



Distribution of chemical forms of mercury in sediments from abandoned ponds created during former gold mining operations in Colombia

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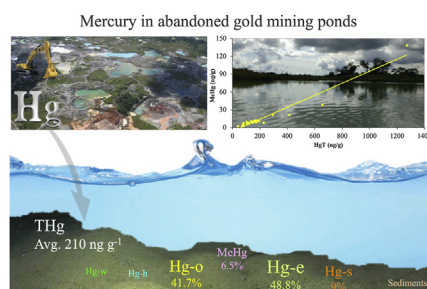
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HIGHLIGHTS

- The distribution and bioavailability of Hg was studied in ponds abandoned by gold mining of Chocó region, Colombia.
- MeHg was significantly correlated with THg, representing 6.5% of T-Hg.
- The chemical forms of Hg do not differ statistically between the abandonment periods.
- Mercury is mainly found as elemental Hg (Hg-e, 48.77%) and organochlorinated Hg (Hg-o, 41.70).
- OM is negatively correlated ($p < 0.05$) with Hg in the oldest ponds.

GRAPHICAL ABSTRACT



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ABSTRACT

Total mercury (THg) and methylmercury (MeHg) were studied in sediments from 27 abandoned gold mining ponds (AGMPs) through small-scale artisanal gold mining in the district of San Juan in Chocó region of Colombia. The AGMPs were abandoned in the last century (1997) and were grouped into three distinct groups (2–6; 7–12; 13–20 years). Overall concentration (in ng g^{-1}) pattern of THg in sediments varied from 39.06 to 1271.32 (avg. 209.57) with 174.81 (13–20 years), 205.56 (7–12 years) and 248.33 (2–6 years) respectively. MeHg concentrations accounted for 3.3–10.9% (avg. 6.5%) of THg and were significantly correlated with THg during all periods. Correlations between organic matter (OM) vs MeHg and THg were negative in the oldest pools, signifying a “dilution effect” or “natural burial” of THg and MeHg. Results for sequential extraction indicate that the fraction of elemental Hg (Hg-e) and organochlorinated Hg (Hg-o) represent the main chemical forms of Hg in the sediments, regardless of the abandonment period, whereas the bioavailable fraction was only 0.12–1.65% of THg. The significant statistical relationship between MeHg, THg and OM suggests that these parameters control the distribution, mobility, toxicity and bioavailability of Hg in the sediments of these abandoned ponds. Evaluation of THg

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with sediment quality guidelines indicates that the values are on the higher side for Threshold effect concentration and Upper continental crust. Comparing of MeHg with many other regions outside Colombia is a worrying factor and needs immediate attention to protect the human health.

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1. Introduction

Mercury (Hg) is one of the most dangerous pollutants that threatens the health of aquatic ecosystems and human populations in many regions around the world (USEPA, 2015). It has a great capacity to bioaccumulate and biomagnify in aquatic and terrestrial ecosystems (Horvat, 2002). Its presence in the environment is related to different sources of emission, both natural and anthropogenic. In particular, small-scale artisanal gold mining (ASGM) contributes 30% of the global Hg (approx. 1400 Mg/year) released into the environment (Meech et al., 1998; UNEP, 2013; Veiga et al., 2014). It is also estimated that nearly 50% of these releases are due to ASGM operations in the Latin American countries (Hinton et al., 2003).

1.1. Presence and behavior of Hg in aquatic environment

In aquatic systems, sediments act as important sinks/sources of Hg, where they are the main sites of methylmercury (MeHg) production (Shi et al., 2005) which bioaccumulates and biomagnifies in the aquatic food web. This often results in a serious threat to wildlife and human health, particularly in aquatic systems that provide protein (i.e. fish) to the human populations. MeHg is especially a worrying factor for human health because it causes severe damage to the central nervous system, particularly in fetuses (Diez, 2009). In this context, fish consumption by human beings remain one of the main route exposed to MeHg.

In aquatic systems, some variations in the chemical or physical conditions of the sediments (eg., pH, Eh, OM, texture, Fe, S, Al) will directly cause changes in the distribution, mobility, solubility, toxicity and bioavailability of the metals (Filgueiras et al., 2002; Liu et al., 2006; Pinedo-Hernandez et al., 2015; Chen et al., 2016; Herrero Ortega et al., 2018). In sediments and soils, Hg can be found in different phases or fractions, for example along with organic matter (OM), Fe-Mn oxyhydroxides, carbonates, sulphides or in its elemental form (Filgueiras et al., 2002). Hg is also being retained in these phases by ion exchange, adsorption, precipitation or co-precipitation mechanisms. Species such as mercury sulfide (HgS) and Hg⁰ have very low mobility and toxicity (Han et al., 2003). In contrast, the alkyl (i.e. MeHg⁺) and inorganic species, i.e. Hg(II), are the chemical species that contribute most to the mobility and toxicity of Hg (Han et al., 2003; Diez, 2009). Each chemical species exhibits a different behavior and mobility. Likewise, concentration of THg (bioavailable) alone is not enough to understand the environmental dynamics of aquatic organisms and its relation to human health aspects. Additional information on the chemical forms of Hg is required to evaluate efficient reduction strategies and to predict the effect of future changes in the environment (Marrugo-Negrete et al., 2015). Sequential extraction procedures are often used to know the different species of Hg in sediments (Bloom et al., 2003), which often makes it possible to characterize the distribution of Hg species according to their greater or lesser degree of solubility, mobility and toxicity to aquatic fauna and the risk to human health (Biester et al., 2000; Davidson et al., 2006; Pinedo-Hernandez et al., 2015).

In many parts of the world Hg is used in its metallic form (Hg⁰)

to amalgamate gold. However, the inefficient Hg recovery procedure often causes the release and deposition of Hg in the sediments surrounding the water bodies (eg. pools/ponds/sedimentation ponds, rivers, marshes) (Van Straaten, 2000). In Colombia, most of the aquatic ecosystems are disturbed by gold mining operations especially Chocó region (Department) is highly impacted by these AGMPs as it is dominated by the mega diversified flora (Reid, 1998). In addition, Chocó (Department) is an important region dominant with AGMPs related mercury emissions and during the last decade approximately 40 Mg of Hg were exposed into the environment.

The main objective of the present study is to understand the geochemical fractionation of Hg, methylmercury their behavior and mobility in the abandoned mining ponds which were deserted in different periods from the last century 1997 to 2017 (2–6; 7 to 12 and 13–20 years) in the mining district of San Juan in the State of Chocó, Colombia.

2. Materials and methods

2.1. Study area

The present study was carried out in twenty seven former abandoned gold mining ponds (AGMPs) located in the municipalities of Tadó and Unión Panamericana in the San Juan mining district (Department of Chocó) in eastern Colombia (5°15'N and 76°33'W - 5°16'N and 76°37'W) (Fig. 1). The region is dominated by both the Afro-Colombian and indigenous population. The municipalities Tadó and Unión Panamericana is criss-crossed by San Juan and Atrato Rivers and are also important waterways draining into the Pacific and Atlantic (in Gulf of Urabá) Oceans. Both the river basins and the adjacent region is strongly impacted by the AGMPs. The average annual precipitation and temperature in the region are 8000 mm and 28 °C, respectively.

Geologically, the region is dominated by conglomerates, fine-grained lithic sandstones, arcillolites, limonites, peat from the Miocene period. Likewise, mudstones, cataclasmic tuffs from the late Cretaceous period and some alluvial terraces of the Quaternary period (Gomez Tapias and Almanza Melendez, 2015). Due to these formations and composition of these in the sediments, high gold and platinum contents are observed in the alluvial terraces, which explains the strong historical presence of gold mining in this region. Mining operations in this region date back to the eighteenth century and they are currently the principal source of economic income for many families in this region. The surface of the artificial ponds varied between 200 and 10,000 m² in size and it varied in depth varying from 1 to 30 m.

2.2. Sample collection

The AGMPs were grouped into three distinct periods which varied from 2 to 6, 7 to 12 and 13–20 years intervals as established by UNEP (2013). The classification of the AGMPs was based on the Minamata Convention to evaluate the short, medium and long term movements of Hg concentration and its mobility in the environment.

