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Mercury contamination level and speciation inventory in Lakes Titicaca & Uru-Uru (Bolivia): Current status and future trends☆

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ABSTRACT

Aquatic ecosystems of the Bolivian Altiplano (~3800 m a.s.l.) are characterized by extreme hydro-climatic constrains (e.g., high UV-radiations and low oxygen) and are under the pressure of increasing anthropogenic activities, unregulated mining, agricultural and urban development. We report here a complete inventory of mercury (Hg) levels and speciation in the water column, atmosphere, sediment and key sentinel organisms (i.e., plankton, fish and birds) of two endorheic Lakes of the same watershed differing with respect to their size, eutrophication and contamination levels. Total Hg (THg) and monomethylmercury (MMHg) concentrations in filtered water and sediment of Lake Titicaca are in the lowest range of reported levels in other large lakes worldwide. Downstream, Hg levels are 3–10 times higher in the shallow eutrophic Lake Uru-Uru than in Lake Titicaca due to high Hg inputs from the surrounding mining region. High percentages of MMHg were found in the filtered and unfiltered water rising up from <1 to ~50% THg from the oligo/hetero-trophic Lake Titicaca to the eutrophic Lake Uru-Uru. Such high % MMHg is explained by a high *in situ* MMHg production in relation to the sulfate rich substrate, the low oxygen levels of the water column, and the stabilization of MMHg due to abundant ligands present in these alkaline waters. Differences in MMHg concentrations in water and sediments compartments between Lake Titicaca and Uru-Uru were found to mirror the offset in MMHg levels that also exist in their respective food webs. This suggests that *in situ* MMHg baseline production is likely the main factor

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controlling MMHg levels in fish species consumed by the local population. Finally, the increase of anthropogenic pressure in Lake Titicaca may probably enhance eutrophication processes which favor MMHg production and thus accumulation in water and biota.

1. Introduction

The Bolivian Altiplano is one of the largest high plateaus in the world containing two large lakes, Lake Titicaca in the north part and Lakes Uru-Uru/Poopó in the central part of an endorheic system consisting in the Titicaca-Desaguadero-Poopó-Coipasa Salt Lake (Revollo, 2001; Delclaux et al., 2007). Lake Titicaca is the most important water resource of the Andean Altiplano, a major source of fish for ~3 million people and the largest navigable water body in the world lying at an altitude of 3809 m above sea level (a.s.l.). Its ecological functioning and limnology have been widely investigated between 1980 and 2000 (Collot et al., 1983; Pourchet et al., 1994; Mourguiart et al., 1998; Dejoux, 1992). Nowadays, the ecological equilibrium of the region is disturbed by a recent but very intensive urban demography and the intensification of mining activities, fisheries and agriculture around the Lake. For example, Puno Bay, on the Peruvian side of Lake Titicaca, has been identified as a contaminated area by urban and industrial effluents since the 1980's (NorthCote et al., 1989). The most preoccupying issue on the Bolivian side of the Lake (Lago Menor – southern basin of the lake) is the extremely rapid development of El Alto city, which population increased from 95,000 inhabitants in 1976 to around 1.2 million according to the last census (Mazurek, 2012) with minimal land planning. Wastewater from El Alto city, its facilities, manufactures and small scale industries, are discharged in the Katari river, which flows to the Lago Menor with less than 50% of water treated (Chudnoff, 2009). Among the emitted pollutants (e.g., nutrients, traces metals and organic contaminants) (Duwig et al., 2014; Archundia et al., 2017), mercury (Hg) contamination is one of the preoccupying issues in this fragile ecosystem. So far, only three studies focused on Hg contamination in the coastal areas of the great Lake Titicaca (Gammons et al., 2006; Molina and Point, 2014; Monroy et al., 2014) revealing high Hg concentrations in all fish species collected in the northern part of the Lago Mayor, particularly at the Mouth of the Ramis River (up to 1840 ng g^{-1} THg, dw in Orestias agassii) where intense gold mining activities are documented. Hg levels in fish muscle from other coastal areas of the Lago Mayor where found below regulatory health guidelines. No data exists yet in Lago Menor which is considered as the most productive area and is also impacted by anthropogenic inputs.

Downstream Lake Titicaca, Lake Uru-Uru, a man-made reservoir, combines diverse metal and organic pollutions since it receives important discharges from urban and mining activities. Recently, several studies evaluating Hg contamination in Lake Uru-Uru have highlighted high concentrations and percentages of toxic MMHg in the water column and biota (Molina, 2015; Alanoca et al., 2016a, 2016b; Lanza et al., 2016).

In this paper, we report for the first time, a complete inventory of Hg levels and speciation, including inorganic Hg(II), elemental Hg (Hg^0) and mono-methylmercury (MMHg), from samples collected between 2010 and 2016 in the different compartments of Lake Titicaca and Uru-Uru. Hg was measured in the atmosphere (total gaseous Hg - TGM), atmospheric fallouts (i.e., filtered and particulate Hg), water column (i.e., filtered, particulate and dissolved gaseous Hg), sediment (i.e., porewater and solid particles) and biota (i.e., plankton, fish and birds). Concentrations of Hg species are compared with previous studies performed in large or elevated lakes. Biogeochemical and anthropogenic factors influencing the sources, distribution and speciation of Hg in the different limnological compartments and selected sentinel organisms are discussed. Based on these discussions and the observed spatial gradients in the ecosystem, we finally propose scenarii of possible future trends in Hg species levels and their impacts on this ecosystem.

