



Baseline investigation of (methyl)mercury in waters, soils, sediments and key foodstuffs in the Lower Mekong Basin: The rapidly developing city of Vientiane (Lao PDR) [☆]



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ABSTRACT

We report here the first inventory of mercury (Hg) contamination in the ecosystem of Vientiane city, a representative emerging city bordering the Mekong River. Total Hg (THg) concentration in soil and sediments of both contrasting non-urbanized (wetland, rice paddy, Mekong River) and urbanized areas (wastewater canal and associated wastewater irrigated wetland) was low (8 to 101 ng g⁻¹), reflecting the essentially non-industrialized status of the capital. Dissolved THg (2.2 ± 2.2 ng l⁻¹) and monomethyl-mercury (MMHg) concentrations (0.06 ± 0.09 ng l⁻¹) were also low in both surface and soil or sediment pore water with higher concentrations (up to 9 ng g⁻¹ THg and 0.53 ng g⁻¹ MMHg) measured in wetland and rice paddy suboxic waters. Dissolved organic carbon was identified as the main carrier in surface water for dissolved Hg transport towards the Mekong River. The measurement of low THg concentrations in rice (6.4 ± 1.0 ng g⁻¹) and fish (51 ± 40 ng g⁻¹) sampled in rice paddies and in the Mekong River confirmed the pristine state of the ecosystem of Vientiane area. Based on these data, we evaluated a low environmental Hg-attributable health risk for the local population whose diet relies on both fish and rice.

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1. Introduction

Mercury (Hg) contamination of tropical ecosystems has been studied in many countries around the world, in part because of the perceived threats to the local human population arising from the consumption of contaminated fish and rice (Brabo et al., 2000; Feng et al., 2008; Hall et al., 1997; Kuwabara et al., 2007). Among Hg species, monomethyl-mercury (MMHg) has been reported as the most dangerous species for local populations (Cheng et al., 2009; Fitzgerald and Lamborg, 2003; Zahir et al., 2005) in part due to its ability to biomagnify in the aquatic food web (Boudou et al., 2005; Durrieu et al., 2005). The main

anthropogenic sources of Hg reported in southern tropical ecosystems are mining activities (i.e., gold and silver mining), industrial waste, fuel and coal combustion and the use of wastewaters for agricultural irrigation (Feigin et al., 1991; Swain et al., 2007).

Currently, little information is available regarding Hg contamination of the Lower Mekong Basin, and in particular in Laotian ecosystem where no published data on Hg are currently available. The rapid growth of the main cities located along the Mekong River during the last few decades, might be a potential source of Hg contamination for ecosystems through wastewater irrigation and waste, fuel or coal combustion (Feigin et al., 1991; Swain et al., 2007). Notably, Vientiane city (Lao PDR) has almost doubled its population during the past 15–20 years, now approaching 300,000 people (Rafiqui and Gentile, 2009). Despite this rapid expansion, Vientiane remains largely non-industrial with the urban fabric of the city being interspersed with paddy fields and orchards, rather than factories (Rafiqui and Gentile, 2009). Wastewater treatment systems are largely absent in the city and most untreated wastewaters from the urban area are discharged into the Houay Mak Hiao (H.M.H.) canal and thence to the large That Luang wetland, where the local population fish and use the water for the irrigation of rice paddies (Whelan et al., 2007).

In this context, we tried to assemble the first inventory of Hg distribution in the aquatic ecosystem of the emerging Vientiane city capital

[☆] Electronic Supplementary Information (ESI) available: Supplementary figures SI.1 and SI.2 show multi-resolution Electrical Resistivity images obtained at the non-urbanized wetland (WL) and rice paddy (RP) sites, Supplementary Table SI.3 shows water chemical parameters obtained in the Vientiane district area, Supplementary Table SI.4 shows the biota characteristics, Supplementary figure and Table SI.5 show the map of complementary biota sampling locations along the Mekong River (from the 2011 MRC campaign) with associated Hg concentrations and locations of known gold mining locations, and Supplementary Table SI.6 shows the biota key characteristics, including mercury concentrations.

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which combines both non-urbanized and urbanized areas. A special emphasis was placed on Hg speciation measurements (i.e., THg and MMHg) in the dissolved phase and THg was measured in the particulate phases of soils and sediments to evaluate the distribution of Hg in both urbanized parts of the city (i.e., the wastewater canal, agricultural areas) and “non-urbanized” areas such as wetlands and the Mekong River. We also measured Hg concentrations in a limited set of terrestrial (rice) and river (i.e., bottom feeder and carnivorous fish) key food stuffs collected in Vientiane in rice paddies and in the Mekong River, respectively, to evaluate potential health risks for the local population.

