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Distribution of Total and Organic Mercury in Superficial Soils in the Upper Manzanares River Watershed, Sucre State, Venezuela

Yahsé Rojas Challa¹, Luisa Rojas de Astudillo¹, Armando Ramirez², Andrés Escalona³ and Gregorio Martínez⁴

¹Department of Chemistry, School of Sciences, Universidad de Oriente, Cumaná, Venezuela.

²Department of Geochemistry, Universidad Central de Venezuela, Caracas, Venezuela. ³Analytic Chemistry Center, Faculty of Sciences, Universidad Central de Venezuela, Caracas, Venezuela.

⁴Department of Chemical Oceanography, Oceanographic Institute of Venezuela, Universidad de Oriente, Cumaná, Venezuela.

Abstract: Total and organic mercury contents were determined from samples of surface soils (0–5 cm), sieved at $\leq 63 \mu\text{m}$, collected from 10 different locations in the upper Manzanares River watershed, using cold vapor atomic absorption spectroscopy. Methylmercury was determined using a HPLC-UV detector. The mean total mercury concentration was $1.3 \mu\text{g} \cdot \text{g}^{-1}$, a value permitted by the Canadian environment quality guidelines for farming soils, but high for European standards. Using certified reference materials, we verified that a modification of the method described by Qian et al. (2000) was effective for organic mercury extraction, with a recovery of 92.17% for DORM-2 and 92.11% for TORT-2. This modified method was applied to soil samples, obtaining concentrations of $0.5\text{--}1.0 \mu\text{g} \cdot \text{g}^{-1}$ of organic mercury. The parameters for determining methylmercury using HPLC-UV were optimized; the best results were obtained with a $4.6 \text{ mm} \times 25 \text{ cm}$ Zorbax CN⁻ column, with a mobile phase of 70/30 V/V of methanol: ammonium acetate $0.05 \text{ mol} \cdot \text{L}^{-1}$, with a flow rate of $0.5 \text{ ml} \cdot \text{min}^{-1}$; the methylmercury was detected at 4.99 min retention time. Methylmercury was not found in the soil samples. Using the certified reference material we proved that the method used produced reliable results. The analysis confirmed the existence of mercury in this farming area.

Keywords: Manzanares River; mercury; methylmercury; soils; Venezuela

Introduction

Most of the anthropogenic Hg deposited in a watershed is retained in the soil, water, and biota for over a decade (Lindqvist and Rodhoe, 1991) and, therefore, has the potential to persist as a toxin. The risk to humans and wildlife occurs as Hg is transported to watersheds and accumulates in the aquatic food chain (Driscoll et al. 2007). Exposure pathways include Hg contamination of aquatic organisms, edible crops, drinking water and air. Human exposure may also occur as a result of direct ingestion of contaminated soil (Revis et al. 1990).

Mercury may be present organically or inorganically in natural environments. Methylmercury is one of the most toxic mercury compounds for the majority of living organisms in the food web (Ramalhosa et al. 2001; Gaona and Valiente, 2003).

Several procedures have been used to separate organic and inorganic mercury. Distillation is one of the most common separation techniques, because it prevents matrix interference, especially when low levels of mercury are determined (Horvat et al. 1993). However, Bloom et al. (1997) proved that during distillation methylmercury is generated abiotically as a result of the action of organic substances on the inorganic mercury of the sample. They proposed the use of acid solutions containing copper sulphate and potassium bromide to extract methylmercury. Bloom et al. (1999) then evaluated this procedure with reference material and proved that there was less abiotic methylmercury production in comparison to the distillation procedure.

In recent years, several methods have been developed to separate mercury species, based on gas chromatography or high resolution liquid chromatography (Ramalhosa et al. 2001). Although gas chromatography is the most frequently used mercury separation technique, it requires volatile derivatives

Correspondence: Luisa Rojas de Astudillo, Department of Chemistry, School of Sciences, Universidad de Oriente, Cumaná, Venezuela. Email: lrojas40@yahoo.com



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of mercury compounds (Fischer et al. 1993). High resolution liquid chromatography allows easier sample treatment without the need of the derivatization process, and the separation of mercury components can be made simply at room temperature (Ramalhosa et al. 2001; Percy et al. 2007). Moreover, mercury species less volatile than methylmercury, as well as non-volatile species, such as organomercurial aromatic components are determined using high resolution liquid chromatography (Hempel et al. 1992).