2. Material and methods

2.1. General settings

2.1.1. Lake Titicaca

Lake Titicaca (Fig. 1a) comprises of two nearly separate basins: the great lake named “Lago Mayor” or “Lago Chucuito” (7131 km^2; mean depth = 100 m; max depth = 285 m) and the smaller lake named “Lago Menor” or “Lago Huiñaimarca” (1428 km^2; mean depth = 9 m; max depth Chua trough = 40 m) (Dejoux, 1992). The two basins are connected by the Strait of Tiquina and a single outlet for the lake, the Río Desaguadero, which drains out the southern end of Lago Menor to the central Altiplano (i.e., to Lakes Uru-Uru and Poopó) (Cross et al., 2000; Dejoux, 1992). Because of its geographical location and high altitude (3809 m a.s.l.), Lake Titicaca is subject to the tropical zone climate (rainy season concentrated between December and March) and its hydrological regime is dominated by evaporation (~95%) while rivers outflow represents ~ 5%. The resulting Lake water is alkaline with a salinity close to 1 g L^{-1} (Dejoux, 1992). Sediments of Lake Titicaca are covered with Totoras (*Schoenoplectus Californicus*) in the inner margin (0–2 m depth) and by macrophytes (mostly *Characeae* spp.) in the photic zones (i.e.,~15 m depth) with maximum development between 4.5 and 7.5 m. Macrophytes constitute more than 60% of the total biomass in Lago Menor (Dejoux, 1992) and colonize a third of its bottom (~436 km^2) between 2 and 15 m in depth (Collot et al., 1983). Major sources of anthropogenic Hg, the gold mining centers, are identified at the mouth of the Ramis and Suchez rivers (Fig. 1a). Two other urban wastewater sources to the lake are located in the Puno Bay (Lago Mayor) and Cohana Bay (Lago Menor) originating from Puno and El Alto cities, respectively (Fig. 1a).

2.1.2. Lake Uru Uru

Lake Uru Uru is located in the central part of the Bolivian Altiplano region (Fig. 1b), south to Oruro city where numerous mining (e.g., Au, Ag and Sn) and smelting activities are concentrated. This shallow aquatic ecosystem is a man-made reservoir supplied mainly by the Rio Desaguadero waters. The Lake surface and depth vary between 120 and 350 km^2 and 0.25–1 m, respectively, as function of the seasons. Fishing activities are practiced year round and are an important protein and financial resource for local communities. A strong contrast exists between the Northern and Southern parts of the lake, with higher density of sedge (*Schoenoplectus totora*), grass (*Ruppia* spp.) and algae (Characeae) in the southern part (Tapia and Audry, 2013). Previous investigation (Alanoca et al., 2016a) studying 24 h biogeochemical cycles demonstrated that diurnal variability (e.g., temperature, oxygen) in

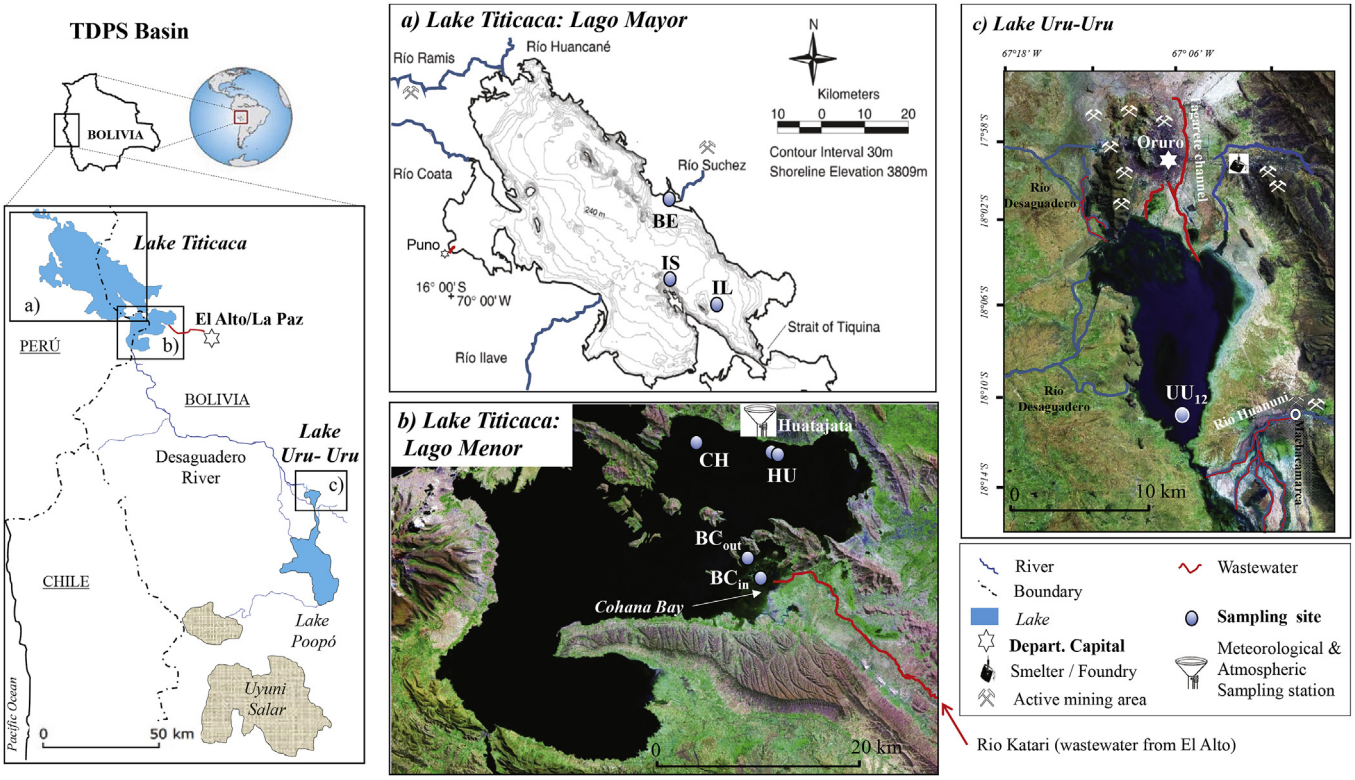

Fig. 1. Map of the Bolivian Altiplano Titicaca-Desaguadero-Poopó-Coipasa Salt Lake (TDPS basin) hydrosystem with (a) Lake Titicaca (Lago Mayor) (b) Lake Titicaca (Lago Menor) and (c) Lake Uru-Uru. Sampling sites (site codes) are for (a) Lake Titicaca, BE: Escoma Bay; IL: Isla de la Luna; IS: Isla del Sol; CH: Chua; HU: Huatajata, BC_{in}: Cohana Bay (inside the bay) and BC_{out}: Cohana Bay (outside the bay) and (b) Lake Uru-Uru: UU_{12}: Uru-Uru.