2. Sampling strategy, material and methods

2.1. Geographic settings

Lao People's Democratic Republic (Lao PDR) is one of the poorest and least developed countries in South-East Asia (Kaufmann, 2003) and with the largest access to the Mekong River. Of the total population (~6.2 million inhabitants in 2008, World Bank, 2010), 65% live along the Mekong and adjacent lowlands (Kaufmann, 2003). Agriculture remains the major sector of the economy providing more than 34% of the Gross Domestic Product (GDP) and employing over 80% of the labor force (NAFRI, 2008). Most agricultural land is used for cultivation of rice which is still the largest single crop (Schiller et al., 2006). The Mekong River is used for irrigation, fishing, a burgeoning aquaculture, deposition of waste (Udomchoke et al., 2010) and provides domestic water for the surrounding communities.

2.2. Sampling locations

Soils, sediments, surface waters and pore waters were sampled across the Vientiane city districts during the two field campaigns

conducted in March 2009 and December 2010 (Fig. 1). The Mekong River was sampled in the main stream from the shore and in shallow waters near river banks and beds during the dry season (March 2009 and December 2010) at two sites located upstream (Mek1 – 17°57'43.28"N 102°36'09.13"E) and downstream (Mek2 – 17°50'14.56"N 102°40'40.36"E) of Vientiane city. Sediments and pore waters were also sampled in shallow stagnant waters at sites Mek1 and Mek2. A non-urbanized wetland (WL – 17°49'49.10"N 102°40'26.46"E) was sampled for soils, surface and pore waters. This wetland is mainly a swamp covered by emergent, floating and creeping macrophytes in a former meander of the Mekong River (see complete description in SI.1). A pond, bordering the wetland, used for fishery, was also sampled for surface water. Finally, two rice paddies were sampled for soils, surface and pore waters; RP1 (17°54'13.96"N 102°39'23.70"E) located in South-East part of Vientiane city (see complete description in SI.2) and RP2 (18°0'10.63"N, 102°40'51.45"E) in the large That Luang wetland located in the North-East part of the city. The rice paddy (RP1) irrigation canal, which is connected to the Mekong River, was also sampled. It must be noted that RP1, RP2 and WL sites are all located in Neogene-alluvial quaternary deposits made of a mix of gravels, clays and sands, a formation which has been recognized as the main water bearing unit from geophysical measurements (Perttu et al., 2011).

To evaluate the impact of Vientiane city on Hg emissions, we sampled the Houay Mak Hiao (H.M.H.) main canal where most untreated wastewaters from the urban area are discharged (Fig. 1). This canal flows through the large That Luang wetland (17°56'N–102°39'E) where the local population fish and use the water for the irrigation of rice fields including RP2 (Whelan et al., 2007). Samples were collected from the same locations as those of the study of Whelan et al. (2007): Ban Sok bridge (BS – 18°00'15.47"N 102°40'49.42"E), Na Kuai bridge (NK – 17°58'12.01"N 102°42'20.37"E) and a third new bridge (BIII – 17°58'12.96"N 102°44'35.43"E).