The objectives of this study were: 1) to verify that the modified method for Hg analysis produces accurate and precise results and 2) to determine the distribution of organic and inorganic mercury in the soils of the upper Manzanares River watershed, where there have been few studies on metal pollution.

Materials and Methods

Sampling area

Soil samples were collected in 10 locations from the upper Manzanares River watershed in October 2004. The climate is tropical humid forest, the temperatures varies between 12 and 27 °C and annual mean rainfall 1328 mm (Márquez et al. 2002), dominated by sedimentary rocks: sand and calcareous (Sánchez and González, 2002). The main threat is due to agriculture, involving both crops and livestock.

The localities chosen for the study are the same that form part of the project “Environmental Assessment and Stakeholder Participation in Pollution Control for the Manzanares River Catchment, Sucre State N° QCL-2324-2288-2661-2102”, jointly funded by the British Embassy in Venezuela and the United Nations Environmental Program, and implemented by the Universidad de Oriente, in Venezuela. The main objective of that three-year project was to assess the level of pollution of the river and the adjacent coastal zone, as well as evaluating point-source and diffuse sources of pollution. In the long term, it will develop a monitoring system, sanitation policy and education plan for the recuperation of this important river (British embassy, 2008).

Figure 1 shows a map of Sucre State, Venezuela, and a complete map of the Manzanares River, with the sampling area in the upper Manzanares River watershed. Portions of several samples were taken

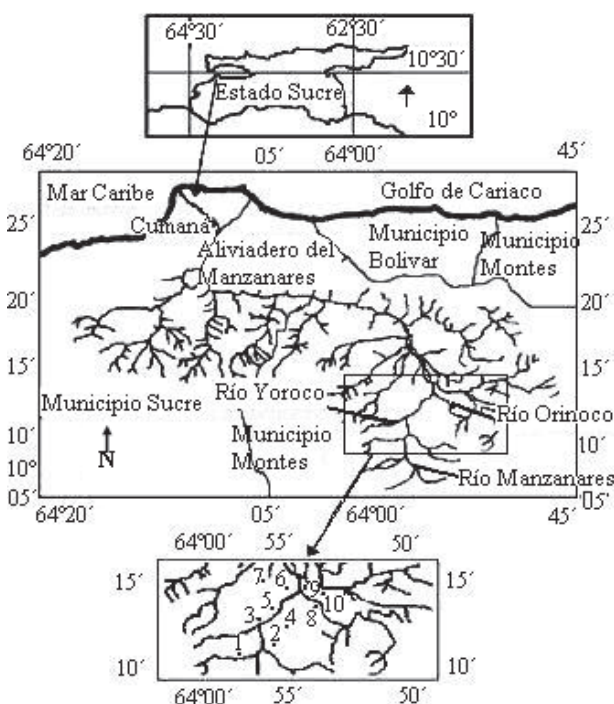


Figure 1. Sampling locations in the upper Manzanares River watershed.

Legend: (1) Cutabano Las Charas; (2) Manzanares-Yoroco; (3) Manzanares I; (4) Yoroco Abajo right; (5) Yoroco Abajo left; (6) Las Trincheras Las Lomas; (7) Fragua; (8) Orinoco La Toma; (9) Peña-Orinoco Border (10) Orinoco Aquaduct.

in a 100 m² area, at a depth of 0–5 cm. The collection area was divided into squares 30 cm wide and 5 cm long, and the collected samples were put into plastic bags.

