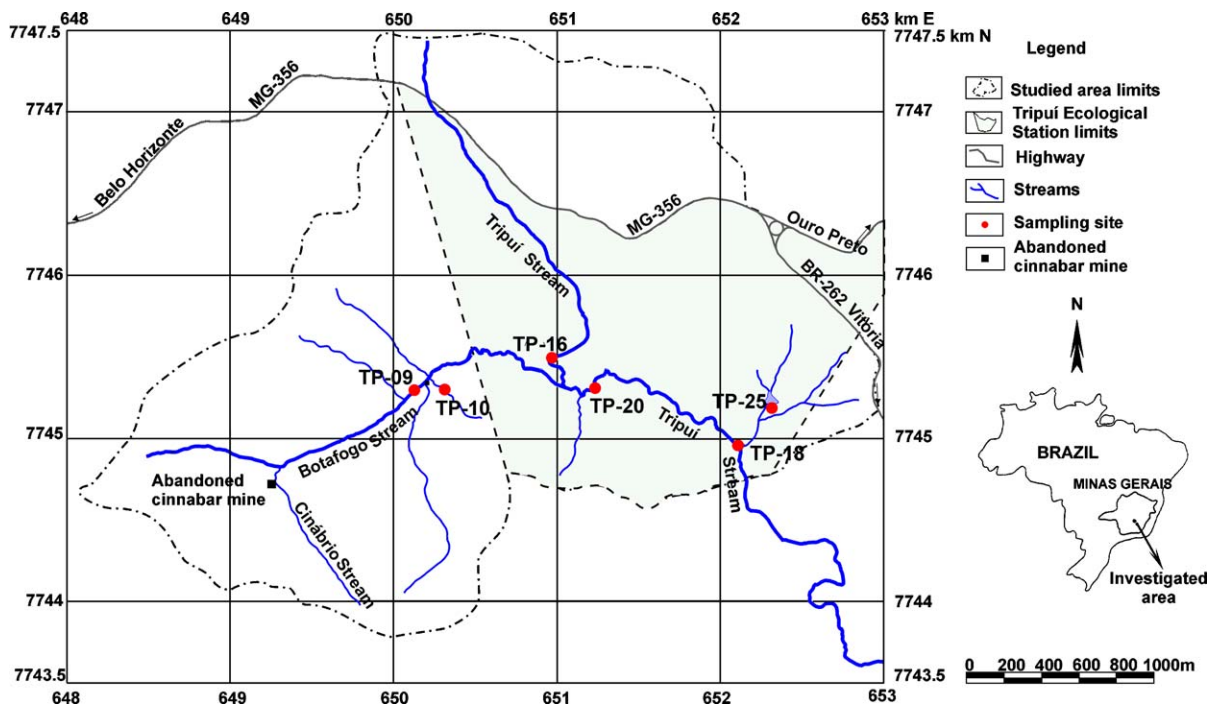

Fig. 1. Sampling site location in the area investigated in Minas Gerais State, Brazil.

km away from Ouro Preto City. One of the main tributaries of Tripuí Stream, Botafogo Stream, flows fast and its riversides present dense vegetation. It meets the Cinábrio Stream at its source, which drains the surroundings of an abandoned cinnabar mine.

3. Methods

3.1. Sample collection and grain size fractionation

Soil samples were collected on stream banks in February 2003 at the following sites: TP-09 (Botafogo Stream), TP-10 (a tributary of Botafogo Stream), TP-16 (Tripuí Stream upstream its confluence with Botafogo Stream), TP-18 and TP-20 (Tripuí Stream downstream its confluence with Botafogo Stream), TP-25 (Fortes pond shore). One track sediment sample (SDT) was also collected at TP-09. Sampling sites are shown in Fig. 1, and sample identifications are given in Table 1.

Approximately 0.5 kg of soil was collected at three different depths, 30, 60 and 90 cm, at all sampling sites using a deep sampling handle (JMC back-saver handle). Samples were kept in polyethylene bags and air dried and fractionated in laboratory by sieving in three grain sizes (2–0.59 mm, 0.59–0.062 mm, and <0.062 mm) to determine the relation between particle size and Hg retention. Each fraction was weighed and the percent weight of the each fraction was calculated (Table 1).