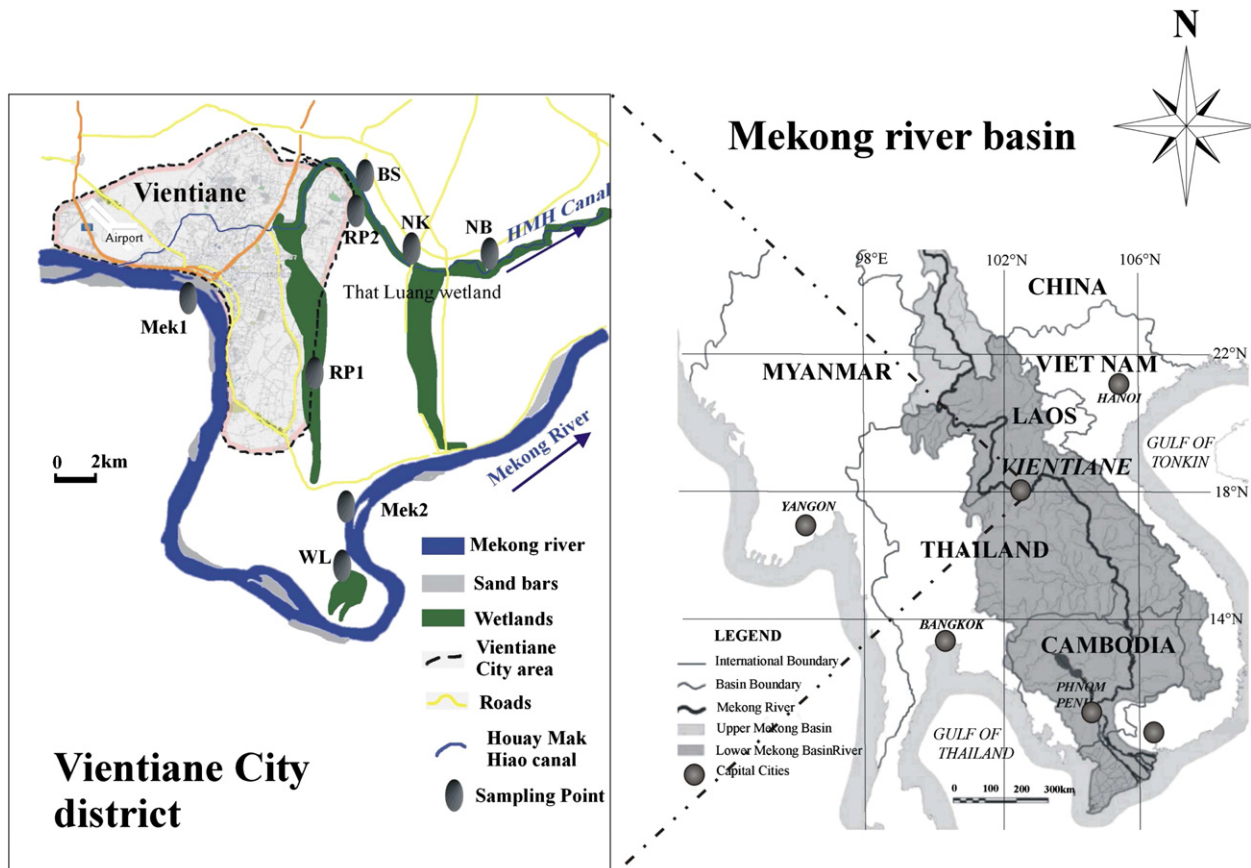


Fig. 1. Sampling location map: soil, sediment and water sampling sites in the Vientiane city area.

During the soil and water sampling in the rice paddies (RP1 and RP2), rice seed samples originating from these fields were also collected from the local farmer. 10 bottom feeder fish (Asian red tail catfish; *Hemibagrus wyckioides* benthopelagic) and 4 benthopelagic carnivorous fish (sharp-nosed catfish; *Pangasius conchophilus*) were sampled by the Mekong River Commission (MRC) during the two fishing campaigns on the 24th and 26th of June 2011 in the Mekong River at Vientiane. Data for other fish and invertebrates sampled and analyzed for mercury along the Mekong River during this 2011 MRC campaign are presented in SI.5.

2.3. Sample collection

Soil profiles were sampled every 10 or 20 cm, to a depth of 2 m, using an auger (SDEC, diameter 70 mm sampling approximately 100 g of soil). All soil samples were collected in sterile plastic bags. Surface sediments (0–10 cm) were sampled with a clean plastic shovel and stored in sterile plastic bags. All solid materials were homogenized and stored in a cooler at 4 °C from the sampling site to the lab.

Water sample collection and treatment for Hg speciation were performed using ultra-clean techniques (Cossa and Gobeil, 2000). All materials in contact with samples were acid-washed (5 days in 50% Normapur HNO₃ v/v, then 3 days in Normapur HCl 10% v/v) and rinsed with ultrapure MQ® (18.2 MΩ cm⁻¹) water before use. Surface water aliquots for total dissolved mercury ((THg)_D) and dissolved monomethylmercury ((MMHg)_D) analyses were filtered with Sterivex®-HV 0.45 μm sterile filters, collected in 250 ml FEP bottles and acidified with HCl (0.5% v/v, Millipore Seastar) (Parker and Bloom, 2005). Soil and sediment pore waters were sampled using MQ® rinsed microporous (0.45 μm membrane) polymer tube samplers (Rhizon® SMS, Rhizosphere Research Products) inserted vertically into the soil or sediment at 5 cm depth (Seeberg-Elverfeldt et al., 2005). Pore water suction was carried out with an acid washed 60 ml syringe set into depression, and pore waters were acidified directly after sampling with HCl 0.5% v/v (Millipore® Seastar). It should be noted that Rhizons preferentially recover water from the soil or sediment macropores (Guédron et al., 2012). Eh potentials were monitored in surface and pore waters several centimeters away from the sampling points. Surface and pore water aliquots for Dissolved Organic Carbon (DOC), total sulfide (ΣS^{II}), ferrous iron (Fe²⁺), anion and major cation analyses were filtered with Sterivex®-HV 0.45 μm sterile filters or with Rhizon samplers. Aliquots for DOC were collected in pyrolyzed (550 °C) Pyrex® amber colored glass bottles and acidified with HCl (1% v/v, Millipore Seastar). Aliquots for total dissolved sulfide (ΣS^{II}) and ferrous iron (Fe²⁺) were fixed directly after filtration with N,N-dimethyl-p-phenylenediamine (methylene blue method: Hach® method 8131 – USEPA standard method 4500) and 1,10-phenanthroline (Hach® method 8146), respectively. ΣS^{II} and Fe²⁺ analyses were performed directly after sampling (see Water analysis section below). Aliquots for anion were stored in full up to 1.5 ml PE cryotubes and aliquots for major cations in PE bottles were acidified with HNO₃, 2% v/v (Normapur).