Before making the analysis, soil samples were dried at room temperature to constant weight. Because mercury is concentrated in the smaller grain sizes, where the specific surface area is higher (Rodrigues-Filho and Maddock, 1997; Wasserman et al. 2001), the samples were sieved to $\leq 63 \mu\text{m}$. Among the physical-chemical properties (like clay mineralogy, organic matter, etc.) that could affect mercury adsorption in soil or sediment samples, texture plays an important role (Yallouz et al. 2007).

Total content of mercury in the soils

Triplicates of each 0.5 g dried soil sample were used for mercury analysis. For each sample, concentrated nitric acid (10 ml) was added, and samples were left to pre-digest overnight at room temperature in a fume hood. A small glass funnel was placed in the mouth of each conical flask, to prevent loss of sample, and the samples were then

refluxed on a hot plate at 100 °C for 3 h. Concentrated sulphuric acid (2.5 ml) and concentrated hydrochloric acid (1.0 ml), sequentially, were then added to each sample, which was allowed to reflux at 130 °C for three additional hours. Potassium manganate (VII) solution (5% m/V) was added drop-wise to each sample until a permanent pink coloration resulted. Hydroxylamine solution (50 µl, 10% m/V) was added to destroy the excess potassium manganate (VII). The digests were filtered into 25 ml volumetric flasks, through Whatman #42 filters, and made up to volume with deionized water rinses of the residues. Mercury in soils was determined by cold vapor atomic absorption spectrophotometry.

The method was validated with a Standard Reference Materials (Montana Soil, 2711, NIST). This reference material was subsequently analyzed with each batch of soil sample, to ensure consistently reliable analysis results. All statistical analyses were performed using the Minitab Statistical Program (Version 15).

Determination of the organic mercury concentrations in the soils

The Qian et al. (2000) method was sequentially applied up to the separation of the organic phase. A mixture of 0.5 g of soil + 6 ml of a solution of CuSO_4 (0.03 mol.l⁻¹) and KBr (0.38 mol.l⁻¹) in H_2SO_4 (5%) was shaken for 2 h. Then 5 ml of CH_2Cl_2 were added and the mixture was shaken for 30 min., and then centrifuged at 3000 rpm for 15 min., to separate the organic phase from the aqueous one. In this study was substituted the following step of Qian et al. (2000) method: A 2.0 ml sub-sample of CH_2Cl_2 layer was pipetted into a 50 ml polypropylene centrifuge tube, and 45.0 ml distilled water was added. The sample was purged with Ar to remove the organic solvent, leaving the extracted methyl mercury in the water matrix. Instead of, organic mercury was converted to inorganic mercury by means of acid digestion (method described in section 1.2, but using only 50% of reagents). The modified method was evaluated with TORT-2 and DORM-2 certified reference materials of the National Research Council Canada. The total and organic mercury (converted into inorganic mercury) measurements were taken with a Perkin Elmer Atomic Absorption Spectrometer (model 3110) coupled with a hydride generator device (MHS-10), and using sodium borohydride as a reducing agent.

Determination of methylmercury concentration in soils using high performance liquid chromatography with a UV detector

Toluene was used to extract methylmercury from samples and dissolve the MeHgCl standard. This solvent was also utilized by Qian et al. (2000) in the extraction of methylmercury from soil samples and with a recovery of 95%. These organic extracts were analyzed using HPLC (Agilent Technologies 1100 series) with a UV-Vis diode array detector and automatic injector to determine methylmercury. The parameters, such as the mobile phase, reverse phase column type and flow rate, were previously optimized at room temperature, varying the flow from 0.4 to 0.5 ml.min⁻¹, and comparing the wavelengths 230 nm, 254 nm and 285 nm. In order to determine the composition of the mobile phase, the proportions of methanol/ ammonium acetate solution 0.05 mol.l⁻¹ (adjusted to pH 5, with 1 mol.l⁻¹ acetic acid) were varied until the best results related to separation and sensitivity were obtained.

Results and Discussion

Total mercury content

The accuracy of the method for determining the total mercury content in soils was verified with the Montana Soil reference material (NIST 2711), and a recovery of 98.4 (± 2.8)% was obtained.