Sampling was carried out in 27 AGMPs deserted after the

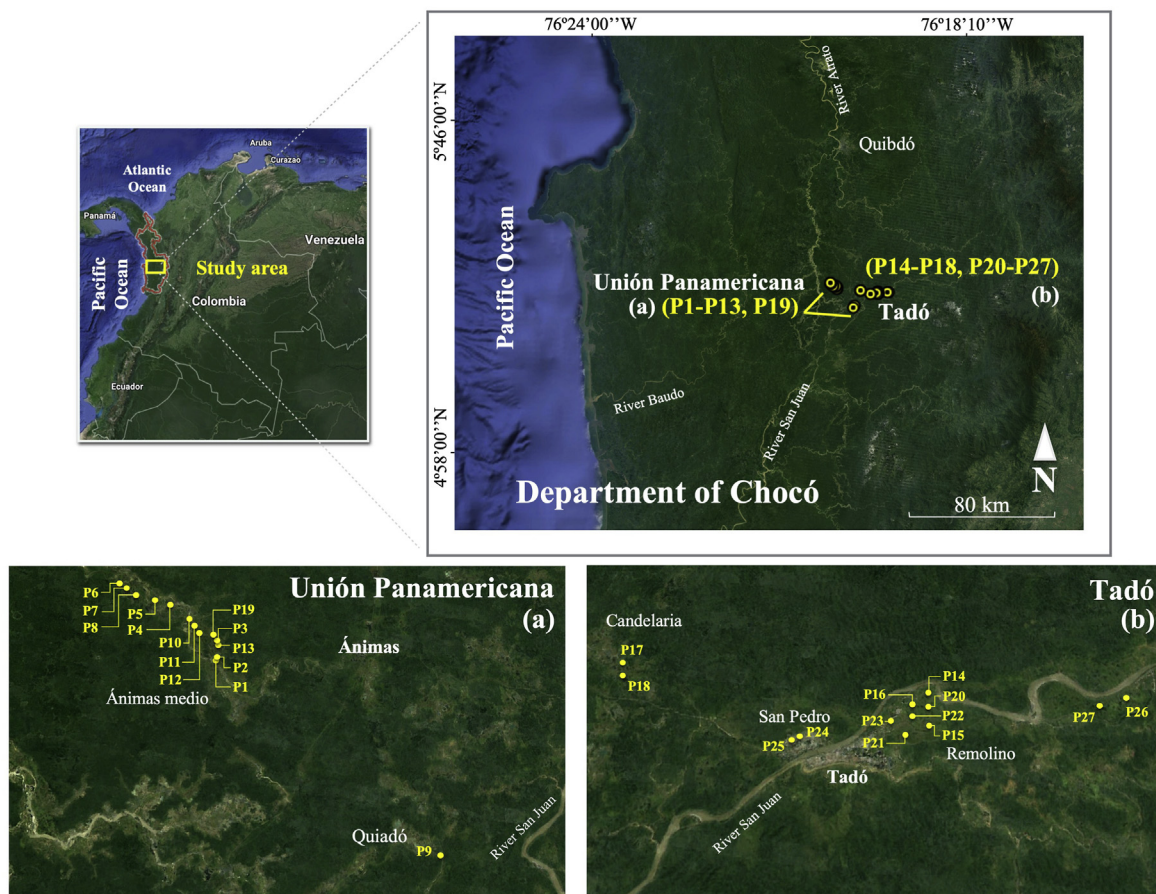


Fig. 1. Location of the sampling sites in abandoned gold mines from Chocó region, Colombia. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

artisanal gold mining operations in the San Juan Mining District during the dry season (March) of 2017 (Fig. 1). Each sample is a composite of representative subsamples of surface sediment (top 5 cm) collected using Eckman dredger in a float boat. Sediment samples were collected from the AGMPs in the municipalities of Unión Panamericana (P1 – P13, P19) and Tadó (P14 – P18, P20 – P27). Immediately after collection, the samples were packed in vacuum plastic bags, labelled preserved in ice and transported to the laboratory. The samples were subsequently dried in a lyophilizer (Telsar LyoQuest) at $-50\text{ }^{\circ}\text{C}$ for 16–24 h. The sampling strategy for the present study was similar to the multi-temporal analysis approach done by Roy et al. (2009), Valois (2016), and Herrero Ortega et al. (2018).

2.3. Sample analysis

THg concentrations were determined following the procedure of USEPA (1998), where 0.5 g of dry sediment was digested with mercury-free $\text{H}_2\text{SO}_4/\text{HNO}_3$ (7:3 v/v) and KMnO_4 (5% w/v) at $100\text{ }^{\circ}\text{C}$ for 1 h (Marrugo-Negrete et al., 2015).

A five-step sequential extraction procedure (SEP) based on Bloom et al. (2003) and modified by Pinedo-Hernandez et al. (2015) was used to study the fractionation of Hg in sediments (Supplementary Table 1). This SEP allows to differentiate 1) the Hg:soluble in water (Hg-w); 2) the human stomach acids (Hg-h); 3) the organo-chelates (Hg-o); 4) the elemental mercury (Hg-e) and 5) the Hg sulfide (Hg-s).

MeHg was determined using the method described by Caricchia

et al. (1997) and modified by Pinedo-Hernandez et al. (2015). An aliquot of dry sediment with 2.0 g was weighed and extracted with 5 mL of $\text{KOH}/\text{CH}_3\text{OH}$ (25%) in an ultrasonic bath for 45 min. Subsequently, after cooling, 5 mL of H_2SO_4 (4 M, saturated with CuSO_4), 5 mL of 4 M KBr and 4 mL of toluene were carefully added and the sample was manually stirred for approximately 3 min. The supernatant organic phase was collected after centrifuging at 2200 rpm for 10 min. The solvent extraction was repeated thrice with 2 mL of toluene and the collected organic extract (10 mL) was subjected to a reverse extraction (twice) for 1.0 mL of a cysteine solution (1.0%). The two cysteine extracts (1 + 1 mL) were collected in the same vial and extracted with a mixture of Toluene (0.5 mL), saturated solution of CuSO_4 (0.5 mL) and 4 M KBr (1.0 mL). After manual stirring, the organic phase was separated from the aqueous phase and 2.0 μL was injected into the GC-ECD system of PerkinElmer, Autosystem XL.

Organic matter (OM) was determined as a percentage of loss by ignition of 2.0 g of sediment in a flask at $450\text{ }^{\circ}\text{C}$ for 4 h (Coquery and Welbourn, 1995). The pH, Eh and CE in the water/sediment mixture were determined in situ using a portable HQ40d analyzer (HACH). The texture (% clay and silt) was determined following the Bouyoucos method (1962). The sediment classification followed the USDA texture class: sand fraction (0.050 mm < % < 2 mm) and clay-silt fraction (% < 0.050 mm).

2.4. Quality assurance

The analytical method used to determine the THg and MeHg in

sediments was validated with a certified reference material "Estuarine sediment" (IAEA - 405, T-Hg = 810 ng g⁻¹ and MeHg = 5.49 ng g⁻¹, dw). The recovery percentages were: 98.0 ± 0.2 for the T-Hg and 97.2 ± 0.5 for the MeHg. The detection limits were 14 ng g⁻¹ dw for THg and 2.5 ng g⁻¹ for MeHg was calculated as the mean plus three times the standard deviation (SD). The fractionation method did not show statistically significant differences ($p = 0.54$) between the ΣHg of the extracted fractions and the THg concentrations determined by digestion of the original sediments, showing that the method used presented good accuracy (<2.5 and < 5.0%).

2.5. Statistical analysis

Generated data are presented as median (min/max) or average ± standard deviation (SD). As the data did not present a normal distribution, statistical analyses were performed using non-parametric methods. Mann-Whitney test was done in order study the comparisons between means and Kruskal-Wallis test for multiple comparisons. Likewise, relationships between variables were investigated using Spearman correlation analysis and regression analysis. Principal component analysis (PCA) with varimax rotation to minimize the number of variables with a high loading on each component was employed with the aim of identifying association among variables. Statistical significance criteria were set at <0.05 and the whole statistical analysis were performed using the SPSS software (Version 23).

3. Results

3.1. Total mercury and methylmercury in sediments

The concentrations of THg and MeHg in the sediments are presented in Table 1. The average concentration of THg in all ponds was 209.57 ± 245.23 (median: 147.03 ng g⁻¹) and for MeHg it was 15.13 ± 25.63 (median: 9.20 ng g⁻¹). There were no statistical differences ($p > 0.05$) in the contents of THg or MeHg for the abandonment periods. However, when assessing the concentration pattern based on average values, MeHg levels were higher in the AGMPs that were abandoned longer ago, with values of (ng g⁻¹) of 9.68 (13–20 years), 9.20 (7–12 years) and 8.23 (2–6 years) respectively.