3.2. Analytical techniques

To determine total mercury, 0.20–0.30 g of soil samples was digested with a mixture of HNO_3/H_2SO_4 (1:2, v/v), potassium permanganate, potassium persulfate in a closed Teflon vessel (22 ml) at 75 °C for 16 h. Before analysis, hydroxylamine hydrochloride was added to reduce excess permanganate, and the sample was diluted to 50 ml with deionized water. Total mercury was determined by CVAAS using a Perkin Elmer flow-injection mercury system, FIMS 400 (detection limit of 5 ng/g). Standard reference material 2709, San Joaquim soil 1.40 ± 0.08 μg/g Hg from the National Institute of Standards and Technology (NIST), USA and GBW 07404 0.590 ± 0.034 μg/g Hg from the National Research Center, China, were used to evaluate the analytical accuracy within 5%. The concentrations measured were 1.32 ± 0.14 μg/g Hg and 0.60 ± 0.07 μg/g Hg, dry weight, with recovery rates of 94% and 102%, respectively. Moisture was determined by weight loss in a separate sub-sample by drying at 110 °C for 2 h.

For pH determination, dry soil was mixed with 1–2.5-fold its water weight and shaken. Measurement was carried out in the supernatant solution 60 min after preparation using Metrohm 744 pH meter.

Determination of Hg phases by solid-phase Hg thermal desorption is based on the specific thermal desorption or decomposition of Hg compounds from solids at different temperatures. Hg thermal desorption curves (TDCs) were obtained according to Windmöller et al. (1996). The system consists of an electronically controlled heating unit and an Hg detection unit. The samples (masses varying from 500 to 3000 mg) were heated at a rate of 33 °C/min from room temperature to 570 °C. A constant nitrogen flow (200 ml/min) passed through the samples carried thermodesorbed vapors to the detection cell of an atomic absorption spectrometer (GBC 932-AA). Mercury was detected at 253.7 nm. Interference, mainly from pyrolytic organic matter, was compensated by continuous deuterium background correction. The Hg TDC shows the release of Hg^0 vs. temperature.

Mercuric sulfide red (99%, Fluka) and cinnabar found in the region studied were used as standards for Hg thermal desorption curve of synthetic red cinnabar (HgS) and natural red cinnabar. Standard materials were prepared by solid dilution with quartz powder. Standard Hg^0 (Raposo et al., 2003) and standard Hg in humic acid (Valle, 2005) were obtained through the same thermal desorption/atomic absorption system and under the same work conditions.

The level of organic matter in soils was assessed by measuring organic carbon in all samples. Organic carbon was determined by the Walkley–Black method (EMBRAPA, 1997). This method is based on the oxidation of C by acid dichromate and titration of excess dichromate with ammonium iron(II) sulfate hexahydrate solution.

Iron, aluminum and sulfur were analyzed by X-ray fluorescence spectrometry (Rigaku 3134), and mineralogical analysis of the samples was carried out with a Rigaku X-ray diffractometer.

The physico-chemical parameters and Hg contents measured were analyzed using STATISTICA for Windows, version 6.0 for linear correlation (Pearson's correlation).

4. Results and discussion

4.1. Sample characterization and Hg quantification

X-ray diffraction analyses of bulk mineralogy reveal that the soil samples consist primarily of quartz (SiO_2),

Table 1
Distributions of mercury and organic carbon concentrations in different size fractions at three soil depths