Lake Uru-Uru can overwhelm seasonal variations with higher daily gradients found during the dry season. Furthermore, the synergistic effect of mining (i.e., acid mine drainage (AMD)) and urban effluents to this shallow lake was proved to enhance Hg methylation with the sediment being the main source of MMHg during the dry season (Alanoca et al., 2016b).

2.2. Sampling location, strategy and elemental analysis

Details on the sampling, site location and analytical protocols are given in the supplementary information 1 (S.I.1 and 2) and in Alanoca et al. (2016a). Briefly, surface water samples were collected during 7 main campaigns performed between 2010 and 2016. Water sampling was performed with a Teflon-coated Go-Flo trace metals sampler and stored unfiltered (UNF) or filtered (F) (0.22 μm PVDF) immediately after sampling. All water samples were stored in acid-washed FEP Teflon containers and acidified with HCl (0.5%, v/v, Ultrex grade - Baker). Dissolved gaseous mercury (DGM) was collected *in situ* from unfiltered water samples, purged within ~0.5 h after sampling and collected on a gold–coated sand traps. Total gaseous mercury (TGM) and atmospheric fallouts were collected on the shore of Lago Menor at Huatajata, nearby the meteorological station (Fig. 1a and S.I.2). Surface sediments were recovered using a gravity corer. Cores were immediately extruded and sediment was collected in centrifuge vials, N_2-flushed and centrifuged at 4000 r.p.m. for 20 min. For each sediment sample, the supernatant (i.e. porewater) was filtered (0.45 μm, PVDF) into 20 ml Teflon vials and acidified with HCl Ultrex. Biological samples representative of the aquatic food webs were collected in Lago Menor (Titicaca) and lake Uru-Uru mostly during the late dry season period (Oct–Nov). Zooplankton samples were collected using nets (Molina et al., 2010) and fish samples were collected by local fisherman using gillnets. Blood samples from two water bird species were collected using reference sampling protocols available elsewhere (Molina and Point, 2014). Mercury concentrations in food web samples are expressed on a dry weight basis.

Dissolved gaseous Hg (DGM), Filtered (F) and UNFiltered (UNF) total mercury concentrations (THg) in surface and pore waters were determined by cold vapor atomic fluorescence spectrometry (CV-AFS) after conversion of all mercury species into Hg^0 followed by detection using a Tekran® (Model 2500) (Bloom and Fitzgerald, 1988; Cossa et al., 2009; Guédron et al., 2015). DGM was analyzed by thermodesorption (600 °C) and CV-AFS.

THg concentrations in sediment and biota were determined by atomic absorption spectrophotometry after dry mineralization and gold amalgamation (Altec, Model AMA 254 and Millestone, DMA80).

Filtered monomethylmercury ($MMHg_F$) concentrations were analyzed using an ethylation purge and trap-gas chromatograph-AFS analyzer (MERX System, Brooks Rand®) and a propylation ID-GC–ICPMS (Monperrus et al., 2008; Bouchet et al., 2013; Guédron et al., 2014; Sharif et al., 2014). For solids, MMHg was extracted from ~100 mg of solid samples with 5 mL HNO_3 (6 N) at 60 °C for 2 h. Digestion aliquots were then analyzed in duplicates and quantified using the standard addition technique.

Dissolved organic carbon concentrations (DOC) were determined using a Non Dispersive Infra-Red (NDIR) CO_2 Shimadzu® (Model VCSN) spectrometer after humid oxidation in a sodium persulfate solution at 100 °C.

2.3. Statistical analyses

Statistical analyses were performed using JMP® software (SAS Institute, USA). One-way ANOVA were performed when comparing

two datasets. Homogeneity of variances were tested using the Brown-Forsythe test. In the case of unequal variances, a Welch ANOVA test was used.

3. Results and discussions

3.1. Mercury speciation in air and atmospheric fallouts of Lake Titicaca

Total gaseous mercury (TGM) concentrations in air on the shore of Lake Menor were not significantly ($p > 0.05$) different between the end of the wet (1.11 ± 0.23, N = 1407) and of the dry season (0.82 ± 0.20 ng m^{-3}, N = 1037). Measured TGM concentrations were in the lowest range of the background concentrations (Table 1) reported for the northern (1.5–2.5 ng m^{-3}) and for the southern hemispheres (mean GEM: 0.84–1.09 ng m^{-3}) (Meuleman et al., 1995; Lin and Pehkonen, 1999; Vette et al., 2002; Campbell et al., 2003a; Cohen et al., 2004; Ryaboshapko et al., 2007; Baya and Van Heyst, 2010; Sprovieri et al., 2016). Such low TGM values suggest little influence of regional urban or industrial activities (e.g., La Paz/El Alto cities) atmospheric emissions. Except for the cement factory in the city of Viacha, there is no combustion process nor industrial process using Hg reported in the region.

THg measured in rain and fallouts sampled at lake Menor (Table 1) were in the same range of reported concentrations for Lake Victoria (Campbell et al., 2003a) and for the great lake region (Hall et al., 2005; Risch et al., 2012). THg concentrations in unfiltered fallouts samples (THg_{UNF}) were twice those in filtered samples (<0.45 μm), suggesting that particulate matter (>0.45 μm) contributes to almost 50% of Hg deposition in fallouts. Filtered MMHg concentrations (0.11 ± 0.06 ng L^{-1}) represented 5.0 ± 3.8% of filtered THg levels in fallouts and were within reported range for concentrations and %MMHg in precipitations collected in the great lake region and elsewhere (Bloom and Watras, 1989; Hall et al., 2005; Graydon et al., 2008). Although the sources of the MMHg measured in fallouts are difficult to diagnose, the presence of MMHg in rain water is likely the result of a combination of the mechanisms occurring in the atmosphere at a regional scale (i.e. atmospheric Hg methylation (Gardfeldt et al., 2003; Malinovsky and Vanhaecke, 2011; Yin et al., 2012) and in a minor extent the photochemical transformations of liberated dimethylmercury (DMHg) to the atmosphere to MMHg (Bloom and Watras, 1989; Prestbo and Bloom, 1995) with the Amazonian side as the major source since most of the rain originates from this region (Roche et al., 1992).