The total data included the proportion of MeHg/THg, which varied between 3.3 and 10.9% (avg. 6.5%) (Table 1). During the periods of abandonment, the differences in the proportions of MeHg/THg were not significant ($p = 0.13$) but were greater in the older ponds. The maximum concentration of THg (1271 ng g⁻¹ dw), MeHg (138 ng g⁻¹ dw) and the highest proportion MeHg/THg (10.9%) is observed in pond P5 in the Unión Panamericana municipality.

Statistical analysis indicates there is a strong and significant positive correlation between the MeHg and THg of the 27 AGMPs studied ($r = 0.86$; $p < 0.0001$) (Table 2). Likewise, there was a positive relationship ($r = 0.90$; $p < 0.001$) in every group of ponds depending on the abandoned period. Analyzing all the ponds, there were no correlations among THg and MeHg or %MeHg with OM. Similarly, there was no correlation during the abandoned periods of 2–6 years and 7–12 years. However, when analyzing the groups of ponds individually in the older ponds (13–20 years), the correlations of THg ($r = 0.83$; $p < 0.01$) and MeHg with the OM was negative and significant ($r = -0.83$, -0.68 ; $p < 0.05$), in contrast with the positive correlation between %MeHg and OM ($r = 0.62$) (Table 2).

The correlations between variables (Hg species, OM, pH and abandoned time), were further analyzed by PCA as shown in

Supplementary Fig. 1, where the two principal components explain 76% of the data variation. The first principal component (PC1), which accounted for 60% of the variance clearly separated the different species of Hg from pH. More specifically, the high positive loading values for Hg species (Supplementary Table 2), suggest a high correlation between them, and a negative correlation with pH. Higher levels of Hg species are related with lower values of pH. On the other hand, PC2 accounted for 16% of the total variance and the second component show high loadings for time and OM. Results in PC2 indicated associations between OM and time, and suggest that as much time of abandonment increase the OM increases (Supplementary Table 2).

3.2. Fractionation of mercury in sediments

The distribution of the five different Hg fractions and their percentage distribution in each of the 27 AGMPs are presented in Table 1 and Fig. 2 respectively. The distribution pattern of the Hg fractions (in avg.) were: Hg-e (48.77%) > Hg-o (41.70%) > Hg-s (8.96%) > Hg-h (0.44%) > Hg-w (0.14%). Total analysis of all samples grouped together indicates that the concentration of Hg in each fraction presented a significant and positive correlation with THg and MeHg ($r = 0.86$; $p < 0.05$) (Table 2). Significantly, MeHg in general showed a strong correlation with Hg-w ($r = 0.60$), Hg-h ($r = 0.45$), Hg-o ($r = 0.62$), Hg-e ($r = 0.50$) and Hg-s ($r = 0.62$) respectively. Similarly, Hg-e vs THg and MeHg presented a positive correlation ($r = 0.63$, 0.50 ; 0.68 , 0.56 ; 0.67 , 0.60 ; 0.38 , 0.22) in all cases, although it is only significant in AGMPs of 2–6 and 7–12 years of abandonment periods ($p < 0.05$). On the other hand, the OM did not show a significant correlation with the Hg fractions comparing to the total data set. However, in the analysis based on periods of abandonment a strong and significant positive correlation was observed between the OM and the Hg-o of the most recent pools, 2–6 years, ($r = 0.70$; $p < 0.05$). Surprisingly, the correlations between the OM and Hg-o became negative and more intense during the periods of abandonment ($r = -0.25$ for 7–12 years) and ($r = -0.53$ for 13–20 years).

Considering the total data set, the bioavailable or interchangeable fraction (Hg-bio = Hg-w + Hg-h) represented an average of 0.58% (median: 0.50%; range: 0.12–1.65%) of the THg (Fig. 3). No statistical significant differences ($p > 0.05$) were observed between the proportions of the bioavailable fractions during the abandoned periods. In general, Hg-bio were higher in the most recent AGMPs: 0.54%, 0.50% and 0.48% in the 2 to 6, 7 to 12 and 13–20 years AGMPs, respectively. The highest values of Hg-bio were observed in AGMPs P5 (1.66%), P26 (1.09%) and P18 (1.01%). Based on the concentrations of the Hg fractions no significant correlations ($p > 0.05$) (Fig. 4a) were observed in the proportions of the different fractions ($p > 0.05$) (Fig. 4b). Low and high inconsistent values of Hg-e in sediments were observed in the more recent AGMPs in contrast to the proportion of Hg-o that increased with reference to the age of the ponds. Overall geochemical distribution of Hg does not differ between the two municipalities ($p > 0.05$).

4. Discussion

4.1. Total mercury and methylmercury in sediments

Usually, gold mining operations sites are subject to have high levels of THg. In this context, the high levels of Hg in the sediments of AGMPs are due to the direct losses of Hg⁰ during the amalgamation processes (dry and wet) of Hg. Moreover, it is due to the mobility of the tailing materials draining towards the aquatic ecosystems due to its inclining topography (Tomiyasu et al., 2012; Odumo et al., 2014; Chen et al., 2016; Benoit 2018). The average

Table 1
Concentrations of THg, MeHg, MeHg/THg ratio, OM, pH, Eh, C and C + Si in AGMPs of Chocó region, Colombia.

Municipality	AGMPs	Hg-w	Hg-h	Hg-o	Hg-e	Hg-s	ΣHg	THg	ΣHg/THg (%)	MeHg	MeHg/THgT	OM (%)	pH	Eh (mV)	C (%)	C + Si (%)	Time (in years)
AGMPs 2–6 years																	
UP	P1	0.44	0.90	47.57	169.29	14.76	232.96	227.82	102.26	8.23	3.61	3.05	6.51	-264.0	10.13	89.87	6
UP	P2	0.22	0.30	55.54	67.58	20.05	143.68	135.37	106.14	10.58	7.82	3.03	6.12	-75.9	18.74	81.26	6
UP	P3	0.44	0.24	37.09	126.42	13.91	178.10	171.73	103.71	12.24	7.13	4.77	6.68	-140.1	20.62	79.38	5
UP	P4	0.21	0.50	152.73	16.66	11.63	181.73	163.43	111.20	10.62	6.50	6.97	6.43	-181.0	31.41	68.59	5
UP	P5	8.43	11.33	300.83	823.14	48.96	1192.69	1271.32	93.82	138.33	10.88	5.31	5.96	-87.9	28.62	71.38	6
UP	P6	<0.10	0.25	29.87	54.83	9.03	94.07	80.65	116.64	7.48	9.28	4.19	6.61	-219.6	21.76	78.24	4
UP	P7	0.13	0.39	72.78	17.38	5.70	96.38	76.11	126.63	<5.0	-	4.62	6.47	-141.3	24.18	75.82	5
UP	P8	0.11	0.39	62.26	20.82	5.51	89.10	69.50	128.20	<5.0	-	5.85	5.28	-60.5	7.76	92.24	6
UP	P9	<0.10	0.30	3.07	38.12	10.10	51.60	39.06	132.10	<5.0	-	2.32	5.66	-5.4	5.70	94.30	4
	Avg.	1.43	1.62	84.64	148.25	15.52	251.15	248.33	113.41	31.25	7.54	4.46	6.19	-130.63	18.77	81.23	5
AGMPs 7–12 years																	
UP	P10	<0.10	1.19	97.07	44.21	12.51	155.06	146.13	106.16	8.87	6.07	6.55	6.79	-132.4	3.12	96.88	9
UP	P11	0.18	1.14	94.08	54.95	11.46	161.81	151.53	106.80	9.24	6.10	5.76	7.31	-198.3	8.07	91.93	9
UP	P12	<0.10	0.55	72.17	131.99	11.83	216.62	193.58	111.88	10.65	5.50	7.08	6.16	-167.9	13.99	86.01	10
UP	P13	0.13	0.72	110.79	53.05	16.35	181.03	173.56	104.28	9.20	5.30	6.79	6.49	-135.1	10.33	89.67	11
T	P14	<0.10	0.34	54.32	95.89	10.96	161.60	155.99	103.59	11.39	7.30	9.80	6.17	-223.6	2.46	97.54	10
T	P15	0.15	0.54	37.84	81.10	18.16	137.79	120.92	113.98	6.80	5.63	14.32	6.67	-200.0	16.47	83.53	10
T	P16	<0.10	1.08	45.25	52.50	17.55	116.46	106.87	108.94	6.31	5.90	5.20	6.56	-141.4	25.12	74.88	11
T	P17	<0.10	0.42	36.77	96.63	15.21	149.05	147.03	101.39	8.67	5.90	11.53	6.39	-111.4	0.18	99.82	7
T	P18	3.01	4.08	107.60	568.98	21.62	705.38	654.43	107.79	38.42	5.87	11.82	5.94	-196.3	13.01	86.99	9
	Avg.	0.87	1.12	72.88	131.03	15.07	220.53	205.56	107.20	12.17	5.95	8.76	6.50	-167.38	10.31	89.69	10
AGMPs 13–20 years																	
UP	P19	1.07	0.68	65.69	322.58	29.20	419.22	414.85	101.05	20.66	4.98	2.69	6.4	-28.4	0.22	99.78	13
T	P20	0.10	0.60	68.40	28.28	15.60	112.98	102.15	110.60	9.68	9.48	11.06	6.34	-195.1	10.4	89.6	17
T	P21	0.12	0.34	34.87	51.56	11.54	98.43	75.39	130.56	5.59	7.41	8.93	6.02	-203.1	15.19	84.81	18
T	P22	<0.10	0.28	19.39	49.68	10.86	80.25	78.97	101.62	5.51	6.98	10.46	6.44	-214.5	12.08	87.92	17
T	P23	0.14	0.90	55.63	62.28	12.42	131.38	117.95	111.39	8.63	7.32	9.47	6.41	-133.1	5.2	94.8	16
T	P24	0.15	1.00	173.44	112.39	17.57	304.54	294.43	103.43	21.82	7.41	8.02	6.24	-183.7	5.47	94.53	16
T	P25	0.19	0.89	132.43	35.39	13.62	182.52	165.81	110.08	11.81	7.12	7.84	6.51	-238.1	8.47	91.53	16
T	P26	0.24	1.81	146.53	19.90	19.90	188.38	183.31	102.77	11.99	6.54	7.58	6.82	-273.8	8.33	91.67	16
T	P27	<0.10	0.49	79.59	67.16	15.32	162.62	140.41	115.81	8.40	5.98	8.53	6.29	-211.3	43.3	56.7	13
	Avg.	0.29	0.78	86.22	83.25	16.23	186.70	174.81	109.70	11.57	7.02	8.29	6.39	-186.79	12.07	87.93	16