Sampling Sites	pH range	Size fractions (mm)	Depth (30 cm)				Depth (60 cm)				Depth (90 cm)			
			Sample	Grain size (%)	Hg (μg/g)	Organic carbon (%)	Sample	Grain size (%)	Hg (μg/g)	Organic carbon (%)	Sample	Grain size (%)	Hg (μg/g)	Organic carbon (%)
TP 09	5.1–5.6	2.0–0.59	SA1d	22	1.08 ± 0.12	5.0 ± 0.2	SA2d	13	1.23 ± 0.12	2.6 ± 0.1	SA3d	13	0.62 ± 0.06	3.8 ± 0.2
		0.59–0.062	SA1g	61	0.91 ± 0.09	4.6 ± 0.2	SA2g	71	0.48 ± 0.05	2.0 ± 0.1	SA3g	72	0.39 ± 0.04	2.0 ± 0.1
		<0.062	SA1h	17	1.18 ± 0.12	5.3 ± 0.2	SA2h	16	0.94 ± 0.09	2.7 ± 0.1	SA3h	15	0.79 ± 0.08	2.8 ± 0.1
TP-10	5.0–5.2	2.0–0.59	SB1d	24	0.21 ± 0.02	3.3 ± 0.2	SB2d	28	0.11 ± 0.01	1.0 ± 0.1	SB3d	23	0.09 ± 0.02	1.8 ± 0.1
		0.59–0.062	SB1g	51	0.17 ± 0.02	3.1 ± 0.2	SB2g	40	0.15 ± 0.01	1.7 ± 0.1	SB3g	55	0.11 ± 0.01	2.1 ± 0.1
		<0.062	SB1h	25	0.23 ± 0.02	3.5 ± 0.2	SB2h	32	0.17 ± 0.02	1.4 ± 0.1	SB3h	22	0.11 ± 0.01	1.4 ± 0.1
TP-16	5.1–5.7	2.0–0.59	SC1d	5	0.16 ± 0.02	6.8 ± 0.2	SC2d	12	0.28 ± 0.03	3.4 ± 0.2	SC3d	5	0.18 ± 0.02	4.6 ± 0.2
		0.59–0.062	SC1g	68	0.12 ± 0.01	2.0 ± 0.1	SC2g	62	0.15 ± 0.01	1.9 ± 0.1	SC3g	57	0.12 ± 0.01	1.7 ± 0.1
		<0.062	SC1h	27	0.16 ± 0.02	1.7 ± 0.1	SC2h	26	0.27 ± 0.03	2.1 ± 0.1	SC3h	38	0.25 ± 0.02	1.7 ± 0.1
TP-18	5.3–5.7	2.0–0.59	SF1d	12	0.27 ± 0.03	12.0 ± 0.3	SF2d	14	0.67 ± 0.07	4.8 ± 0.2	SF3d	24	0.70 ± 0.07	5.8 ± 0.2
		0.59–0.062	SF1g	52	0.38 ± 0.04	3.9 ± 0.2	SF2g	42	0.55 ± 0.05	2.7 ± 0.1	SF3g	50	0.47 ± 0.05	2.9 ± 0.1
		<0.062	SF1h	36	0.60 ± 0.06	3.5 ± 0.2	SF2h	44	0.75 ± 0.07	1.9 ± 0.1	SF3h	26	0.63 ± 0.06	2.4 ± 0.1
TP-20	5.2–5.7	2.0–0.59	SD1d	7	0.29 ± 0.03	2.7 ± 0.1	SD2d	10	0.22 ± 0.02	1.3 ± 0.1	SD3d	16	0.28 ± 0.03	0.8 ± 0.1
		0.59–0.062	SD1g	80	0.22 ± 0.02	1.0 ± 0.1	SD2g	77	0.21 ± 0.02	0.8 ± 0.1	SD3g	75	0.24 ± 0.02	0.4 ± 0.1
		<0.062	SD1h	13	0.37 ± 0.04	2.3 ± 0.1	SD2h	13	0.43 ± 0.04	1.6 ± 0.1	SD3h	9	0.39 ± 0.04	1.3 ± 0.1
TP-25	5.7–6.0	2.0–0.59	SE1d	9	0.76 ± 0.08	3.4 ± 0.2	SE2d	10	0.88 ± 0.09	2.7 ± 0.1	SE3d	10	0.88 ± 0.09	2.3 ± 0.1
		0.59–0.062	SE1g	40	0.38 ± 0.04	1.4 ± 0.1	SE2g	40	0.53 ± 0.05	0.7 ± 0.1	SE3g	41	0.58 ± 0.06	1.2 ± 0.1
		<0.062	SE1h	51	0.51 ± 0.05	<0.1	SE2h	50	0.77 ± 0.08	<0.1	SE3h	49	0.83 ± 0.08	<0.1

kaolinite $(Al_2Si_2O_5(OH)_4)$, goethite (FeO·OH) and muscovite $(KAl_2(AlSi_3O_{10})(OH)_2)$. Minor amounts of hematite (Fe_2O_3), gibbsite $(\alpha\text{-}Al_2O_3 \cdot 3H_2O)$, magnetite (Fe_3O_4), chlorite $(Mg_3(Si_4O_{10}) \cdot (OH)_2 \cdot Mg_3(OH)_6)$ were also observed. The silt and clay fraction is predominantly composed of quartz, muscovite and kaolinite, with minor amounts of goethite, hematite and gibbsite. At TP-25, the predominant minerals were quartz, muscovite and kaolinite. Diffractograms of samples SA1d, SE2h, SF2d and SD1h are shown in Fig. 2.