3.2. Hg spatial distribution, speciation and partitioning in surface sediments

THg concentrations in surface sediments of Lake Titicaca were variable between sites (Table 2) with lowest concentrations found in shallow (water column depth between 2 and 15 m - HU: average ± SD: 19 ± 4 ng g^{-1}) and very shallow (water column depth < 2 m – BCin: 38 ± 13 ng g^{-1}) coastal areas of the Lago Menor and highest concentrations in the deep sites of the lake (IS and CH: 77 ± 34 ng g^{-1}). These values are in the higher range of reported THg concentrations for high altitude Tibetan lake but in the lower range for other great lakes worldwide (Table 2). MMHg concentrations in sediments also varied between sites and never exceeded 4% of THg. The highest concentrations and percentages were found in coastal contaminated sites (BCin: 0.98 ± 0.50 ng g^{-1} and 2.2± 1.1%, BE: 1.1 ± 0.3 ng g^{-1} and 1.6 ± 0.2%) and shallow sites (HU: 0.66 ± 0.08 ng g^{-1} and 3.5 ± 0.5%) followed by deep sites (CH: 0.51 ± 0.01 ng g^{-1} and 0.5 ± 0.1%) while the lowest were found in very shallow pristine areas (BCout: 0.07 ng g^{-1} and 0.3%). THg concentrations in sediment of Lake Uru-Uru were 5–10 time higher than in Lake Titicaca illustrating the great impact of mining and urban effluent inputs to this shallow lake. MMHg in sediment of Lake Uru-Uru covered a large range of concentrations (1.09 ± 1.93 ng g^{-1}) but exhibit relatively low percentage MMHg (i.e., 0.7 ± 1.1%) which are in the same range as for coastal contaminated sites of Lake Titicaca.

MMHg distribution in sediment porewater ($MMHg_{PW}$) showed different distribution than for sediment matrix with highest concentrations measured in shallow and very shallow sites (5.8 ± 5.6 ng L^{-1}) rising up to 12.2 ng L^{-1} at HU site (sediment covered by *Characeae* and biofilms) and lowest in the deep sites (CH: 0.84 ± 0.23 ng L^{-1}). Interestingly, elevated % MMHg was encountered at almost all sites reaching 47 ± 26% in very shallow, 39 ± 27% in shallow sites and 23 ± 15% in deeper sites. Highest $MMHg_{PW}$ concentrations were encountered particularly in the shallow carbonate sediments (e.g., HU) where high sulfate contents in both sediment and water (~250 mg L^{-1} - (Iltis et al., 1992)) are likely the major drivers for Hg methylation by sulfate reducing bacteria (SRB), the most probable Hg methylators in such environments (King et al., 1999; Achá et al., 2010; Parks et al., 2013).

An opposite trend is observed for Hg distribution between sediment porewater and solid phase and we suggest it is related both to the nature of sediment matrix (e.g., OM vs carbonate) and to different sedimentation rates amongst sites. Firstly, sediment enriched in OM (i.e., deep and very shallow sites - Rodrigo and

Table 1
Comparison of filtered and unfiltered total mercury (THg), filtered monomethylmercury (MMHg) in atmospheric depositions and total gaseous mercury (TGM) concentrations, measured at Huatajata station, in Lake Titicaca with literature data for world's great lakes. Superscripts (a & b) refer to bibliographic reference (right column) from which data originate.

Area	Altitude (m a.s.l)	Sampling period	TGM (ng m^{-3})	THg_F (ng L^{-1})	THg_{UNF} (ng L^{-1})	$MMHg_F$ (ng L^{-1})	Reference
Titicaca (Lago Menor)	3809	2013–2016	0.74–2.67 (N = 1407)[a] (mean = 1.11 ± 0.23)[a] 0.51–1.35 (N = 1037)[b] (mean = 0.82 ± 0.20)[b]	1.38–7.14 (N = 14) (2.96 ± 1.75)	2.60–13.7 (N = 10) (mean = 5.9 ± 3.07)	0.03–0.21 (N = 12) (mean = 0.11 ± 0.06)	This study ([a] late wet season and [b] late dry season)
Lake Victoria	1133	1994/95[a] & 1999[b]	1.05–1.52[a]		1.8 1–3.0[b]		Campbell et al. (2003a, 2003b)[a]
Lake Baïkal	456	1992–1993[a]	0.73–6.1	2–21		0.1–0.25	Meuleman et al. (1995)[a]
Great Lakes region	~180	1998–2003		1–130		0.01–0.85	Hall et al. (2005)
Lake Michigan	176	1993[a], 1994-1995[a,b]	1.5–3.6[b]	5.08 ± 1.55[a]	21.6 ± 13.9[a]	0.10 ± 0.10 [a]	Lamborg et al. (2002)[a], Vette et al. (2002)[b]

Table 2
Comparison of total mercury (THg) and monomethylmercury (MMHg) concentrations in sediment and filtered porewater Lake Titicaca and Uru-Uru with literature data for world's great lakes. Superscripts (a & b) refer to bibliographic reference (right column) from which data originate.