UP – Unión Panamericana; T – Tadó. AGMPs: Abandoned Gold Mining Ponds; C: Clay; Si: Silt. Hg-w: water soluble; Hg-h: human stomach acid soluble; Hg-o: organo chelated; Hg-e: elemental mercury; Hg-s: mercuric sulfide. All values in ng g⁻¹.

concentration of THg in the sediments of present study is consistent with the results reported for the West Wits mine, Gauteng, South Africa (Lusilao-Makiese et al., 2016). The heterogeneity in the contents of THg in the sediments of AGMPs in these aquatic environments are the result of the different amalgamation techniques applied during the extraction of gold (Lacerda and Salomons, 1998; Veiga and Baker, 2004), and the differences in the age of the sites (Leiva and Morales, 2013).

In the present study the different AGMPs are complex and the ponds differ in surface area, depth, type of sediments, vegetation and the type/intensity of mining, which often confuses the relation of Hg with that of the age of the ponds. However, in order to evaluate the Hg methylation, the same set of data with reference to the ponds has to be evaluated over time. Based on this concept, we tried to understand the Hg-age interactions using a set of confirmed known ponds, where the abandonment age varied between 2 and 20 years in the municipality of Tadó and Unión Panamericana (Table 1). In general, the ponds in these municipalities almost share similar weather conditions, chemical composition, morphology and weathering levels (data not shown), type of mining and similar average levels of THg. With the exception of the considerably high concentrations (in ng g⁻¹) recorded in P5 (138.33) and P18 (38.42), the distribution of MeHg was homogeneous in the AGMPs of 2–6, 7–12 and 13–20 years. This homogeneity as well as the spatial content of MeHg is similar in both the regions due to the low-flow conditions in the water column, which easily causes its bioaccumulation in the food chain present in the aquatic organisms, eventually affecting the wildlife and human health (Ikingura and Akagib, 1999; Ikingura et al., 2006; Lino et al., 2019). Despite the lack of significant differences in the contents of

THg and MeHg during different periods ($p > 0.05$), there is a tendency of increased MeHg content in the younger ponds. It is likely that the lower values of pH (avg. 6.19, 6.50, 6.39), Eh (avg. -130.63, -167.38, -186.79) and the type of natural OM (allochthonous and/or autochthonous) (avg. in %: 4.46, 8.76, 8.29) are improving the Hg methylation efficiency (Kelly et al., 1997; Roy et al., 2009; Kim et al., 2011; Lei et al., 2019), and as a consequence MeHg concentration increases in the sediments of the ponds of 13–20 years old.

On the other hand based on the concentration the calculated ratio of MeHg/THg makes it possible to describe the degree of contamination in a particular environmental system. In general, the uncontaminated aquatic sediments usually show MeHg/THg proportions less than 1.5% (Ullrich et al., 2001; Boszke et al., 2003; Issaro and Abi-Ghanem, 2009). In the present study, MeHg/THg ratios varied from 3.6 to 10.9% indicating the active Hg methylation processes occurring in the ponds and its potential risk of MeHg accumulation in the aquatic food web. Likewise, the calculated higher ratios of MeHg/THg (>7.0% at several sample locations) observed in the different AGMPs (2–6, 7–12 and 13–20 years) indicate that the factors controlling methylation are not specifically related to the abandoned time period (Table 1). The ratios recorded in this study (3.3–10.9%) are higher compared to those reported by Shi et al. (2005) in the Haihe River (0.1–2.4%), China; 1.5–3.7% in aquatic environments impacted by gold mining in the Mojana region, Colombia (Pinedo-Hernandez et al., 2015) and is consistent with the proportions (3–11%) in the Ciénaga de Ayapel and the swamp Grande Achi, Colombia (Marrugo-Negrete et al., 2015). In the Wujiangdu reservoir, northern part of Quebec, Canada MeHg/THg ratios of up to 30% were recorded in the humic horizon of a

Table 2
Correlation matrix of different fractions of Hg in surface sediments from Chocó region, Colombia.