The distribution of total mercury, organic carbon, Al, Fe and S concentrations in different grain-size fractions at three depths and at six sampling sites is summarized in Tables 1 and 2. The mercury concentrations presented in Table 1 are reported as μg/g dry weight. Total mercury concentration in soil samples ranged from 0.09 to 1.23 μg/g, significantly higher than the concentration of <0.1 μg/g established by Fergusson (1990) for unpolluted soils. Hg content in the sediment sample (SDTh) was 0.62 μg/g. The values obtained for organic carbon (0.6–4.8%) agree with the typical content values of organic matter in tropical soils of South America (0.5–21.7%) reported by Alloway (1995).

Soil was found to consist mainly of fine and medium sand texture (0.59–0.062 mm). Clay and silt ranged from 9% to 51%. At site TP-25 (Fortes pond), the predominant size fraction was <0.062 mm. At this site, abundant fine grains were deposited. In most of the samples of this study, sand (2–0.59 mm) and silt and clay (<0.062 mm) fractions contained similar Hg concentrations. The same was observed for Fe, Al and organic carbon (except at TP-25). Sulfur concentration appeared to be independent from particle size. The behavior of mercury in association with the finest granulometric class of clay in soil was observed in previous studies (Busher, 1992; Leoni and Sartori, 1997). According to Tessier et al. (1982), increased metal concentration in coarse fractions had already been observed, and it is believed that coarse particles may document anthropogenic inputs better because of their limited transport and longer residence time at any particular site.

Sample pH values were between 5.0 and 6.0. Hence, this acid soil can be associated with the humid climate of this region, where possibly frequent leaching tends to produce protonated clays, which lowers the pH.

4.2. Mercury phases in soils

TDCs of standard mercury compounds or mercury binding forms, which might potentially occur in soils of TES, are shown in Fig. 3.

Hg TDCs were carried out in all samples, and the representative curves are shown in Fig. 4. Most of them display a characteristic pattern defined by peaks with one maximum between 280 and 380 °C (Fig. 4a). This suggests the presence of mercury in the form of Hg^{2+} bound to organic matter according to the curve of
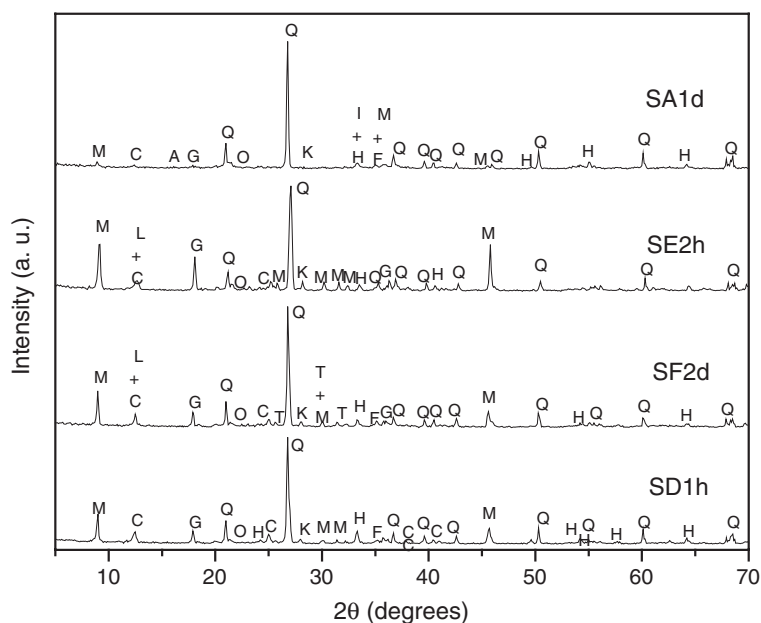

Fig. 2. Diffractograms of samples SA1d, SE2h, SF2d, and SD1h. Mineral peaks: M (muscovite); C (kaolinite); A (albite); L (chlorite); G (gibbsite); Q (quartz); O (goethite); H (hematite); T (tourmaline); K (microcline); I (ilmenite); F (magnetite).