Fish samples were collected in the Mekong at Vientiane city and were identified (common name and species name), and the length and weight were determined on site. Samples were then grouped by species and stored in a cooler until dissection. After dissection, muscle samples of a similar species were pooled in plastic bags, stored in dry ice and shipped for analysis in France. In the laboratory, pooled fish muscles were then freeze-dried and grounded to <100 μm.

2.4. Sample analysis

2.4.1. Soil, sediment and biota analysis

Once in the laboratory, soil and sediment sub-samples from each site were separated for analysis of water content (Heiri et al., 2001), grain size distribution, loss on ignition at 550 °C (LOI_{550 °C} – a proxy for organic content), and measurements of THg. The water content was obtained

by the difference in sample weight measured before and after freeze drying. Total organic matter content was estimated on freeze-dried samples through the Loss On Ignition (LOI) method after the pyrolysis of ~5 g of samples burnt at 550 °C for 2 h (Guédron et al., 2013; Heiri et al., 2001). The grain size distribution was measured on wet samples using a particle size analyzer Coulter® LS-100 (Beckman Coulter, Fullerton, CA, USA), following ultrasonic dispersal in de-ionized water (Loizeau et al., 1994). The proportions of three major size classes (clay <2 μm; silt 2 to 63 μm; and sand 63 to 2000 μm) were determined from the size distributions, as well as the median grain size.

Samples (soil, sediment and biota) for THg analysis were freeze-dried. Soil and sediment were sieved, and the <2 mm fraction was subsequently ground to <63 μm. Biota samples were entirely ground to <63 μm. Total Hg concentrations ([THg]) were determined by atomic absorption spectrophotometry after dry mineralization and gold amalgamation using an automatic mercury analyzer (Altec, Model AMA 254) with a relative precision of ± 10% (Guédron et al., 2009; Roos-Barraclough et al., 2002). Concentrations obtained for repeated analyses of certified reference materials (CRM, i.e.; CRM 7002: 0.086 ± 0.006 μg g⁻¹, N = 9 and MESS-3: 0.088 ± 0.005 μg g⁻¹, N = 9) were in the range of certified concentrations for standards CRM 7002 (0.090 ± 0.012 μg g⁻¹) and MESS-3 (0.091 ± 0.008 μg g⁻¹), respectively. The analytical quality was controlled by analyzing every sample twice. The measurement error was usually about 5% and always below 10%. The detection limit (3SD_{blck}) was 0.005 μg g⁻¹.

2.4.2. Water analysis

Samples were analyzed for total dissolved mercury [(THg)_D] and dissolved monomethylmercury [(MMHg)_D], by cold vapor atomic fluorescence spectrometry (CV-AFS) after conversion of all mercury species into Hg⁰ (Bloom and Fitzgerald, 1988) followed by detection using a Tekran® (Model 2500) mercury detector equipped with a high sensitivity mirrored quartz fluorescence cuvette (2009). The principles of the methods follow the Bloom and Fitzgerald (1988) gold amalgamation method for (THg)_D, and the Filippelli et al. (1992) hydruration method for (MMHg)_D modified by Cossa et al. (2009). QA/QC for (THg)_D was checked by repeating the analysis of the certified reference material (CRM) ORMS-3 – concentrations found (12.3 ± 0.2 pg g⁻¹, N = 3) agreed with the certified concentration (12.6 ± 1.1 pg g⁻¹). The analytical quality for (THg)_D measurements was assured by analyzing several samples twice with measurement error on replicates (N = 15) always lower than 15%. Blank replicate concentrations were 0.053 ± 0.006 ng l⁻¹ (N = 12) and the detection limit (defined as three times the blank standard deviation, 3SD_{blck}), was 0.02 ng l⁻¹. Quantification of (MMHg)_D was performed after checking for possible interference with internal spikes (Coquery et al., 2003) and the accuracy of analysis was checked using a certified reference material (CRM) ERM-AE670 (IRMM – European Commission). The measurement error on replicates was usually about 10% and was always lower than 15%. The blanks were always below 1 pg l⁻¹ (N = 12), the quantification limit (3SD_{blck}) was 0.004 ng l⁻¹ and the absolute detection was 1 fmol of MeHg. Dissolved trace elements (i.e., As and Mn) were measured by ICP-AES (Varian model 720ES – SI.3) with detection limits better than 10 μg l⁻¹ for all measured elements. Dissolved sulfate ([SO₄²⁻]) analysis was performed by ion chromatography (Metrohm Compact, model 761 – SI.3) with a detection limit (3SD_{blck}) of 5 μg l⁻¹. Dissolved ferrous iron ([Fe²⁺]) and sulfide ([ΣS^{II}]) concentrations were measured on site using a Hach® (model DR/850) spectrophotometer (methods 8146 and 8131 for [Fe²⁺] and [ΣS^{II}], respectively), with 20 and 5 μg l⁻¹ quantification limits, respectively. Dissolved organic carbon concentrations ([DOC]) were determined using a NonDispersive Infra-Red (NDIR) CO₂ Shimadzu® (Model VCSN) spectrometer. Eh, pH and conductivity were performed in situ using a WTW® 340i multi-parameter set calibrated on site with pH and redox buffer solutions.