	Hg-w	Hg-h	Hg-o	Hg-e	Hg-s	THg	MeHg	MeHg %	OM	pH	Eh	C	C + Si	Years
Total sampling points (n = 27)														
Hg-w	1.00													
Hg-h	0.40*	1.00												
Hg-o	0.45*	0.70**	1.00											
Hg-e	–	–	–	1.00										
Hg-s	0.55**	0.55**	0.39*	0.51**	1.00									
THg	0.62**	0.58**	0.61**	0.63**	0.65**	1.00								
MeHg	0.60**	0.45*	0.62**	0.50**	0.62**	0.86**	1.00							
MeHg/THg	–	–	–	–	–	–	–	1.00						
OM	–	–	–	–	–	–	–	–	1.00					
pH	–	–	–	–	–	–	–	–	–	1.00				
Eh	–	–	–	–	–	–	–	–	–0.39*	–0.38*	1.00			
C	–	–	–	–	–	–	–	–	–	–	–	1.00		
C + Si	–	–	–	–	–	–	–	–	–	–	–	–	1.00	
Years	–	–	–	–	–	–	–	–	0.63**	–	–	–	–	1.00
AGMPs 2–6 years (n = 9)														
Hg-w	1.00													
Hg-h	–	1.00												
Hg-o	0.50*	0.73*	1.00											
Hg-e	0.67*	–	–	1.00										
Hg-s	0.81**	–	–	0.75*	1.00									
THg	0.91**	–	–	0.68*	0.80**	1.00								
MeHg	0.81**	–	–	0.56*	0.81**	0.88**	1.00							
MeHg/THg	–	–	–	0.55*	0.63*	0.50*	0.71*	1.00						
OM	–	–	0.70*	–	–	–	–	–	1.00					
pH	–	–	–	–	–	–	–	–	–	1.00				
Eh	–	–	–	–	–	–0.50*	–	–	–	–0.77*	1.00			
C	–	–	0.67*	–	–	0.50*	0.56*	–	0.58*	–	–	1.00		
C + Si	–	–	–0.67*	–	–	–0.50*	–0.56*	–	–0.58*	–	0.50*	–	1.00	
Years	0.66*	0.58*	0.56*	–	–	–	–	–	–	–	–	–	–	1.00
AGMPs 7–12 years (n = 9)														
Hg-w	1.00													
Hg-h	0.50*	1.00												
Hg-o	0.42*	0.67*	1.00											
Hg-e	–	–	–	1.00										
Hg-s	–	–	–	–	1.00									
THg	–	–	0.60*	0.67*	–	1.00								
MeHg	–	–	0.55*	0.60*	–	0.90**	1.00							
MeHg/THg	–	–	–	–	–0.57*	–	–	1.00						
OM	–	–	–	0.70*	–	–	–	–	1.00					
pH	–	–	–	–0.80**	–	–0.70*	–0.58*	–	–0.50	1.00				
Eh	–	–	–	–	–	–	–	–	–	–	1.00			
C	–	–	–	–	0.57*	–	–	–0.54*	–	–	–	1.00		
C + Si	–	–	–	–	–0.57*	–	–	0.54*	–	–	–	–	1.00	
Years	–	–0.76*	–	–	–	–	–	–	–	–	–	–	–	1.00
AGMPs 13–20 years (n = 9)														
Hg-w	1.00													
Hg-h	0.72*	1.00												
Hg-o	0.44*	0.75*	1.00											
Hg-e	–	–	–	1.00										
Hg-s	0.67*	0.62	0.67*	–	1.00									
THg	0.76*	0.70*	0.70*	–	0.85**	1.00								
MeHg	0.80**	0.80**	0.77*	–	0.87**	0.90**	1.00							
MeHg/THg	–	–	–	–	–	–0.50*	–	1.00						
OM	–0.83**	–0.53*	–0.53*	–	–0.67*	–0.83**	–0.68*	0.62*	1.00					
pH	–	–	–	–0.55*	–	–	–	–	–	1.00				
Eh	–	–	–	0.73*	–	–	–	–	–	–0.52*	1.00			
C	–0.79*	–0.70*	–	–	–0.55*	–0.68*	–0.73*	–	0.50*	–	–0.53*	1.00		
C + Si	0.79*	0.70*	–	–	0.55*	0.68*	0.73*	–	–0.50*	–	0.53*	–	1.00	
Years	–	–	–	–0.53*	–0.61*	–0.79*	–0.50*	0.73*	0.66*	–	–	–	–	1.00

Clay (C); $p < 0.05^*$; 0.01^{**} Hg-w: water soluble; Hg-h: human stomach acid soluble; Hg-o: organo chelated; Hg-e: elemental mercury; Hg-s: mercuric sulfide.

podzolic soil after 10 years of flooding (Lucotte et al., 1999; Reis et al., 2010). Similarly, higher content of MeHg (138.3 ng g^{-1}) and proportion of MeHg/THg (10.9%) at the pond site P5 is a sediment characterized with high THg content (Veiga and Baker, 2004; Marrugo-Negrete et al., 2015).

Despite the relatively low concentrations of THg (median: 147.03 ng g^{-1}) in the AGMPs these mining districts act as environmental hotspots, where some critical sites have higher concentration with high capacity to methylate the THg. This process

especially demands government attention and the implementation of remediation programs for control and reduction of ecological risk and also on human populations. In general, the concentrations of THg and MeHg in the sediments remain high at least during the first 20 years after abandoning the sites.

The biological production of MeHg is often favoured by multiple environmental factors, (i.e) low pH levels, high OM content, methylation efficiency, microbial activity and the availability of Hg^{2+} for the methylation bacteria (Yong-kui et al., 2007). These

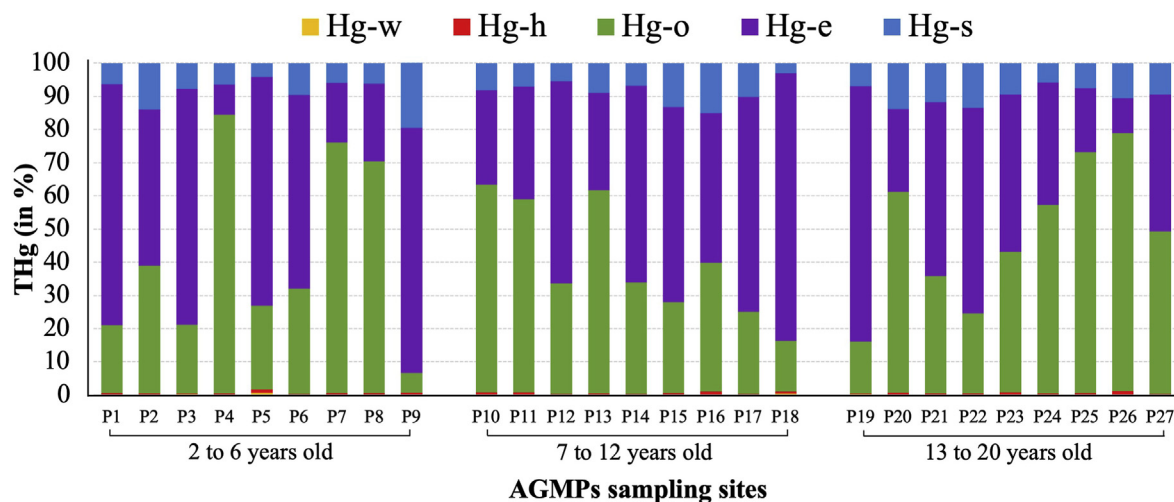


Fig. 2. Percentage distribution of the Hg fractions in the sediments of AGMPs (for all abandonment scenarios) based on sequential extraction method (Table 1).

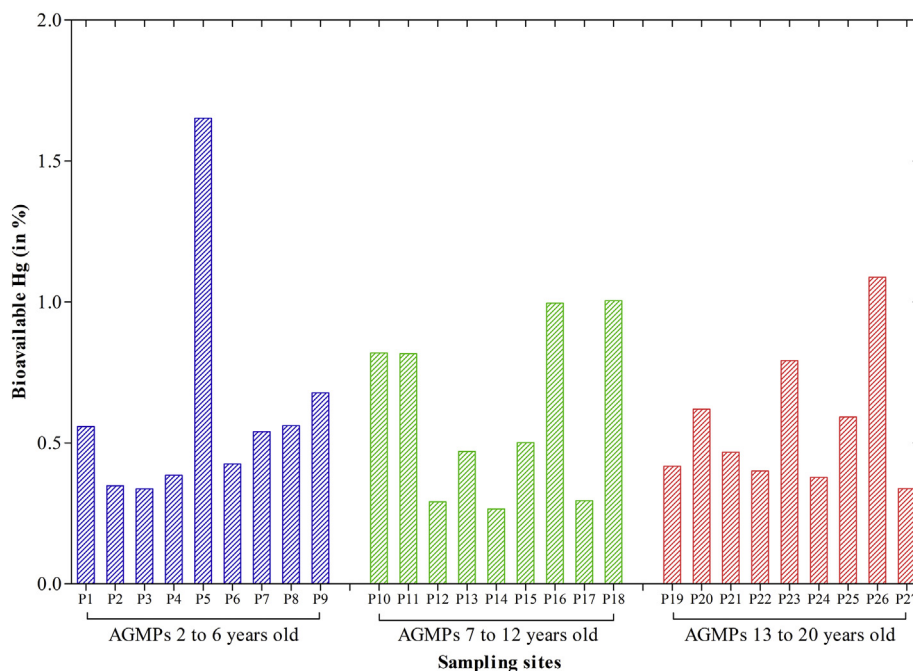


Fig. 3. Distribution in percentage of the bioavailable Hg species ($Hg\text{-bio} = Hg\text{-w} + Hg\text{-h}$) in the sediments of AGMPs of Chocó region, Colombia.

factors cause the methylation efficiency to vary from one ecosystem to another, and it also limits the general understanding of Hg dynamics (Winfrey and Rudd, 1990; O'Connor et al., 2019). Our results indicate that despite the wide range of THg concentrations recorded in this study, the strong correlation ($r = 0.88, 0.90, 0.90$) observed between MeHg and THg (Table 2) suggest that at high concentrations THg is being methylated indicating higher concentrations (Rudd et al., 2018). Likewise, the production of MeHg in the surface sediments of AGMPs is mainly controlled by the concentration of THg. Similar observations have been reported in aquatic ecosystems impacted by gold mining in the Haihe River, China (Shi et al., 2005), Mojana region, Colombia (Pinedo-Hernandez et al., 2015) and Kedougou region, Senegal (Gerson et al., 2018). In the present study, the lentic nature of the ponds together along with the association with sediment properties like low pH levels (<6.8 , except in P11), high OM (3–14%) and low levels Eh values

(<200 mV) provides favourable conditions that promotes Hg methylation by anaerobic bacteria regardless of the period of desertion (Kim et al., 2011; DeLaune et al., 2004; Lei et al., 2019).