Table 2
Distributions of aluminum, iron, and sulfur concentrations in different size fractions at three soil depths

| Sampling sites	Size fractions (mm)	Depth (30 cm)				Depth (60 cm)				Depth (90 cm)			
		Sample	Al (%)	Fe (%)	S (μg/g)	Sample	Al (%)	Fe (%)	S (μg/g)	Sample	Al (%)	Fe (%)	S (μg/g)
TP-09	2.0–0.59	SA1d	6.1 ± 0.6	12.4 ± 1.2	490 ± 50	SA2d	6.2 ± 0.6	11.7 ± 1.2	240 ± 20	SA3d	5.5 ± 0.5	11.1 ± 1.1	260 ± 30
	0.59–0.062	SA1g	6.1 ± 0.6	11.1 ± 1.0	490 ± 50	SA2g	5.3 ± 0.5	8.4 ± 0.8	200 ± 20	SA3g	4.6 ± 0.5	7.8 ± 0.8	190 ± 20
	<0.062	SA1h	6.6 ± 0.7	12.3 ± 1.2	520 ± 50	SA2h	8.1 ± 0.8	12.2 ± 1.2	260 ± 30	SA3h	7.5 ± 0.7	11.5 ± 1.2	240 ± 20
TP-10	2.0–0.59	SB1d	10.1 ± 1.0	6.1 ± 0.6	180 ± 20	SB2d	12.6 ± 1.3	5.2 ± 0.5	<100	SB3d	11.9 ± 1.2	6.0 ± 0.6	140 ± 10
	0.59–0.062	SB1g	8.1 ± 0.8	4.6 ± 0.5	190 ± 20	SB2g	10.1 ± 1.0	4.4 ± 0.4	120 ± 10	SB3g	10.4 ± 1.0	4.7 ± 0.5	170 ± 20
	<0.062	SB1h	10.8 ± 1.0	6.9 ± 0.7	210 ± 20	SB2h	11.7 ± 1.2	6.0 ± 0.6	<100	SB3h	11.7 ± 1.2	6.5 ± 0.6	130 ± 10
TP-16	2.0–0.59	SC1d	6.2 ± 0.6	13.2 ± 1.3	450 ± 40	SC2d	7.7 ± 0.8	11.5 ± 1.2	260 ± 30	SC3d	7.1 ± 0.7	12.7 ± 1.3	250 ± 20
	0.59–0.062	SC1g	4.0 ± 0.4	9.6 ± 1.0	160 ± 20	SC2g	5.8 ± 0.6	9.0 ± 0.9	200 ± 20	SC3g	4.8 ± 0.5	8.7 ± 0.9	140 ± 10
	<0.062	SC1h	7.7 ± 0.8	18.8 ± 1.9	200 ± 20	SC2h	8.9 ± 0.9	15.3 ± 1.5	230 ± 20	SC3h	9.2 ± 0.9	14.8 ± 1.5	180 ± 20
TP-18	2.0–0.59	SF1d	8.9 ± 0.9	8.4 ± 0.8	1370 ± 140	SF2d	9.7 ± 1.0	9.2 ± 0.9	500 ± 50	SF3d	9.2 ± 0.9	8.4 ± 0.8	600 ± 60
	0.59–0.062	SF1g	6.2 ± 0.6	5.5 ± 0.5	380 ± 40	SF2g	8.6 ± 0.9	6.7 ± 0.7	250 ± 20	SF3g	8.0 ± 0.8	6.9 ± 0.7	300 ± 30
	<0.062	SF1h	9.4 ± 0.9	10.1 ± 1.0	280 ± 30	SF2h	10.0 ± 1.0	9.4 ± 0.9	140 ± 10	SF3h	10.0 ± 1.0	9.3 ± 0.9	220 ± 20
TP-20	2.0–0.59	SD1d	6.2 ± 0.6	21.2 ± 2.1	220 ± 20	SD2d	8.4 ± 0.8	14.2 ± 1.4	<100	SD3d	3.3 ± 0.3	14.8 ± 1.5	<100
	0.59–0.062	SD1g	3.7 ± 0.4	11.8 ± 1.2	<100	SD2g	8.3 ± 0.8	14.1 ± 1.4	<100	SD3g	4.1 ± 0.4	15.2 ± 1.5	<100
	<0.062	SD1h	6.7 ± 0.7	18.7 ± 1.9	180 ± 20	SD2h	9.0 ± 0.9	19.2 ± 1.9	110 ± 10	SD3h	9.5 ± 0.9	13.7 ± 1.4	120 ± 10
TP-25	2.0–0.59	SE1d	8.6 ± 0.9	6.7 ± 0.7	<100	SE2d	8.3 ± 0.8	6.6 ± 0.7	120 ± 10	SE3d	8.6 ± 0.9	6.6 ± 0.7	<100
	0.59–0.062	SE1g	6.2 ± 0.6	3.7 ± 0.4	<100	SE2g	6.6 ± 0.7	3.4 ± 0.3	<100	SE3g	6.5 ± 0.6	3.7 ± 0.4	<100
	<0.062	SE1h	9.6 ± 1.0	6.7 ± 0.7	<100	SE2h	9.8 ± 1.0	6.6 ± 0.7	<100	SE3h	10.2 ± 1.0	6.8 ± 0.7	<100
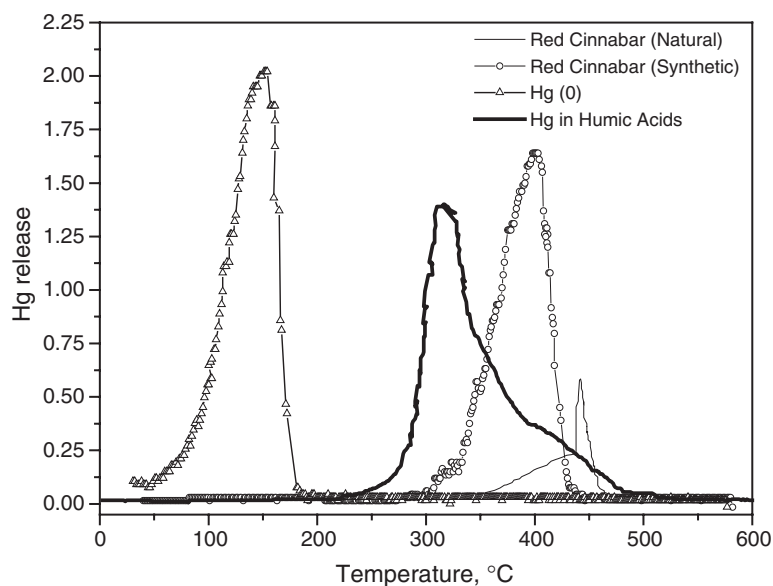
Fig. 3. Comparison of thermal desorption curves of standard mercury compounds.