2.5. Statistical analysis

Since most of the data were not normally distributed, we have listed in tables, as suggested by Webster (2001), the 6 following parameters: the mean, the standard error of the mean, the median, 25th percentile (25th perc.), 75th percentile (75th perc.) and the number of observations (N). We accordingly used nonparametric tests, such as the Mann–Whitney rank sum test (*U* test), or the Kruskal–Wallis one way analysis of variance on ranks (*H* test) in order to compare two, or more than two sets of data. Spearman's correlations were computed to compare multiple data set pairs. Correlation coefficients (CC) and *P* values (*P*) are reported. All statistical analyses were performed using Sigmastat®.

3. Results and discussion: low mercury concentrations in the ecosystem of Vientiane city area

3.1. Baseline inventory of mercury in soil and sediment

Total mercury concentrations ([THg]) measured in soil and sediment of Vientiane area (Fig. 2) were low, being in the range of concentrations found in the Mekong River delta sediments (22–90 ng g⁻¹, Cenci and Martin, 2004) or in other non-urbanized environments (e.g., 30–100 ng g⁻¹, Heyes et al., 2000; Roulet and Lucotte, 1995) and far below the probable effect concentration (PEC) for Hg (1060 ng·g⁻¹); the concentration above in which harmful effects are likely to be observed in sediment-dwelling organisms (MacDonald et al., 2000). The lowest [THg] were measured in the Mekong sandy sediments (range = 7.7 to 16.7 ng g⁻¹, see box plot (right panel) in Fig. 2) and the highest [THg] in silty and organic soils of rice paddy (50.4 to 101 ng g⁻¹, see soil profiles (left panel) in Fig. 2) and wetland (62.8 to 100.9 ng g⁻¹, see soil profiles in Fig. 2) sites, respectively. In the countryside, the distribution of soil [THg] with depth, for both rice paddy and wetland soils was related to the organic matter content (OM) and to the silty-clay distribution.

Although the wastewaters of Vientiane city were discharged directly into the Houay Mak Hiao (H.M.H.) urban canal, THg concentrations in sediments remained in the same range as those obtained in the Mekong

sediments showing minimal Hg release from this largely non-industrialized city. [THg] increased moderately along the stream from the Ban Sok bridge (BS, 16.1 ± 0.1 ng g⁻¹) to the Na Kuai bridge (NK, 42.5 ± 5.7 ng g⁻¹) and at the new bridge (NBIII, 43.0 ± 0.2 ng g⁻¹) probably due to fine soil particle inputs from the rice fields of the That Luang wetland surrounding the canal.

3.2. Baseline inventory of mercury and methylmercury in surface and pore water

In the filtered samples, total dissolved Hg concentrations ($[(\text{THg})_{\text{D}}]$) in both surface and pore waters of the non-urbanized areas (i.e., the Mekong River, mean = 1.3 ± 0.4 ng l⁻¹, the wetland, 3.4 ± 2.9 ng l⁻¹ and the rice paddies – 3.7 ± 1.8 ng l⁻¹, Fig. 3a–e) were in the same order of magnitude as those measured in the urbanized areas (H.M.H. urban canal – mean = 0.7 ± 0.3 ng l⁻¹, Fig. 3a–c). These concentrations are typical of pristine tropical environments (0.4 to 2.8 ng l⁻¹, Balogh et al., 2005; Coquery et al., 1995; Guédron et al., 2011; Lechler et al., 2000; O'Driscoll et al., 2009; Roulet et al., 1998a; Selvendiran et al., 2008) and far below the USEPA guideline (770 ng l⁻¹) recommended to protect against chronic effects to aquatic wildlife (USEPA, 2009). The proportion of dissolved methylmercury concentrations ($[(\text{MMHg})_{\text{D}}]$) within the THg was relatively higher ($[(\text{MMHg})_{\text{D}}] / [(\text{THg})_{\text{D}}] = 3$ to 13%) in waters of the Mekong River and wetland site (0.1 to 30%) than in the other studied sites (typically below 2% – which is commonly reported in the literature, Coquery et al., 1997; Fitzgerald and Lamborg, 2003). As for THg, higher $[(\text{MMHg})_{\text{D}}]$ were measured in both surface and pore waters of wetlands (0.08 ± 0.15 ng l⁻¹, Fig. 3f and g) and rice paddies (0.07 ± 0.10 ng l⁻¹, Fig. 3f and g) than in the Mekong (0.05 ± 0.03 ng l⁻¹, Fig. 3c) and the H.M.H. canal waters (Fig. 3c). Such $[(\text{MMHg})_{\text{D}}]$ were in the range of values reported for the Mekong Delta (Noh et al., 2012) and other pristine environments (Fitzgerald and Clarkson, 1991; Guédron et al., 2011; Meuleman et al., 1995; Watras et al., 1994).