Statistical correlation analysis between organic matter and the Hg (THg and MeHg) are usually positive that receive indirect contributions of the ionic forms of Hg in some aquatic regions, where direct release of elemental Hg is received from the local environment (Lacerda and Salomons, 1998; Veiga and Baker, 2004; Shi et al., 2005; Pinedo-Hernandez et al., 2015). The above inferences coincide with the results reported for river sediments receiving direct discharges of metallic Hg^0 from gold mining in the Madeira River in the Amazon basin (Pfeiffer et al., 1993) and rivers/waste lagoons in gold mining environments in the Ivory Coast (Mason et al., 2019).

In the present study, the absence of correlation among MeHg, THg vs OM, in recent AGMPs (2–6 and 7–12 years), suggests that

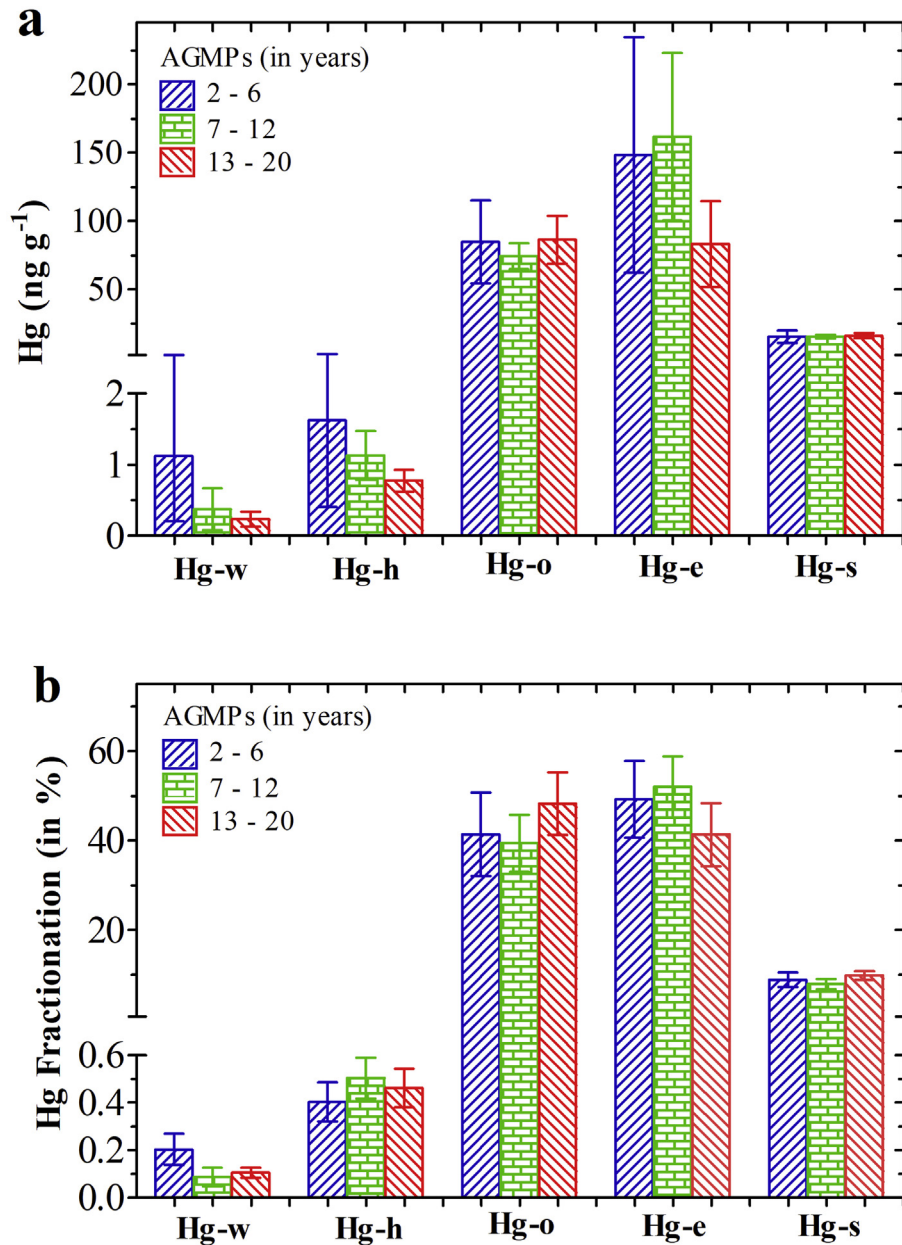


Fig. 4. Average distribution of the different Hg fractions: soluble in water (Hg-w), soluble in human stomach acids (Hg-h), organ-chelated (Hg-o), elemental mercury (Hg-e) and mercury sulfide (Hg-s) in the three abandonment scenarios in relation to (a) THg and (b) percentage of Hg fractions.

concentration of Hg⁰ is more important than the adsorption capacity of the organic material in the sediment (Green et al., 2019). In contrast, the significant negative correlation between MeHg, THg vs the OM in the sediments of AGMPs 13–20 years (Table 3) show a progressive increase in the organic matter content in the sediments which brings in a “dilution effect” or “natural burial” of THg and MeHg in this matrix (St. Louis et al., 2000; Bravo et al., 2017; Lei et al., 2019). The negative correlation between Hg-o and OM in the group of 13–20 years AGMPs support the above inference.

Our results of MeHg concentration in the present study suggest that OM controls the net methylation of MeHg and the bioavailability in the sediments of older AGMPs. The main criteria to control this are: 1) dilution of the concentrations of THg and MeHg by OM and 2) a greater efficiency of methylation of the THg to MeHg ($r = 0.62$; Table 2) supported by the high content of OM in the sediments stimulating the growth of Hg methylators such as

sulfate-reducing bacteria. However, the role of molecular composition of OM on Hg methylation processes in AGMPs remains uncertain. The molecular composition of OM (e.g. algal-derived, humic matter or fulvic) often reflect the source and biological reactivity with the Hg (Kothawala et al., 2014; Pestana et al., 2019), which helps to improve the understanding Hg methylation processes of Hg in these environments. The important fact is that the OM quality rather than its quantity may account for MeHg production (Bravo et al., 2017; Herrero Ortega et al., 2018; Lei et al., 2019; Pestana et al., 2019). For instance, the phytoplankton-derived organic compounds often enhances Hg methylation rates through a global increase in the bacterial production rate (Bravo et al., 2017). Conversely, the sediments rich in terrigenous OM has lower methylation rates. The negative relationships between Hg and OM have also been reported in other studies related to the biogeochemistry and bioaccumulation of Hg in aquatic ecosystems

Table 3
Concentration of Hg in sediments in the abandoned gold mining ponds with other regions around the World.