standard Hg in humic acid (Fig. 3). Hg release temperatures varied with grain size, indicating a slightly stronger Hg interaction with the silt and clay fraction (Fig. 4a and c, samples SA2h, SE2h). In some topsoil layer, samples from sites TP-20 and TP-18 and in one sediment sample (SDT) from TP-09, Hg TDCs display a basically bimodal pattern with peaks at about 280–380 °C and 400–500 °C (Fig. 4b). This suggests the presence of mercury bound to organic matter and the existence of red cinnabar as shown in the natural cinnabar curve from the region studied (Fig. 3). According to Biester et al. (2000), the thermal decomposition of red cinnabar shows sharp Hg peaks due to the breakdown of the cinnabar lattice, which causes the sudden release of high amounts of metallic Hg. They also found that the mercury release temperatures of red cinnabar varies slightly with crystallinity and grain size. Synthetic cinnabar (Fig. 3) showed Hg release temperatures lower than those of the fully crystalline cinnabar of the region studied. It is interesting to note that sample SD1h (Fig. 4b) and others that present similar peaks are from the topsoil layer, which indicates a possible detrital origin of cinnabar. According to Alloway (1995), cinnabar is resistant to normal oxidation and weathering processes, and therefore, it enters the geochemical cycle mainly in the form of mechanically degraded particulate material. Metallic mercury is released below 200 °C (Fig. 3), but it was not detected in the soil samples studied as would be expected in the case of anthropogenic Hg input due to the gold amalgamation process.

TP-25 samples showed Hg release temperatures higher than 400 °C (Fig. 4c), indicating that in these samples, mercury is more strongly bound to the matrix in comparison to the other samples evaluated here. This high release temperature is comparable with that of Hg bound to ferrihydrite (Valle, 2005). Due to its low crystallinity, this iron oxide presents a large surface area and high reactivity. This hypothesis is quite reasonable, since the soil of TES is rich in iron oxides.