Area	Altitude (m a.s.l)	Period	THg_{sed} (ng g^{-1})	THg_{PW} (ng L^{-1})	$MMHg_{sed}$ (ng g^{-1}) (% MMHg)	$MMHg_{PW}$ (ng L^{-1}) (% MMHg)	Reference
Titicaca – Lago Mayor	3809	2013–2015	45–79	N.A.	0.93–1.36 (1.6 ± 0.2%)	N.A.	This study
Titicaca – Lago Menor	3809	2013–2015	16–114	2.9–17.6	0.51–1.33 (1.8 ± 1.5%)	0.67–12.2 (37 ± 22%)	This study
Lake Uru-Uru	3686	2010–2011	79–404	2.4–239.1	0.17–7.9 (0.7 ± 1.1%)	0.04–35.8 (30 ± 44%)	This study
Tibetan Lakes	2813–4652	2006–2007	8–67[a,b]				Wang et al. (2010)[a]; Yang (2010)[b]
Lake Victoria	1133	1990–1995[a,b]	74–450 [a,b]	5–85.5	0.18–0.24	0.21–2.54 [b]	Ramlal et al. (2003)[a]; Campbell et al. (2003a, 2003b)[b]
Lake Superior	180	1988[a] & 2000[b]	4–380 [a,b]	DL - 780 [a]	2.15–6.45 [b]		Matty and Long (1995)[a]; Rolfhus et al. (2003)[b]
Lake Michigan	176	1988[a] & 1994–1995[b]	2–450 [a,b]	DL - 220 [a]	0.01–0.45 [b]		Matty and Long (1995)[a]; Mason and Sullivan (1997)[b]

Wirrmann, 1992) show the highest sorption capacity for Hg and MMHg as illustrated by high partition coefficients (i.e., $logK_D = log[Hg]_{sed} - log[Hg]_{PW}$) found at CH ($logK_{D\ THg} = 4.42 \pm 0.23$, $logK_{D\ MMHg} = 2.79 \pm 0.12$) and BCin ($logK_{D\ THg} = 3.78 \pm 0.24$, $logK_{D\ MMHg} = 2.45 \pm 0.22$). The lower Hg content in very shallow sediment results from the high sedimentation rates (0.22–1 cm yr^{-1} - (Binford et al., 1992; Pourchet et al., 1994) due to large local OM production and catchment inputs trapped in the dense totoras cover which contributes to almost 95% of the sedimentation (Pourchet et al., 1994). In deep areas, higher Hg concentrations results from a 10 to 50 times lower sedimentation rate (0.05–0.1 cm yr^{-1} - unpublished data) of OM originating from decomposition of plankton which are known to scavenge Hg from the water column (Mason and Jenkins, 1995). Secondly, carbonate rich (~60% $CaCO_3$ - (Rodrigo and Wirrmann, 1992)) sediment in shallow areas exhibit the lowest Hg concentrations and $logK_D$ at HU and BCout (mean ± SD = 2.81 ± 0.65 and 2.43 ± 0.65 for THg and MMHg, respectively) due to the weak affinity of Hg for carbonate matrix (Guédron et al., 2013) and high sedimentation rates resulting from large *Characeae* spp. production (Binford et al., 1992; Pourchet et al., 1994). Finally, the Hg contaminated and OM rich sediments of Lake Uru-Uru (Alanoca et al., 2016b) illustrate similar characteristics as for OM rich sediments of Lake Titicaca with a high Hg storage capacity as illustrated by higher $logK_D$ (mean = 4.45 ± 0.84 and 2.86 ± 1.59 for THg and MMHg, respectively).

3.3. Mercury speciation in surface water of Lakes Titicaca and Uru-Uru

Dissolved gaseous Hg (DGM) was low at most locations in both investigated lakes and never exceeded 1%THg_F. Such DGM levels were similar to those found in other great lakes of lower altitude (Table 3) demonstrating that both Titicaca and Uru-Uru lakes have limited gaseous Hg production in agreement with the low TGM levels measured in the air (Table 1). Although these levels were low, highest concentrations were observed in open waters of Lago Mayor and Menor suggesting higher Hg photo-reduction to elemental Hg in open water where DOC content is low (Fig. 2).

Filtered and unfiltered THg levels (THg_F and THg_{NF}) in surface water (Fig. 2) were low in the entire Lake Titicaca and fell in the lowest range of reported concentrations for other great lakes worldwide (Table 3) (Mudroch et al., 1988; Meuleman et al., 1995; Mason and Sullivan, 1997; Campbell et al., 2003a, 2003b; Ramlal et al., 2003; Rolfhus et al., 2003) illustrating the general pristine state of Lake Titicaca. However, an increasing trend in concentrations was observed with lowest THg_F and THg_{UNF} concentrations measured in the oligotrophic Lago Mayor (IL) and highest concentrations in the heterotrophic Lago Menor (Fig. 2). The average particulate THg (THg_{UNF} - THg_F) in surface water represented 39± 16%, 46± 23% and 50± 20% of THg_{UNF} measured in Lago Menor, Lago Mayor and lake Uru-Uru, respectively (S.I.3), showing that almost half of THg is present as truly dissolved or colloidal Hg. THg and MMHg concentrations in filtered and unfiltered water also vary with depth along the water column due to the variable abundance and distribution of plankton (S.I. 4) that act as carrier phase for Hg. Mean $MMHg_F$ concentrations in Lago Mayor (0.008 ± 0.006 ng L^{-1}; 0.8 ± 0.4 %THg) and Lago Menor (0.035 ± 0.044 ng L^{-1}; 13 ± 26 %THg) were within the range of reported values for Baikal (Meuleman et al., 1995) and Laurentian (Mason and Sullivan, 1997; Rolfhus et al., 2003) Lakes. Highest $MMHg_F$ concentrations were found in shallow coastal areas such as Cohana Bay where $MMHg_F$ represented 26± 30% of THg_F. Despite lower $MMHg_F$ concentrations in Lake Titicaca water, their relative abundance in the THg fraction is much more elevated compared to other great lakes where %MMHg rarely exceed 1% (Table 3). Downstream, THg_F, THg_{UNF}, $MMHg_F$ and $MMHg_{UNF}$ in surface waters of the shallow eutrophic Lake Uru-Uru were 3–10 times higher than those measured in Lake Titicaca (Fig. 2). Particularly high % MMHg (44± 53% of THg) in Lake Uru-Uru highlights high production and accumulation of MMHg in this urban and mine impacted ecosystem (Tapia and Audry, 2013; Alanoca et al., 2016a).