Two different patterns in the distribution of dissolved Hg species were evident between stream waters (i.e., Mekong River and H.M.H. canal) and stagnant waters (i.e., wetland and rice paddies, Fig. 3). In the Mekong River, waters and superficial pore-waters were mainly oxid, pH was basic (pH = 7.5 to 8.5) and the main carrier for $(\text{THg})_{\text{D}}$

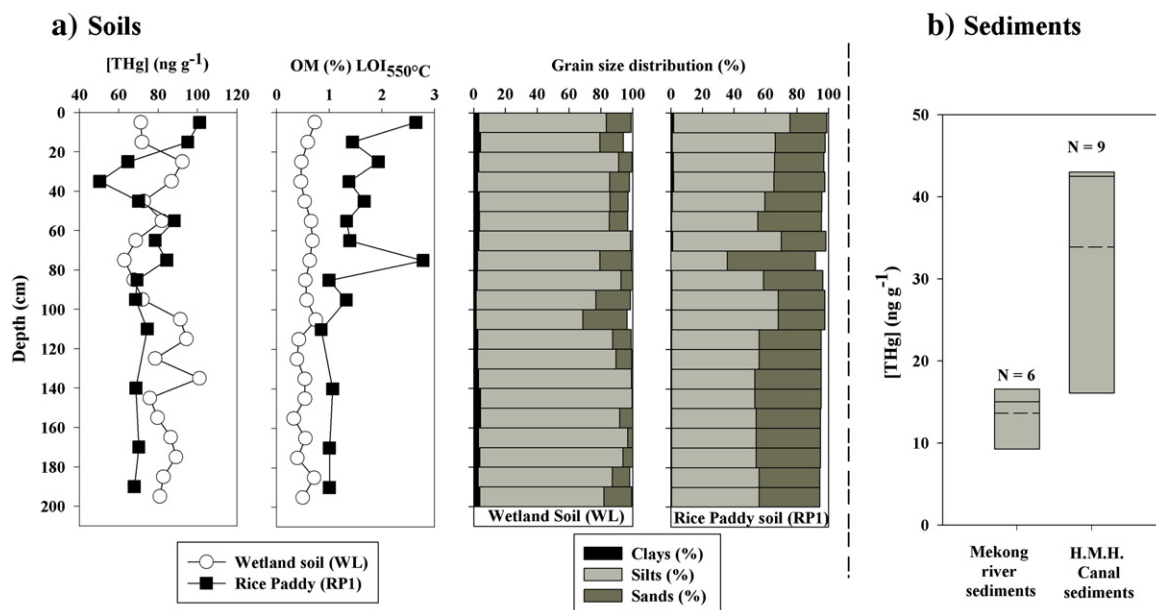


Fig. 2. (a) Total mercury content [THg] (ng g⁻¹), organic matter (OM) in % obtained from LOI₅₅₀°C, and grain size distribution in wetland (WL) and rice paddy (RP1) soils. (b) Box plot of total mercury content ([THg]) in sediments of the Mekong and the Houay Mak Hiao (H.M.H.) canal in the Vientiane district, showing the minimum, median (dotted line) and mean (full line), and maximum of each data set (N is the number of samples).