4.3. Correlation analysis

With the objective of evaluating correlations between Hg concentrations and the physico-chemical parameters analyzed at 3 depths and at 5 sites, Pearson linear correlation coefficient test was used. The obtained correlation matrix is presented in Table 3. TP-25 data were not included in this correlation due to its different behavior, as already demonstrated by Hg TDCs. The correlations in bold are significant at $p < 0.05$ ($N = 15$). As can be seen in Table 3, Hg correlated with organic carbon ($r = 0.64$) and sulfur ($r = 0.77$), and organic carbon strongly correlated with sulfur ($r = 0.88$). Shuster (1991) stated that mercury exhibits a large affinity for organic matter in soils and sediments due to its strong affinity for S-containing functional groups frequently found in organic molecules. Busher (1992) found a significant correlation between Hg and organic matter content in sediments from Tripuí Stream and observed that sulfur is most likely associated with sulfide minerals, mainly pyrite,

and possibly with sulfur-bearing organic matter. It was also concluded through thermal desorption technique that Hg in sediment samples from Carmo River, Minas Gerais, Brazil (FEAM et al., 1999) was mostly associated to humic acids. The results of this study suggest that the Hg–S–organic matter interaction occurs with a large part of Hg present in soils. Although the clay and silt (<0.062 mm) mineralogy of site TP-25 is predom-
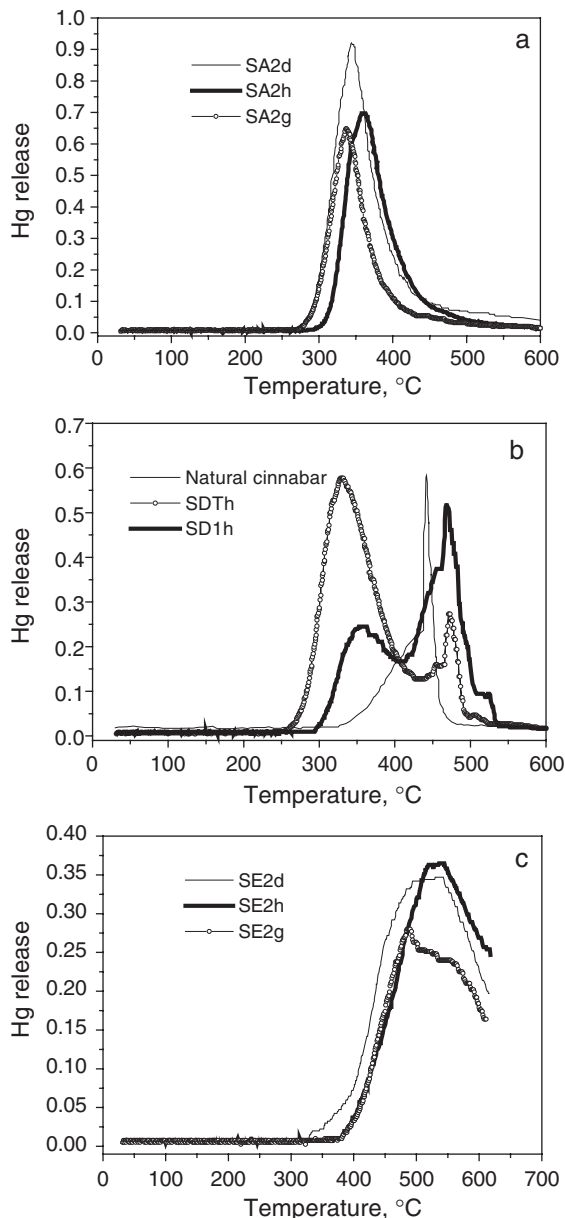
Table 3
Pearson's correlation between selected parameters in soils at three depths (N=15, p<0.05)

	Depth	Hg	Organic carbon	pH	Al	Fe	S
Depth	1.00						
Hg	− 0.14	1.00					
Organic carbon	− 0.42	**0.64**	1.00				
pH	0.28	0.28	0.22	1.00			
Al	0.13	− 0.16	0.11	− 0.03	1.00		
Fe	− 0.05	0.01	− 0.39	− 0.06	**− 0.74**	1.00	
S	− 0.27	**0.77**	**0.88**	0.45	− 0.12	− 0.10	1.00

inantly of minerals quartz, kaolinite and muscovite and lesser amounts of hematite, goethite and gibbsite, thermal desorption results suggest that Hg is strongly bound as in Hg-ferrihydrite (Valle, 2005).