When data from both lakes are gathered, positive correlations ($p < 0.01$) are found between concentrations of DOC and $MMHg_{UNF}$ ($r = 0.89$), $MMHg_F$ ($r = 0.76$) or $\%MMHg_F$ ($r = 0.65$). Thus, the rise of DOC and salinity (including sulfate) combined with neutral to alkaline pH along the continuum (from Lago Mayor to Lago Menor and Lake Uru-uru) support the hypothesis of rising favorable conditions for sulfate-reducing bacteria to produce MMHg (Acha et al., 2017). In parallel, the % MMHg associated to truly dissolved and colloidal fraction (i.e. < 0.22 μm) rose in surface water from Lago Mayor (43± 33%) to Lago Menor (53 ± 16%) and Lake Uru-Uru (68± 22%) (S.I.3) together with DOC content suggesting the idea that in this ecosystem organic ligands stabilize dissolved MMHg. Furthermore, high DOC content in shallow waters are probably more effective to quench UV radiation penetration in surface water (and thus photo-demethylation) than to enhance photosensitization of photochemical pathways. Altogether, these results suggest an important *in situ* MMHg production and/or limited degradation favoring its accumulation in water of these high altitude endorheic lakes.

3.4. Mercury levels and biomagnification in food webs

Total Hg concentrations increased significantly across the food webs of the Lago Menor and Lake Uru-Uru illustrating clearly Hg

Table 3
Comparison of filtered and unfiltered total mercury (THg), monomethylmercury (MMHg) and dissolved gaseous mercury (DGM) concentrations in Lakes Titicaca and Uru-Uru with literature data for world's great lakes. Superscripts (a & b) refer to bibliographic reference (right column) from which data originate.

Area	Altitude (m a.s.l)	Sampling period	THg_F (ng L^{-1})	THg_{UNF} (ng L^{-1})	$MMHg_F$ (ng L^{-1}) (%$MMHg_F$)	$MMHg_{UNF}$ (ng L^{-1}) (%$MMHg_{UNF}$)	DGM (pg L^{-1})	Reference
Titicaca – Lago Mayor	3809	2013 & 2015	0.11–0.37	0.08–0.49	0.003–0.015 (1.5 ± 1.1%)	0.013–0.021 (5.4 ± 5.2%)	7.11–11.2	This study
Titicaca – Lago Menor	3809	2013 & 2015	0.10–0.82	0.18–1.81	0.007–0.243 (16 ± 13%)	0.024–0.306 (20 ± 12%)	0.78–17.3	This study
Lake Uru-Uru	3686	2013 & 2015	0.98–2.26	2.06–5.76	0.09–1.03 (42 ± 17%)	0.72–1.83 (35 ± 6%)	0.05–16.5	This study
Lake Victoria	1133	1996 to 1998[a]	3–15.5 [a,b]		0.064–0.133[b]			Ramlal et al. (2003)[a]; Campbell et al. (2003a, 2003b)[b]
Lake Baïkal	456	1992 & 1993[a]	0.14–0.77[a]		0.002–0.038 [a]			Meuleman et al. (1995)[a]
Lake Superior	180	2000[b]		0.44–0.64[b]	0.004–0.006 [b]		17–23 [b]	Mudroch et al. (1989); Rolfhus et al. (2003)[b]
Lake Michigan	176	1994 & 1995[b,c]	0.17–0.55[a,b]	0.28–0.70[b]	0.009–0.018[b]		14–26 [c]	Mudroch et al. (1988)[a]; Mason and Sullivan (1997)[b]; Vette et al. (2002)[c]

biomagnification processes in these high altitude lake ecosystems (Fig. 3). THg levels measured across the food webs in the Lago Menor increased by two orders of magnitude, ranging from 16 ± 3 ng g^{-1} (dw) in Andean Coot *Fulica ardesiaca* blood samples to 1787 ± 291 ng g^{-1} in White-Tufted Grebe *Rollandia rolland* blood samples. In the middle of the trophic chain, THg levels were lower in benthopelagic omnivorous fishes (*Orestias Spp.*; 337 ± 32 ng g^{-1}), relative to piscivorous pelagic fishes (*O. bonariensis;* 723 ± 268 ng g^{-1}) foraging at a higher trophic level. Overall, THg concentrations in each comparable species and tissue matrix were significantly higher ($p < 0.05$) in Lake Uru-Uru relative to the Lago Menor except for piscivorous pelagic fishes (*O. bonariensis*) for which bigger individuals were collected in lake Titicaca (210 ± 20 mm, N = 11) relative to lake Uru-uru (150 ± 30 mm, N = 11). THg concentrations in lake Uru-uru food webs ranged from 174 ± 45 ng g^{-1} in Andean Coot *Fulica ardesiaca* blood samples (herbivorous, lowest trophic position) to 2685 ± 755 ng g^{-1} in White-Tufted Grebe *Rollandia rolland* blood samples (piscivorous, highest trophic position), respectively.

Hg speciation analysis on selected biological samples indicated that MMHg accounted for 58± 12% of HgT (N = 5) and 26± 16% of HgT (N = 21) in zooplankton from lake Uru-Uru, and in the Lago Menor, respectively. Methylmercury was found to be the dominant Hg compound in *Orestias Spp.* and *O. bonariensis* muscle tissues, accounting for 92± 10% (N = 20), and 94± 6% (N = 20) of HgT concentrations, respectively in both lakes.