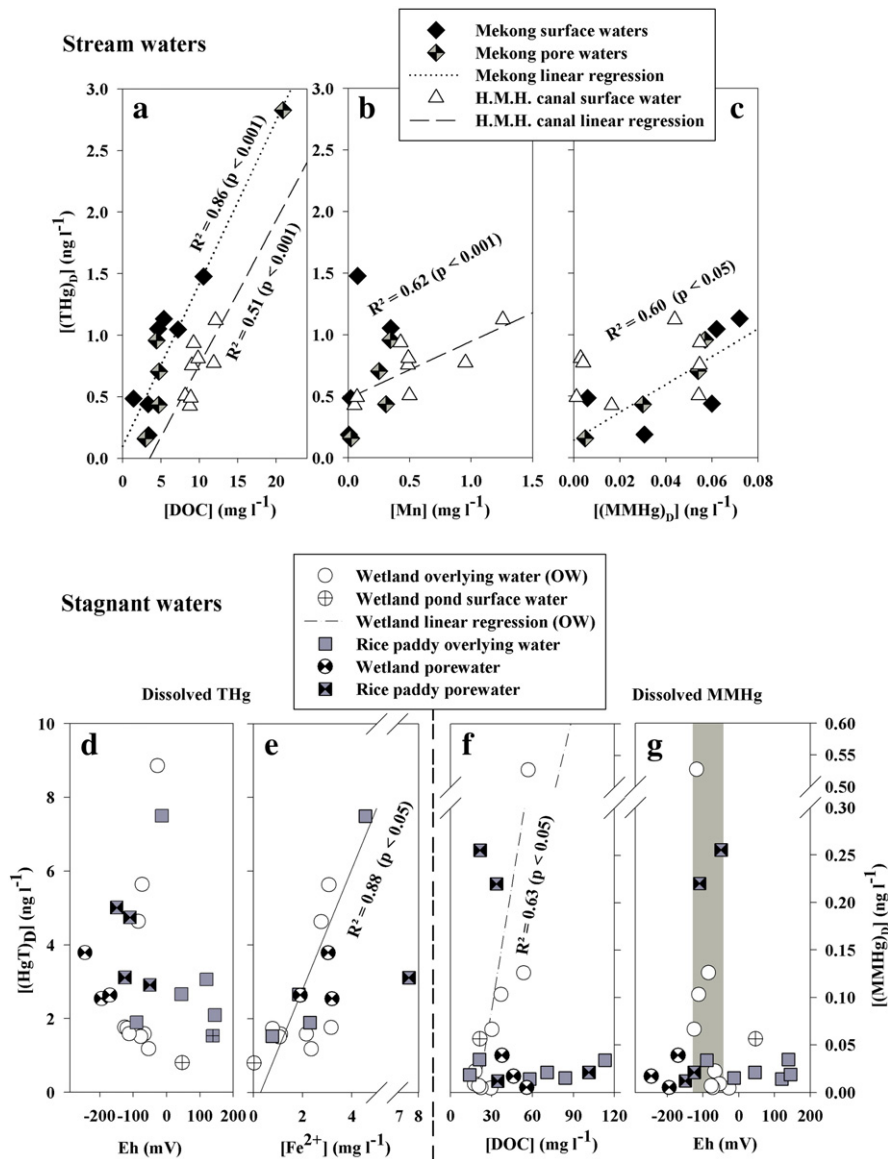


Fig. 3. Upper panels: stream waters (Mekong and Houay Mak Hiao (H.M.H.) canal): Total dissolved mercury (THg) versus (a) dissolved organic carbon (DOC), (b) manganese (Mn) and (c) monomethylmercury (MMHg) concentrations. Dotted line is the linear regression for surface and pore water samples of the Mekong River and long dash line is the linear regression for the H.M.H. water samples. Bottom panel: stagnant water (rice paddy and wetland sites). Left panels: Total dissolved mercury versus (d) Eh potential and (e) dissolved ferrous iron (Fe^{2+}) concentration. Solid line is the linear regression (THg vs Fe^{2+}) for the entire set of water samples. Right panels: Total dissolved methylmercury versus (f) DOC concentration and (g) Eh potential. Medium dash-dot line is the linear regression (MMHg vs DOC) for the Mekong River surface water samples.

and $(\text{MMHg})_D$ was DOC as shown by their good correlations (H test, $P < 0.05$, Fig. 3a). This observation corroborates those made by Selvendiran et al. (2008) in temperate wetland environments. In the wastewater H.M.H. urban canal originating from the Mekong, $(\text{THg})_D$ was correlated not only with DOC ($r^2 = 0.51$, $P < .001$) but also with Mn^{2+} ($r^2 = 0.62$, $P < 0.001$) suggesting that both DOC and filter passing Mn oxides are major carrier phases for $(\text{THg})_D$ (Quémerais et al., 1999; Rondeau et al., 2005) as is observed in large river systems (Maia et al., 2009; Quémerais et al., 1998). In this fluvial system, the predominance of large grain size fractions (i.e., quartz sands and silts), which have low adsorption capacity, leads to a relatively high dissolved THg concentration compared to THg in solid sediments. Indeed, log partition coefficients between pore water and sediments ($\log K_D = \log [(\text{THg})_D]_{\text{sediment}} - \log [(\text{THg})_D]_{\text{porewater}}$) ranged from 3.7 to 4.1, being 1 to 2 orders of magnitude lower than the published data for other continental freshwaters ($\log K_D = 5$ to 6, Coquery et al., 1995; Guédron et al., 2011; Muresan et al., 2007; Roulet et al., 1998b). In contrast, in the mainly anoxic and acidic surface and pore waters of the wetland

(pH = 5.5 to 5.8) and rice paddy (pH = 6.5 to 6.9) sites, $(\text{THg})_D$ was not associated with DOC. At both sites, $(\text{THg})_D$ was dramatically variable with the highest concentrations found with the highest $[\text{Fe}^{2+}]$, in the anoxic pore-water and sub-oxic overlying waters (Fig. 3 and SI.3). In parallel, the highest $[(\text{MMHg})_D]$ were measured in slightly reducing areas (i.e., -150 to -50 mV, Fig. 3) similar to Hg contaminated French Guyana flooded soils (Guédron et al., 2011). In the wetland site, a good correlation was found between $[(\text{MMHg})_D]$ and $[\text{DOC}]$ ($r^2 = 0.63$, $P < 0.05$, Fig. 3) in the suboxic surface waters suggesting that these waters are potential MMHg contributors to the main Mekong stream when waters are renewed during high flood periods. In addition, the high density of vegetation cover at this site (i.e., thick root mats and long bullrushes) was also favorable to the preservation of MMHg since it limited UV-B radiation to penetrate overlying waters and consistently attenuate potential abiotic (photochemical) demethylation. In contrast, the rice paddy sites were only weakly covered by vegetation when samples were collected (dry season, high solar incidence) being at the growing season, i.e., before rice plants reach their mature size. Finally, in both wetland and rice

paddy sites, $\log K_D$ values were slightly higher (4.5 ± 0.3 and 4.4 ± 0.2 , respectively) than in the Mekong River probably due to the higher clay and OM (Guédron et al., 2012) content in soil or sediments originating from soil erosion.