4.4. Mercury distribution in soil profiles

Mercury concentration profiles (30, 60 and 90 cm) at six TES sites are shown in Fig. 5. The mercury concentration at each depth was calculated by the weighted mean of the Hg concentration in the three different grain sizes studied. In most sites, Hg was homogeneously distributed throughout the depths. At TP-09, the concentration of Hg decreased with the depth, whereas at TP-25, the opposite was observed. The retention of Hg at TP-09 is probably related with the organic carbon content (Anderson, 1979), which is the highest in the topsoil layer. The low organic carbon content, acid pH and the oxidizing conditions (Fergusson, 1990) may explain the presence of Hg in the deepest layer at TP-25. Within the soil profiles, organic matter content was the highest in the surface horizon, and the concentrations of Fe, Al and S were almost always homogeneously distributed throughout the depths. According to Fergusson (1990), variations in the concentrations of heavy elements in soil profile are not consistent and are as readily interpreted as in water and sediment profile. Several factors can influence the level of an element in a soil profile: the nature of the parent material, pedogenic process, organic and clay content, proportion of iron-containing minerals, pH, soil topography, rainfall, microbial activity and the level of pollution. The relevance of the factors will vary from site to site.

5. Conclusions

The distribution of mercury in TES soils presented Hg concentrations ranging from 0.09 to

Fig. 4. Hg thermal desorption curves of TES samples: (a) different size fractions of sample SA2; (b) natural red cinnabar; track sediment sample SDTh (<0.062 mm); soil sample SD1h; (c) different size fractions of sample SE2.
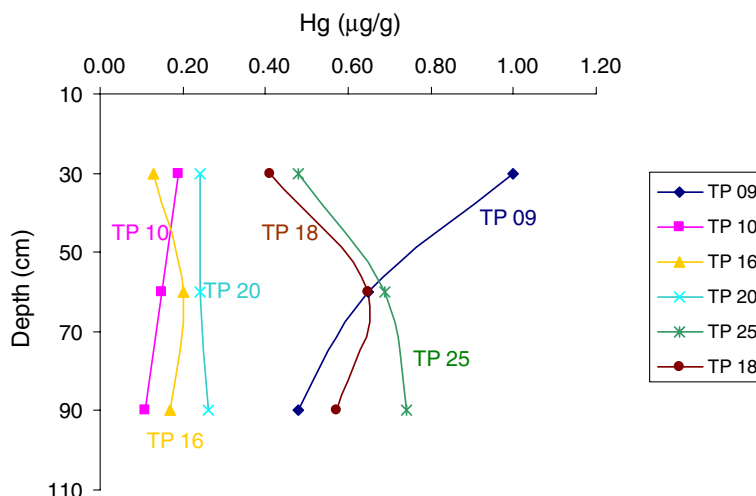
Fig. 5. Mercury profiles at six sites in Tripuí Ecological Station.

1.23 μg/g. The highest contents were found at the site nearest to an abandoned cinnabar mine, TP-09, and at the sites that receive direct influence from this mine through Botafogo Stream (TP-18 and TP-20). Although Fortes pond (TP 25) was not affected by the cinnabar mine, it showed a high Hg content. As Hg^0 was not detected in soil samples, it can be concluded that if there were metallic Hg input through gold amalgamation process in past times, it was oxidized to Hg^{2+} and sorbed onto soil components.

The results showed that Hg concentration depends on the distribution of different soil grain size fractions. Hg concentration was similar in the sand size fraction (2–0.59 mm) and in the silt and clay size fraction (<0.062 mm) of all soil layers studied. The same was observed for Fe, Al and organic matter, with the exception of site TP-25.

TDCs revealed the presence of mercury in the form of Hg^{2+} bound to organic components in most of the samples as well as the presence of red cinnabar in some. Data correlation analysis confirmed that mercury is associated with organic matter and sulfur and possibly with sulfur-bearing organic matter in soils.

The results suggest that mercury has been introduced into the soils along the years mainly via erosion process in the abandoned cinnabar mine rather than by anthropogenic origin.

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