In situ MMHg baseline production is likely the driver of this Hg concentration offset documented among the food webs in both Lakes since higher MMHg levels are reported in both sediment and surface water of Lake Uru-Uru compared to Lago Menor (Table 2 and Fig. 2). Similarly, the comparison of Hg levels in fish to existing data from the Lago Mayor (S.I.5) revealed that THg contents in *Orestias* and *O. bonariensis* fish were respectively approximately 2 and 5 times lower in Lago Mayor (Monroy et al., 2014) than those from the Lago Menor (this study). This relative difference among Lake Titicaca sub-basins is also consistent with the significantly lower MMHg levels measured in surface water samples from Lago Mayor compared to Lago Menor (Fig. 2 and Table 3). However, Hg concentrations reported for two fish species (325–1840 ng g^{-1}, S.I.5) at the Ramis river mouth in Lago Mayor (Fig. 1) which is largely affected by intense Hg emission due to gold mining activities (Monroy et al., 2014; Gammons et al., 2006) are significantly higher (*t*-test, $p < 0.05$) than all Hg levels measured in our study. Apart from these point source impacted fish species at the Ramis river mouth, Hg levels in fish from the Lago Mayor are of the same order or slightly higher than the lowest values reported for other high altitude pristine regions from central US, Europe and Canada and the Tibetan plateau (S.I.5). Hg levels in fish from the Lago Menor and Lake Uru-Uru are similar to those documented in the Tibetan plateau at locations where moderate Hg contamination is suspected (Shao et al., 2016; Zhang et al., 2014). Overall, Hg levels in the two dominant fish species consumed by the Bolivian and Peruvian local populations are significantly lower than the threshold (500 ng g^{-1} ww, estimated to 2000 ng g^{-1}, dw, applying a moisture content of 75%) established by the European Union commission (2006). An exception exists for fish collected in the vicinity of the Ramis river mouth (affected by intense gold mining activities) where Hg contents are close to the safety limits considered by the European Union commission (EUC, 2006).

3.5. Hg contamination of lakes from the Altiplano: current status and future trends

The unique set of results obtained in our study demonstrates that major sources of Hg contamination (i.e., urban and mining effluents), despite their significant amount, have limited dispersion in Lake Titicaca. This can be explained by their retention in the coastal areas where the dense cover of totoras traps more than 95% of particle (Pourchet et al., 1994). Furthermore, Hg contamination due to mining emissions is attenuated at the mouth of Suchez (this study) and Ramis rivers (Gammons et al., 2006) due to the remoteness of mining centers. In opposition, Lake Uru-Uru depicts a higher Hg contamination state due to the higher density and vicinity of urban and mining centers around this shallow ecosystem (Alanoca et al., 2016b).

Despite generally low or moderate THg levels, the specificity of the Altiplano Lakes compared to other great lakes is the relatively high proportion of MMHg in water which reaches up to 50%. As discussed in the previous section, these high MMHg percentages can be explained by (i) high MMHg production in an environment favorable to methylating micro-organisms (e.g., sulfate rich water and sediment, lower dissolved oxygen levels, neutral to alkaline water, shallow areas etc …), (ii) stabilization and accumulation of MMHg in waters due to abundant (in)organic ligands and (iii) low degradation of MMHg in organic rich waters.

The recent eutrophication event in the Lago Menor (April 2015; Acha et al., 2017) which lead to the deoxygenation of water and the rise of hydrogen sulfide and MMHg in surface water highlighted the vulnerability of this ecosystem to anthropogenic pressure. Due to its shallow water column (average 9 m) and rising urban