Locations	Extraction type*	¹ Hg-w	² Hg-h	³ Hg-o	⁴ Hg-e	⁵ Hg-s	THg	MeHg	MeHg (%)
<i>Worldwide</i>									
^a Stream, Randfontein, South Africa	¹ Water; ² CH ₃ COOH + HCl; ³ KOH	27 (3)	297 (33)	360 (40)	207 (23)	9 (1)	900	–	–
^a Wetlands, Randfontein, South Africa	¹ Water; ² CH ₃ COOH + HCl; ³ KOH; ⁴ HNO ₃ ; ⁵ HCl + HNO ₃	240 (20)	312 (26)	420 (35)	228 (19)	–	1200	–	–
^b Aquatic deposits in gold mining sites, Johannesburg, South Africa	–	–	–	–	–	–	140	0.8	0.6
^c Artificial reservoirs and rivers, Ivory Coast	–	–	–	–	–	–	–840	–9.2	–1.7
^d Mining ponds, Kedougou, Senegal	–	–	–	–	–	–	2.4	0.03	0.2
^e Mine, Kedougou, Senegal	–	–	–	–	–	–	–147	–1.3	–5.0
^f Reservoir and river region, Zimbabwe	–	–	–	–	–	–	3279	3.6	–
^g Carmo river region, Minas Gerais, Brazil	³ KOH; ⁴ HNO ₃ +HF + HCl	–	–	5.8–17.7 (0.9)	80–328 (42)	–	180	–	–
^h Fluvial sediments from AGMPs, Minas Gerais, Brazil	⁴ HNO ₃ +HF + HCl (prior heating of the sample)	–	–	–9.8)	–56)	–	–690	–	–
ⁱ Samuel Hydroelectric Reservoir, Brazil	–	–	–	–	–	–	140	–	–
^j Samuel Reservoir, Brazil	–	–	–	–	–	–	40.6	0.69	1.5
^k Petit-Saut reservoir, French Guiana Muresan et al., 2008	–	–	–	–	–	–	–	–	0.66
^l Pond, Cuyuni river basin, Venezuela	–	–	–	–	–	–	220.6	25.9	11
<i>Colombian region</i>									
^m Swamp, Ayapel, Colombia	¹ Water; ² CH ₃ COOH + HCl; ³ KOH; ⁴ HNO ₃ ; ⁵ HCl + HNO ₃	15 (5)	17 (7)	100 (43)	50 (19)	60 (25)	235	18	7.7
^m Swamp, Achi, Colombia	¹ Water; ² CH ₃ COOH + HCl; ³ KOH; ⁴ HNO ₃ ; ⁵ HCl + HNO ₃	23 (3)	38 (5)	225 (33)	210 (32)	170 (27)	722	40	5.5
ⁿ Mojana region, Colombia	¹ Water; ² CH ₃ COOH + HCl; ³ KOH; ⁴ HNO ₃ ; ⁵ HCl + HNO ₃	9.0 (1.7)	24.6 (4.7)	253.7 (48.4)	98.0 (18.7)	139 (26.5)	524.2	14.5	2.6
Present study	¹ Water; ² CH ₃ COOH + HCl; ³ KOH; ⁴ HNO ₃ ; ⁵ HCl + HNO ₃	0.3 (0.14)	0.92 (0.44)	87.4 (41.7)	102 (48.8)	18.8 (8.9)	209.6	15.1	6.5
<i>Sediment Quality Guidelines (SQGs)</i>									
^o Threshold Effect Concentration (TEC)	–	–	–	–	–	–	180	–	–
^o Probable Effect Concentration (PEC)	–	–	–	–	–	–	1060	–	–
<i>Background level</i>									
^p Upper Continental Crust (UCC)	–	–	–	–	–	–	50	–	–
^p Region soils	–	–	–	–	–	–	50	–	–

* Only Hg fraction; Average concentrations of Hg fractions (percentage value in brackets and bold); All values in ng g⁻¹. (Hg-w: water soluble; Hg-h: human stomach acid soluble; Hg-o: organo chelated; Hg-e: elemental mercury; Hg-s: mercuric sulfide)

^a Malehase et al., 2016.

^b Lusilao-Makiese et al., 2016.

^c Mason et al., 2019.

^d Niane et al., 2014.

^e Gerson et al., 2018.

^f Green et al., 2019.

^g Varejão et al., 2009.

^h Cesar et al., 2011.

ⁱ Pestana et al., 2019.

^j Guimarães et al., 1995.

^k Santos-Francés et al., 2011.

^m Marrugo-Negrete et al., 2015.

ⁿ Pinedo-Hernández et al., 2015.

^o Mac Donald et al., 2000.

^p Rudnick and Gao (2014).

in other regions of the world like the Long Island Sound, New York (Hammerschmidt and Fitzgerald, 2004), the Bay of Fundy, Canada (Sunderland et al., 2006) and mangrove sediments from Jiulong River Estuary, China (Wu et al., 2011). On the other hand, for a better understanding of the biogeochemistry of Hg in the sediments of mining ponds, the rates of Hg methylation and demethylation should also be examined.

It is also likely that the absence of a significant trend in the MeHg/THg correlations vs OM or C + Si in the most recent ponds (2–6 and 7–12 years) indicate that the direct supply of MeHg does not exert a dominant control over the distribution of the observed MeHg/THg ratios (Dong et al., 2018). However, the strong and significant correlation between MeHg vs MeHg/THg in AGMPs of 2–6 years, as well as the strong correlation between MeHg vs C + Si suggest that Hg methylation is in situ particularly in fine grain

sediments are primarily responsible for the accumulation and distribution of MeHg (Dong et al., 2018).

4.2. Fractionation of Hg in sediments

The Hg-w fraction includes Hg species present in the pore water and those bound to the dissolved organic matter (without an Hg-carbon bond) or suspended mineral particles (Wallschläger et al., 1998; Ramasamy et al., 2012). This fraction extracted with water can be easily mobilized by natural processes and they also serve as a substrate in the Hg methylation process (Ullrich et al., 2001; Boszke et al., 2003). The percentages of Hg-w recorded in this study (<0.01–0.71%) were low compared with sediments of Lake Vembanad, India (2.28–41.9%; avg. 8.51%) (Ramasamy et al., 2012), sediments from former gold mining sites in Descoberto, Brazil

(0.84–3.58%) (Cesar et al., 2011) and from the River Ji Yun in China (0.05–1.22%) (Ching and Hongxiao, 1985). The Hg-h fraction is operatively defined as reactive Hg species, which is mainly associated with carbonates (Kot, 2004). In some specified regions, carbonates can be an important adsorbent for many metals when OM and Fe-Mn oxides are less abundant in the aquatic system (Filgueiras et al., 2002). However, this phase is very susceptible to changes in pH, therefore, Hg is easily solubilized and is often made available for transfer to aquatic biota. It also includes the Hg species bound to the OM, which is absorbed on the surface of the minerals (Bloom et al., 2003). The average percentage of Hg-h observed in this study (0.44%) is consistent with the average values (0.6%) reported in China (Shi et al., 2005) lower than the average values (6.61%) in India (Ramasamy et al., 2012), and Colombia (4.7% by Pinedo-Hernandez et al., 2015).

In this study, the Hg-w + Hg-h fractions represent the bioavailable fraction (Hg-bio or labile Hg species). Despite the low proportions (0.12–1.65%) of Hg-bio from THg they represent the greatest risk since it will be easily transferred to the water column and subsequently will bio-accumulate in the biota or serve as a substrate for Hg methylation (Ullrich et al., 2001; Shi et al., 2005). This process is clearly observed in the present study where high content and ratios of MeHg were noted in sediments and high content of Hg in fish (data not shown).

The bioavailability of Hg found in the present study was slightly lower in older reservoirs than in more recent reservoirs as described before (Munthe et al., 2007; Hodson et al., 2014; Herrero Ortega et al., 2018) which is mainly due to the greater absorption of available Hg by the dense native vegetation in the oldest ponds, as well as a greater sequestration of Hg in sediment organic matter (Rodríguez et al., 2009).

The organoquellated Hg (Hg-o), is considered as a semi-mobile and semi-available fraction that is largely mobilized by microbial action (Yuan et al., 2010). This fraction contains Hg complexed acids like humic, fulvic and amino acids (without Hg-carbon bonds) (Ramasamy et al., 2012). In addition, the small amounts of Hg₂Cl₂ are often associated with live and dead biota along with Hg, MeHg (Bloom et al., 2003) and the reduced sulfur species binds to the Hg present in the OM (Xia et al., 1999; Hesterberg et al., 2001). A part of the Hg in the OM also binds to the oxygen and nitrogen atoms, but in a much lower concentration level (Hesterberg et al., 2001). However, high proportions of Hg-o as those recorded in this study (eg. ranging from 72.9 to 86.2 ng g⁻¹) have been frequently observed in sediments containing high humic acids (Bloom et al., 2003; Varejão et al., 2009; Male et al., 2013), which they also exhibit a high potential for Hg methylation. Apart from this, the OM is also acting as a chelating agent, which temporarily traps controlling the mobility and bioavailability of Hg in the sediments. Finally, the greater proportion of Hg-o in the sediments from older AGMPs suggest that the degree of complexation of the Hg increases with the age of the ponds (Hodson et al., 2014).