Figure 2 shows the mercury concentrations for the 10 localities studied. One-way analysis of variance (ANOVA), at $\alpha = 0.05$ probability, was used to assess the relation of mercury concentration and sites, the results showed that mercury concentration in each site was statistically different from one another ($F = 51.07$, $P < 0.001$).

Since Venezuela have no established soil quality guideline at this time, the European Union and Canadian guidelines were used as interim measure to assess whether the concentrations of mercury in soils could have adverse biological impact. The concentrations were between 1.0 and 3.0 µg.g⁻¹, which is below the level established by the Canadian environment quality guidelines (6.6 µg.g⁻¹) for farming soils (CCME, 2001). Nevertheless, recent evidence suggests that mercury is responsible for a reduction of micro-biological, activity vital to the terrestrial food chain in soils, over large

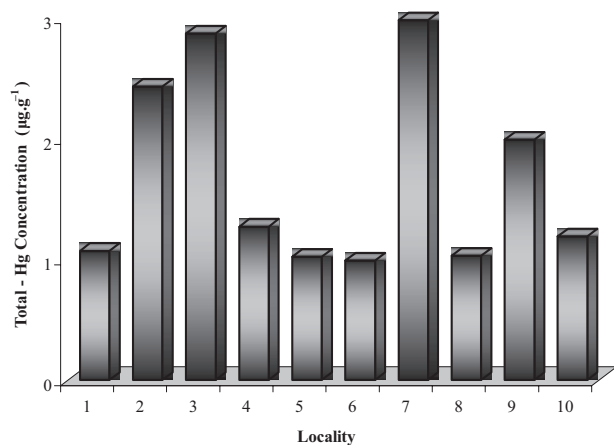


Figure 2. Total mercury content in the localities of the upper Manzanares River watershed.

Legend: (1) Cutabano Las Charas; (2) Manzanares-Yoroco; (3) Manzanares I; (4) Yoroco Abajo right; (5) Yoroco Abajo left; (6) Las Trincheras Las Lomas; (7) Fragua; (8) Orinoco La Toma; (9) Peña-Orinoco Border; (10) Orinoco Aquaduct.

parts of Europe—and potentially in many other places in the world with similar soil characteristics. Preliminary critical limits to prevent ecological effects due to mercury in organic soils have been set at 0.07–0.3 mg/kg for the total mercury content in soil. The limits were developed by an international expert group on effect-based critical limits for heavy metals, working within the framework of the UN ECE Convention on Long-Range Transboundary Air Pollution (Pirrone et al. 2001). Taking the preliminary critical limits into account, the soils of the upper Manzanares River watershed are contaminated.

It is difficult to determine the origin of mercury in the localities studied. However, as Venezuela is under the influence of the inter-tropical area of low equatorial pressures, where the northeast and southeast trade winds (alises) converge, it is likely that these winds carry the mercury from the mining areas of Bolivar State, in the south, towards the north of Venezuela. Mercury is used there to separate gold from mineral fractions and it is widely used by non-organized miners in many tropical countries (Brazil, Bolivia, Colombia, and Venezuela) (Carrasquero and Adams, 2002; Telmer et al. 2006). Mercury can be readily transferred between air, water, and soils and can be transported long distances in the atmosphere (UNEP, 2002; Panyametheekul, 2004). The Venezuelan State has no information about the quantity of mercury used by non-organized miners; however, according to the United Nations Industrial Development Organization, between 1985 and 1991, five tons of mercury

were deposited into the lower Caroni river area (downstream from the Guri Reservoir) as a result of mining activities. The highest quantities of mercury are launched into the environment as a result of the open-air burning of mercury amalgams (Valdirio and Costa, 2001). Hg is often emitted by fossil-fuel burning power plants and can travel great distances in the atmosphere, however, in the upper Manzanares River watershed, this atmospheric source seem to be considerably less important than regional contamination from the burning of amalgamated gold. According to Meili et al. (2003), the predominant source of Hg in most watersheds is atmospheric deposition, which has increased 2- to >20-fold over the past centuries.