3.3. Mercury concentration in key foodstuffs and risk assessment for populations

Total mercury concentrations in rice (*Oryza sativa* L.) grains from RP sites (5.6 to 7.1 ng g^{-1}) were below the maximum permissible limit of total mercury in food crops (20 ng g^{-1}), as recommended by the Chinese National Standard Agency (Krisnayanti et al., 2012). In parallel, [THg] in analyzed sampled bottom feeder fishes (22.7 ± 0.3 ng g^{-1} , ww) and benthopelagic carnivorous fishes (79.2 ± 2.2 ng g^{-1} , ww) were low and over 4 to 13 fold lower than WHO guidelines (300 ng g^{-1} , ww), reflecting the low level of Hg in the Mekong River (SI.4). This range of [THg] was similar to those measured in fish sampled at various locations along the Mekong River during this MRC fishing campaign but slightly lower than those measured in sampling sites of the Mekong River located downstream the confluence with rivers flowing through known gold production areas (SI.5 and SI.6). These data were also in the range of previously reported concentrations in fish from Cambodia (Agusa et al., 2005; Murphy et al., 2008), and from rivers and reservoirs in locations bordering China (Feng and Qiu, 2008; Liu et al., 2012) but they were significantly lower than reported concentrations for Amazonian environments (40 to 3770 ng g^{-1} , ww, Barbosa et al., 2003; Benefice et al., 2010; Durrieu et al., 2005; Malm et al., 1995; Roulet et al., 1999). Unfortunately, Hg concentrations within the two fish species could not be compared with any of the fish characteristics (e.g. length and mass, SI.4) since fish samples were pooled per species after dissection and Hg concentration could not be measured on individual fish samples. Although the number of data is limited, we can assess the potential risk of Hg exposure for population using the Joint FAO/WHO Expert Committee on Food Additives (JECFA) hazard characterization of mercury expressed as the Provisional Tolerable Weekly Intake (PTWI = 1.6 μg of MMHg per kg body weight) (UNEP/WHO, 2008; WHO, 2004). Assuming that about 90% of THg in fish muscle is typically found in the form of MMHg, and that almost 25% of THg in rice is present as MMHg (Horvat et al., 2003; Krisnayanti et al., 2012), THg measurements can therefore be used to approximate MMHg concentrations in keyfood stuff (Bloom, 1992; Francesconi and Lenanton, 1992; Grieb et al., 1990; Hammerschmidt et al., 1999). Therefore, considering the reported average weekly fish consumption of 550 g in Lao PDR (Hortle, 2007) with a weekly rice consumption of 2.8 kg (Chen et al., 2002), we can assess the MMHg intake per kilogram body weight per week ($\mu\text{g Hg/kg-bw/week}$) which is equal to the amount of fish and rice ingested per week (g/week) multiplied by the MMHg concentrations in the fish ingested (mean = 0.051 $\mu\text{g g}^{-1}$) and rice (mean = 0.006 $\mu\text{g g}^{-1}$) divided per kilogram body weight (kg-bw). Therefore, considering a mean body weight of 60 kg, the weekly intake of MMHg would be 0.54 to 0.71 $\mu\text{g kg-bw}^{-1}$ for the population living in Vientiane area. We can finally conclude that, based on our calculations, the risk of health impact is very limited despite the high fish and rice consumption in these regions. This is consistent with the studies of UNIDO (2003) in the Luang Prabang district and other more recent studies in Cambodia (Agusa et al., 2005, 2007).

4. Conclusion

Regarding Hg contamination, the ecosystem of Vientiane city district is in a pristine state according to low concentrations of THg (and MMHg) measured in water, soil and sediment of both non-urbanized and urbanized areas of the city and to its non-industrialized status. Although this set of data is not exhaustive, it presents the first baseline inventory of Hg and MMHg in Lao PDR which could be used as a baseline

reference in the region for future work with regard to the extremely rapid development of this region. The measurements of THg in keyfood stuffs (i.e., rice and fish) confirmed this low level of contamination. Therefore, although Lower Mekong Basin inhabitants consume large amount of fish and rice, the current low Hg contamination in this region means that there are mostly only minimal environmental Hg-attributable health risks – this contrasts with industrialized contaminated sites where people consume less fish but with much higher MMHg contents (Cizdziel et al., 2002; Dorea and Barbosa, 2007; Garcia-Bravo et al., 2009; Ullrich et al., 2007).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.gexplo.2014.03.020>.

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