Considering the pH-Eh results, the chemical fractionation process indicates a greater preference of Hg which forms organic chelates and subsequently inorganic sulphides. It is very well supported by the relative abundance of OM, which provided more binding sites in the present study in both the regions (Campbell et al., 1988; Krupadam et al., 2007). The study on fractionation indicates high contents and proportions of Hg-e (ranging from 83.25 to 148.3 ng g⁻¹) (Hg⁰, Fe and Mn oxides), which is a typical character of mining sites that receive direct contributions of Hg⁰ during gold recovery processes (Cesar et al., 2011; Nartey et al., 2012; Lusilao-Makiese et al., 2016; Green et al., 2019). However, Hg⁰ has low solubility and mobility and it tends to concentrate in the areas near the discharge site (Van Straaten 2000). In addition, it tends to persist in soils and sediments under suitable Eh-pH conditions

which is available for chemical and biological transformation that results in the formation of more toxic chemical species (i.e. MeHg) (Biester et al., 2002). The present results are consistent with those observed in the sediments affected by Brazilian gold mines (Varejão et al., 2009). The high Hg-e found in the present study is also similar to other areas (sedimentation ponds) directly impacted by gold mining in the River Camaqua basin in Brazil (82.0–83.1%) (Pestana et al., 2000) and the old gold mines in Bibiani, Ghana (20.77–95.12%) (Nartey et al., 2012).

The Hg-s fraction result (ranging from 15.07 to 16.23 ng g⁻¹) suggests that Hg is associated with inorganic sulphide complexes and that this Hg is not available for methylation. However, if the environmental conditions in the sediments become aerobic (e.g. decreased organic load) the Hg in this phase will be released as Hg (II) and will become available for methylation (Ullrich et al., 2001; Boszke et al., 2003). With respect to other similar other studies, the average percentage of Hg in this phase (8.96%) was higher than those in India (1.02%) (Ramasamy et al., 2012).

In the present study most of the Hg fractions were significantly correlated, indicating that the changes in one fraction are often reflected the transformations to other fractions independently of the abandonment period of the ponds (Table 3). Likewise, Hg-e showed positive correlations with THg ($r = 0.63$) and MeHg ($r = 0.50$) in all the AGMPs which used Hg⁰ in gold amalgamation processes (Marrugo-Negrete et al., 2015). The positive correlations between the interchangeable fractions (Hg-w and Hg-h) and MeHg reflects the toxicity potential, bioaccumulation and bio-magnification process indicating that Hg represents a tropical network in these aquatic environments. In addition, the high content of OM in the sediments increases the dissolved organic matter and are subsequently linked with the Hg-w and Hg species (Wang et al., 2004).

In relation with sediment texture, the highest levels of Hg are often observed in the sandy sediments in most of the AGMPs which also indicates low positive correlation values, which is similar to other observations from AGMP in Senegal (Niane et al., 2014). Likewise, the negative correlations of C + Si with THg, MeHg in the most recent lagoons suggests that the Hg is mainly in the form of metallic or amalgamated droplets with residual gold particles (Guedron et al., 2009). On the contrary, the relatively strong correlation of Hg with the finer sediments of the oldest ponds ($r = 0.68$ for THg; $r = 0.73$ for MeHg) indicates that due to the larger surface area in the finer sediments a larger capacity to absorb THg, MeHg and Hg-bio that enters the ponds exists (Wang and Chen 2000; Boszke et al., 2004; Varejão et al., 2009). In general, careful analysis of the AGMPs showed that the Hg contents in the sediments decrease with the increase of grain size.

5. Comparative studies

Table 3 compares the results of Hg concentrations obtained in this study with other works in aquatic ecosystems affected by AGMPs. The average concentrations (values in ng g⁻¹) of THg in sediments (39.1–1271; avg. 210) indicates a two-fold lesser magnitude than those reported for sediments in ponds contaminated with Hg in Venezuela (Santos-Frances et al., 2011) and from mining ponds in Senegal (Niane et al., 2014). In general, they are at the lower end in THg concentrations reported by other similar studies (Muresan et al., 2008; Cesar et al., 2011; Lusilao-Makiese et al., 2016; Mason et al., 2019; Green et al., 2019).

Compared with the SQGs, 26% of pond sediment samples evaluated in our study presented higher concentrations of THg above the TEC level indicating that adverse effects on benthic organisms are expected to occur frequently. Only one sample (P5) in the study presented higher THg concentrations above the PEC value.

Nevertheless, this aspect suggests the existence of other ponds with higher THg concentrations in this mining region and therefore further detailed studies are needed since these ponds represent a human risk since local communities obtain food (fish) from these sites (Salazar-Camacho et al., 2017).

On the other hand, the concentrations of MeHg (values in ng g^{-1}) (<5.0 to 138.33, avg. 15.13) and MeHg percentage (avg. 6.5%) were very above than the reported values in a Brazilian reservoir (Guimarães et al., 1995; Pestana et al., 2019), water deposit in gold mining sites, Johannesburg (Lusilao-Makiese et al., 2016) and the artificial reservoirs, Ivory Coast (Mason et al., 2019). Nonetheless, these values fall within the range exhibited by other ecosystems affected by gold mining that act as hotspots for MeHg production (Muresan et al., 2008; Marrugo-Negrete et al., 2015; Pinedo-Hernandez et al., 2015). Although the concentrations of THg in the sediments of the present study are not very alarming compared to other studies, their high capacity for MeHg production is worrying, which subsequently puts human health and wildlife at risk.

Finally, in this study the average proportions of Hg (in %): Hg-e (48.8), Hg-e (47.1) and Hg-s (8.9) are consistent with the values registered by Marrugo-Negrete et al. (2015), Pinedo-Hernandez et al. (2015) and Malehase et al. (2016) in lentic systems that receive important contributions of Hg^0 from gold mining with high OM contents in the surface sediments. However, the average proportions of Hg-e observed in our study were lower compared to similar locations like Minas Gerais, Brazil (Varejão et al., 2009; Cesar et al., 2011), and which report average proportions of Hg-e of up to 78% in lotic systems with low OM content in the sediments.

6. Conclusion

Based on our results, the average contents of Hg-w, Hg-h, Hg-o, Hg-e, Hg-s and MeHg in surface sediments showed no significant variability between the different periods of desertion of these ponds. Primarily Hg in the surface sediments of AGMPs by gold mining in the San Juan mining district indicates elemental Hg-e is bound to amorphous materials. In addition, it is associated with organic matter (Hg-o) and the sulfur-bound mercury (Hg-s). Moreover, the elemental Hg fraction (Hg-e) is abundant in most of the mining areas in the Chocó region, Colombia. Despite the low Hg contents recorded in the first two fractions (Hg-w and Hg-h) Hg methylation in the present study is an important process in these AGMPs. Since the studied AGMPs are located in former gold mining regions the high percentages of Hg-e in these sites is due to the use of elemental mercury during gold recovery processes. MeHg concentrations in sediments showed a similar trend with THg, demonstrating their dependence partially along THg.

The results from the sequential extraction method proved to be a valuable technique to generate useful information about the mobility and bioavailability of Hg in the sediments. The level of Hg in the sediments of these AGMPs are partially governed by the OM which dilutes the overall concentration of THg. However, even after 20 years of abandonment, the enrichment and contamination by MeHg, THg continues and persists in the sediments of these ponds.

Overall, the geochemical distribution of Hg and MeHg indicates that Hg represents a serious threat in these water bodies (especially ground water sources) which needs special attention. Moreover, it is also specified that due to the concentration of THg and MeHg in the region these AGMPs should be prohibited for any human use including pond culture practices especially fish harvesting.

Declaration of competing interest

The authors do not have any conflict of interest in this study.

CRedit authorship contribution statement

Harry Gutiérrez-Mosquera: Conceptualization, Data curation, Formal analysis, Investigation, Project administration, Software, Visualization, Writing - original draft, Writing - review & editing. **José Marrugo-Negrete:** Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing - original draft, Writing - review & editing. **Sergi Díez:** Investigation, Visualization, Writing - original draft, Writing - review & editing. **Gladis Morales-Mira:** Data curation, Formal analysis, Methodology, Supervision. **Luis Javier Montoya-Jaramillo:** Data curation, Formal analysis, Methodology. **M.P. Jonathan:** Software, Writing - original draft, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2020.127319>.

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