Another source of mercury pollution in farming soil is the use of fertilizers and agrochemicals (Haygarth and Jones, 1992). Many of the raw materials used in the preparation of nitrogen, phosphorus and potassium fertilizers, organic fertilizers and fertilizers with high zinc content may contain toxic metals (EPA, 1999). An analysis of 29 fertilizers revealed the presence of 22 toxic metals, one of which was mercury (Shaffer, 2001).

The highest content of mercury was found in Fragua, which is an area surrounded by crops, suggesting that it is probable that fertilizers have contributed to the high level of the metal there. The inhabitants of these localities are unlikely to have any knowledge about the level of heavy metals allowed in fertilizers, as this is not always shown on the labels; only the beneficial nutrients, such as zinc or phosphate are shown. Also, the fertilizers are sold directly to the public, and consumers are not warned about the presence and high quantities of toxic metals.

Organic mercury content

At the present time, there are many certified reference materials for the concentrations of mercury in several matrices (sediments, soils, water, plants and tissues) of different origins. However, only a few reference materials of marine origin are certified for components of methylmercury. Natural levels of methylmercury in soils are measured in parts per billion (ppb) and, as yet there are no certified reference materials available. For this reason, certified sediment reference materials are used as a substitute (Qian, 2001), but only two reference materials for sediment have been validated, and controversies have emerged about their

precision for the determination of methylmercury concentrations.

This study confirmed the efficiency of the modified method taken from Qian et al. (2000) using certified reference materials from the National Research Council Canada, DORM-2 (Dogfish muscle), which contains methylmercury of $4.47 (\pm 0.32) \mu\text{g}\cdot\text{g}^{-1}$ and TORT-2 (lobster hepatopancreas) with a value of $0.152 (\pm 0.013) \text{g}^{-1}$. The change was made in the technique of quantification: The organic mercury was quantitatively converted into inorganic mercury using acid digestion and measurements were taken using cold vapor atomic absorption spectroscopy.

The recoveries were 92.17% for DORM-2 and 92.11% for TORT-2 (Table 1). The results of this study confirm that methylmercury in both biotic and abiotic systems bonds strongly with organic and inorganic sulphides. To break these bonds it is necessary to chemically treat the samples before separation using copper and bromide ions. Copper (II) ions permit a complete liberation of the organic mercury from the thiol groups, and they have been successfully used in the separation of mercury in fish and sediments (Longbottom et al. 1973). Additionally, bromide ions in the copper solution, as a source of halides, provide a high recovery of mercury (Qian et al. 2000). Bromide attracts methylmercury and facilitates the distribution of the organomercury bromide compounds between the aqueous and organic phases. Dichloromethane proved to be the best option for the extraction of organic mercury and its conversion into inorganic mercury. A complete digestion of the organic layer of dichloromethane in nitric acid was reached, producing reliable results.

The procedure described was applied to the soil samples. Figure 3 shows the concentrations of mercury obtained from five locations, in other areas the content of mercury was below the detection limit ($31 \text{ng}\cdot\text{g}^{-1}$). Values were between 0.53 and $1.00 \mu\text{g}\cdot\text{g}^{-1}$. According to these results, the

locations with the highest content of organic mercury were Yoroco Abajo, Yoroco Arriba and Las Trincheras-Las Lomas, which are located in the highlands and surrounded by abundant wild vegetation. Altitude may be a relevant factor in the origin of the high contents of organic mercury in these areas, mainly due to atmospheric deposition. Frontera Peña-Orinoco is another place with a high content of mercury; it is situated in flat zone with houses and banana crops. It is possible that the mercury found in farming areas is due to the use of fertilizers and fungicides. Orinoco La Toma is the location with the lowest content of organic mercury; it has abundant wild vegetation and it is approximately 300 m away from the village.