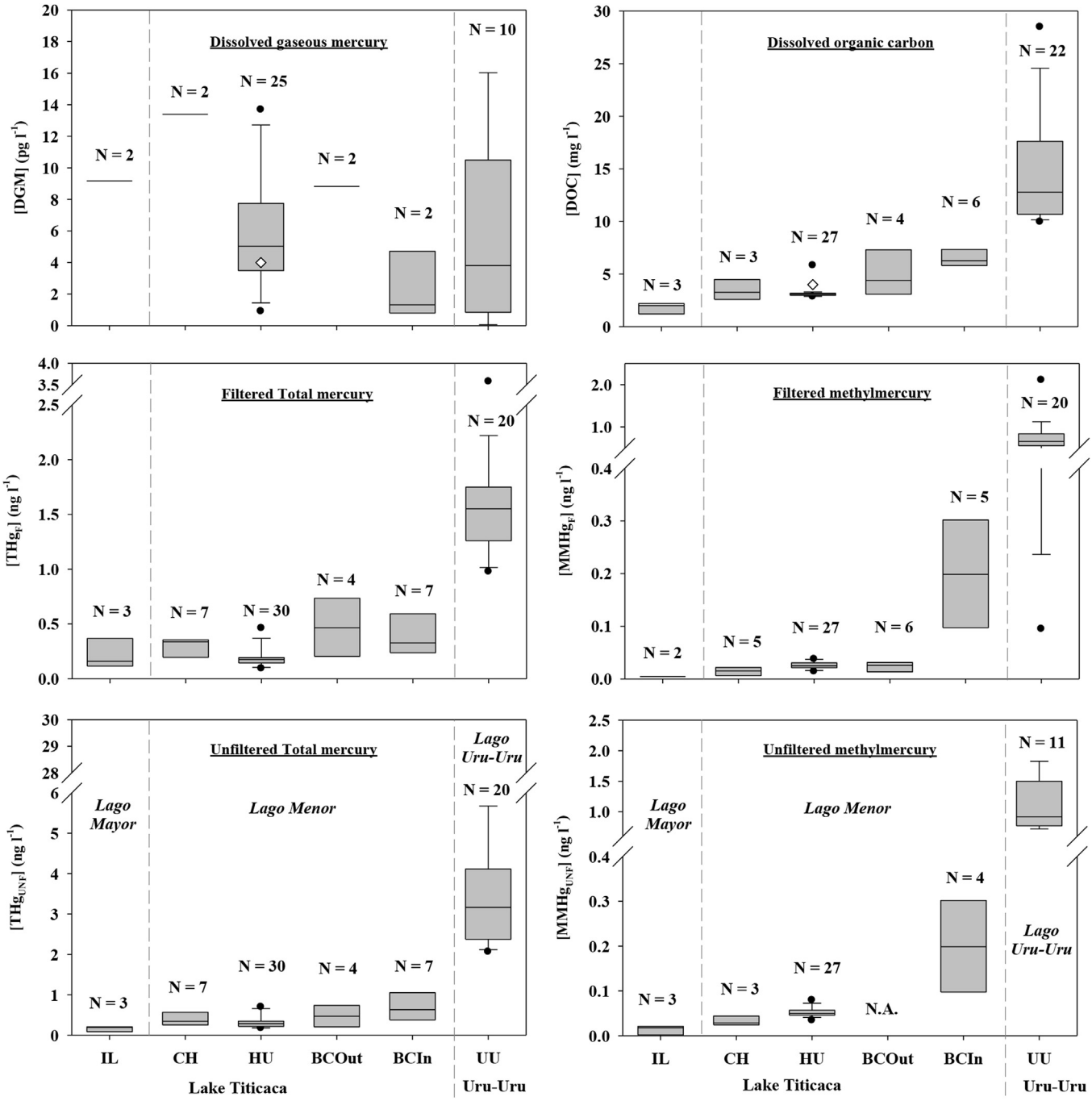

Fig. 2. Box plot presentation of dissolved gaseous mercury (DGM), dissolved organic carbon (DOC), total filtered (F) and unfiltered (UNF) mercury and methylmercury in surface waters (0–1 m) along the upstream – downstream gradient from Lake Titicaca to Uru-Uru. Box plots show the minimum, median (full line), and maximum of each data set (black point are outlier of the 5th/95th percentiles and N is the number of samples). Data from Uru-Uru Lake are from the campaign sampled at point UU12 during the late wet and dry season 2014 and 2015. IL: Isla de la Luna, CH: Chua, HU: Huatajata, BC: Cohana Bay, UU: Uru Uru.

development, Lago Menor might be subject to recurrent eutrophication events (Acha et al., 2017) and chemical contaminants inputs (Duwig et al., 2014) in the upcoming years. For such a scenario, Lake Uru-Uru would be the best current analogue of extreme eutrophication state. This scenario is less likely in Lago Mayor which has a water volume more than 70 times larger than Lago Menor. Considering the current trends of growing population and urbanization around Lake Titicaca possible Hg pollution scenarii could be (i) an increase in Hg inputs (e.g., riverine and atmospheric) resulting in increasing Hg levels in all environmental compartments likely to Lake Uru-uru, (ii) the shift from oligotrophic to heterotrophic or even eutrophic state due to increasing OM and nutrients input which may result in enhanced MMHg production and accumulation in the water column and eventually biota (Soerensen et al., 2016), and (iii) long lasting anoxic events, as a consequence of recurrent eutrophication events, resulting in increased H_2S concentrations and consequently higher MMHg production in the water column (Acha et al., 2017). Although such scenarii, tend to favor the hypothesis of a rise in MMHg concentrations at the ecosystem scale, the risk for humans has to be moderated since levels remains on or below the EUC, WHO & UNEP guidelines, mainly due to the short trophic chains (and local

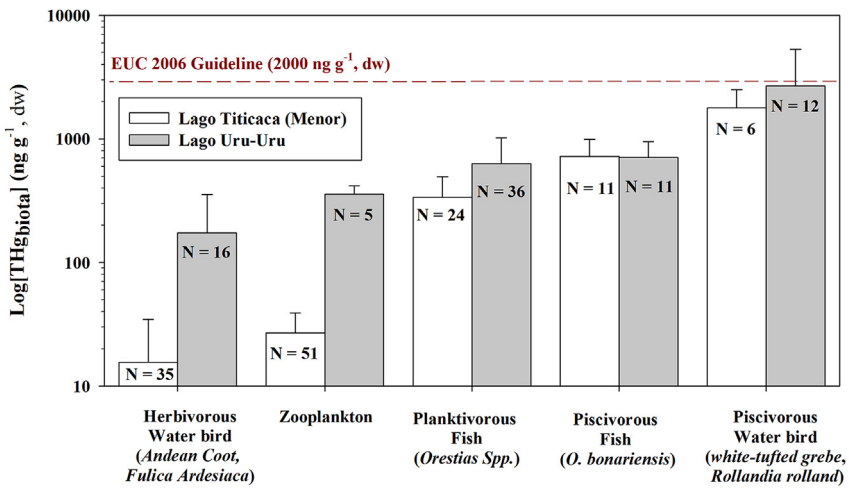

Fig. 3. Mean total mercury (THg) concentrations (ng g^{-1}, dw) in key sentinel biological organisms collected in Lake Titicaca (Lago Menor) and Lake Uru-Uru. Error bars represent one standard deviation and N is the number of samples. THg levels in fish were determined on freeze-dried muscle samples. THg levels in water birds were determined on freeze-dried whole blood samples. European Commission (EUC, 2006) Hg concentrations guidelines are indicated for comparison.

population diet is not only based on fish consumption). We conclude that the current state of Hg contamination in most of the Lake Titicaca is not as critical as warned by the study from Monroy et al. (2014), in which Hg guideline values were not reported correctly (i.e., dry weight instead of wet weight), and led to a biased statement of Hg contamination in fish in Lake Titicaca. Indeed, our results show that besides isolated "hotspots" such as Rio Ramis and Lake Uru Uru, most of the Lake Titicaca hydrosystem exhibits Hg levels in biota that remain of concern, but which are comparable to other great lakes in the world investigated so far. However, efforts must be made to reduce the actual trend with increasing anthropogenic emissions to the fragile Lago Menor ecosystem (and some coastal shallow areas of Lago Mayor) to avoid eutrophication events and large multi-contaminants inputs. Our results will also provide new insights to the synthesis made by Molina and Pouilly (2014) and the help Bolivian and international institutions to better develop an action plan for mercury emission regulation in the framework of the Minamata_Convention (2014).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2017.08.009.

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