Determination of methylmercury using HPLC-UV

Column type selection

A column with a cyanide (CN^-) functional group was used in this study. The stationary phase linked to the cyanopropyl is relatively polar and is used in the normal separation mode with relatively non-polar mobile phases, such as methylene chloride/hexane mixtures. This can be used for separations in reverse phases using highly polar mobile phases, such as mixtures of water/methanol or water/acetonitrile. This column can be used to separate moderate polar components (DuPont Instruments, 1985).

In this study, the column was used in reverse phase. At first we used the 15-cm long Adsorbosphere CN^- column, but this column did not separate the blank signal with that of methylmercury and formed one peak with a retention time of 4.75 min. We then replaced the column by a longer one, the 25-cm Zorbax CN^- . Analyzing the blank, the retention time for toluene increased, and several low peaks and a high one were detected at 8.96 min., and the methylmercury signal was observed at 4.98 min. Figure 4 shows the separation between

Table 1. Concentration of MeHg and percentage of recovery obtained with the reference material using the method from Qian et al. (2000) modified in this study.

Standard reference material	Certified value of MeHg ($\mu\text{g}\cdot\text{g}^{-1}$)	Obtained concentration of MeHg ($\mu\text{g}\cdot\text{g}^{-1}$)	% Recovery
DORM-2	4.47 ± 0.32	4.12 ± 0.45	92.17
TORT-2	0.152 ± 0.013	0.140 ± 0.024	92.11

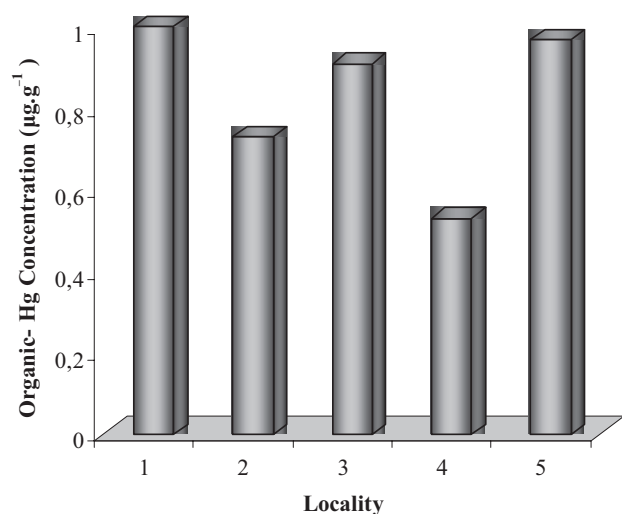


Figure 3. Organic mercury concentrations in the different localities, obtained using the method Qian et al. (2000) modified in this study.

Legend: (1) Yoroco Abajo right; (2) Yoroco Abajo left; (3) Las Trincheras Las Lomas; (4) Orinoco La Toma; (5) Peña-Orinoco Border.

the methylmercury and toluene signals. This was the column chosen to make the subsequent analyses.

Selection of the mobile phase

The best separation of methylmercury was achieved using the mobile phase 70/30 (V/V) methanol/

ammonium acetate 0.05 mol.l⁻¹ at pH 5 and at a wavelength of 230 nm.

Calibration curve

The calibration curve was made based on the dilution of 1 mg.l⁻¹ of the methylmercury standard; six working standards were used, showing an R² value of 0.996, indicating consistent results. The limit of detection estimated on the base of the calibration curve was 6.3 ng.ml⁻¹.

Analyte addition technique

The recovery of an analyte is an important factor for the validation of an analytical method (Hubert et al. 1999). To obtain it, 20 µl of a standard solution of 50 ng.ml⁻¹ was added to the extracts from Frontera Peña-Orinoco (which did not show evidence of containing mercury) in a 1:1 proportion (Fig. 5). The recovery was 78.2%, a level considered adequate, according to the United States Geological Bulletin, who give a recovery ranging from 75.0% to 93.2% as being acceptable for evaluating the accuracy of methylmercury procedures. DeWild et al. (2004) assessed the accuracy of the KBr/CuSO₄/CH₂Cl₂ methylmercury extraction procedures in soil samples using a certified reference material and the analyte addition technique, and the recovery

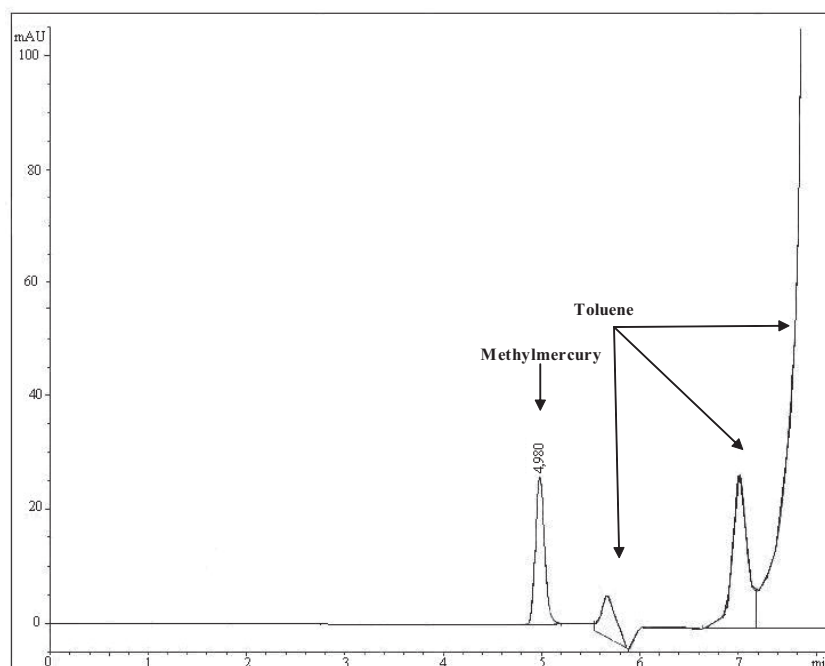


Figure 4. Chromatogram of MeHgCl standard using a 25-cm Zorbax CN⁻¹ column.

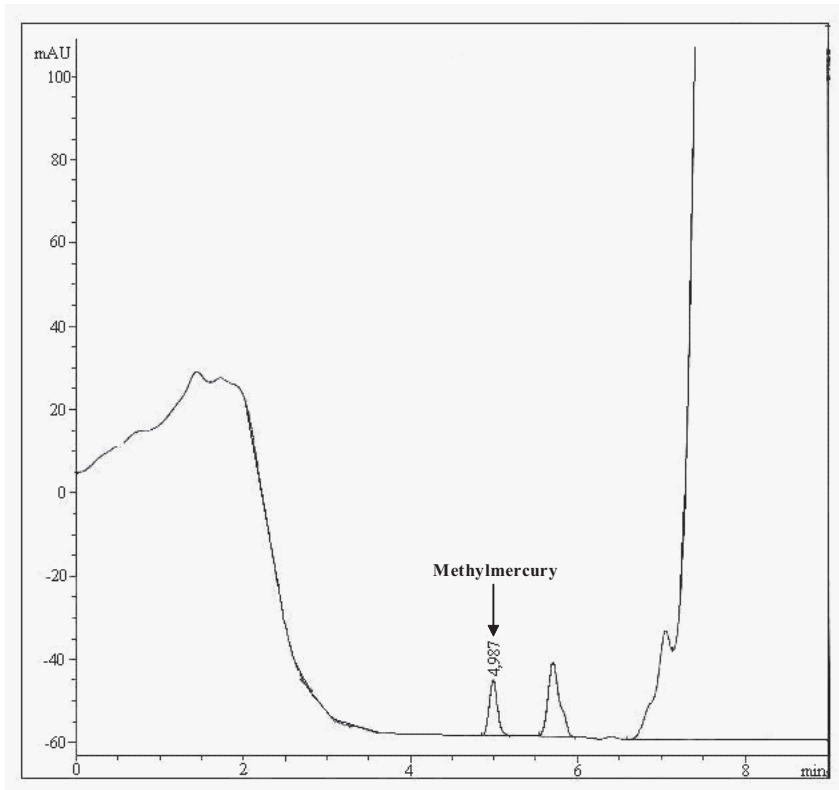


Figure 5. Chromatogram of the locality Frontera Peña—Orinoco contaminated with methylmercury standard of 50 ng.ml^{-1} , in a proportion 1:1. Retention time for MeHg = 4.99 minutes.

for spiked soil samples was 66.2% to 88.8%, with an average value of 82.0%.

Content of methylmercury in the soil samples

The analyses were made in order to determine the content of methylmercury in the locations where organic mercury was detected, following the modified version of the Qian et al. (2000) methodology. The chromatograms of the extracts of the soil samples showed no signal of methylmercury.

Either the values of methylmercury were lower than the detection limit (6.3 ng.ml^{-1}) or the soil samples there did not have methylmercury. This might confirm that mercury in soil is not always available for methylation.

Among the factors affecting the specific rates of methylation/demethylation of mercury is the pH (Sadiq, 1997; Pavlogeorgatos et al. 2006). Thus, the absence of methylmercury in analyzed soil samples might be due to the pH, which was between 5.9 and 7.4 (Table 2). Several investigations have found an inverse relationship between

Table 2. pH values, texture and organic matter of the soil samples with organic mercury.

Locality	pH	% Organic matter	% Clay	% Silt	% Sand	Texture
Yoroco Abajo right	6.78	13.30	26.30	22.71	50.98	Sandy clay loam
Yoroco Abajo left	6.56	12.68	27.57	32.42	40.01	Loam
Las Trincheras Las Lomas	5.94	11.92	14.30	16.71	68.99	Sandy loam
Orinoco La Toma	7.33	10.63	10.31	28.68	61.01	Sandy loam
Peña—Orinoco Border	7.44	8.27	6.31	6.31	74.99	Sandy loam

Hg methylation and pH; low pH is associated with an increase in methylation (Rogers, 1977; Bloom et al. 1991; Regnell, 1994).

The textures of the soil samples with organic mercury concentrations (Table 2) were similar to those evaluated by Rogers (1977), who found that the production of methylmercury was affected by soil texture, pH, soil moisture content and soil temperature. There was a decrease in the occurrence of methylmercury when the solution pH was above 4.5. Additionally, Grigal, (2003) observed that MeHg production in areas of well drained soils is scarce. The mean of content of organic matter in soils analyzed in this study was $(11.4 \pm 1.9)\%$ (Table 2), and there was a positive correlation ($R^2 = 0.71$, $p < 0.02$) between organic matter content and concentration of organic Hg; therefore, is unlikely to become methylated (Wallschlaeger et al. 1998; Biester et al. 2002; Ravichandran, 2004).

Conclusions

Mercury concentrations were within the limits of the Canadian environmental quality norms (6.6 mg/kg), but, under the European Union's rules (0.07–0.3 mg/kg), all sites were contaminated.

The highest concentrations of organic mercury were found in Yoroco Abajo, Frontera Peña-Orinoco and Las Trincheras-Las Lomas. The first and third locations were mountainous soils with steep slopes, whilst the second was situated in a farming area.

The Qian et al. (2000) method was modified and evaluated with certified reference materials of the National Research Council Canada, DORM-2 and TORT-2, to determine the content of organic mercury (such as methylmercury), resulting in recovery of 92.17% and 92.11%, respectively. This ensures the effectiveness of the method.

The content of methylmercury was best determined using HPLC-UV with a 25-cm Zorbax CN⁻ column, a mobile phase of 70/30 (V/V) of methanol/ammonium acetate 0.05 mol.l^{-1} , and a flow rate of 0.5 ml.min^{-1} . Retention time for methylmercury was of 4.99 min. The recovery for spiked samples was 78.2%.

The soil samples with organic mercury showed no signal of methylmercury, which may be associated with pH levels and soil texture not permitting the methylation.

Acknowledgements

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