
# Mercury speciation at the oxic/anoxic transition of a meromictic lake (Lake Pavin, Massif Central, France)

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## Introduction

Lake Pavin is a unique permanently stratified maar lake in France with anoxic bottom waters. It is stratified with an oxygenated mixolimnion overlying an anoxic monimolimnion from ~55m to the bottom at 92m. A turbidity layer enriched with Fe and Mn (oxy)hydroxides is located around 55m (Fig.1).


*Lake Pavin, a permanently stratified lake.*

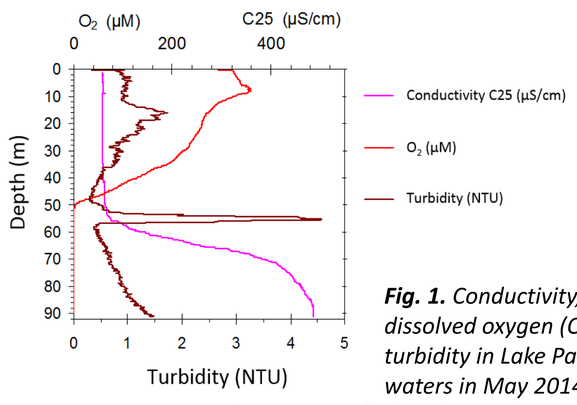



***Fig. 1.*** *Conductivity, dissolved oxygen ($O_2$) and turbidity in Lake Pavin waters in May 2014.*

Mercury (Hg) speciation in aquatic systems consists of zero and divalent species, namely elemental Hg ($Hg^0$), inorganic ($Hg^{II}$), monomethylmercury (MMHg), dimethylmercury (DMHg). MMHg is a neurotoxic species and has the ability to bioaccumulate and bioamplify throughout the aquatic food chain, leading to human exposure. It is thus of major importance to understand how and where methylation processes take place. The aim of our study is to determine Hg speciation on filtered (F) and unfiltered waters (UNF), including dissolved gaseous Hg (DGM=$Hg^0$+DMHg, UNF), total mercury THgF and THgUNF, and total methylated mercury (MeHg=MMHg+DMHg, F and UNF), to understand Hg transformations near the oxic-anoxic interface in relation with Fe, S chemistry, and bacterial activity.

## Methods

Sampling was performed from the surface to the bottom, at the middle of the lake on a 3x3m sampling platform, using a Niskin bottle. Samples were unfiltered (UNF) and filtered (F, 0.45µm PVDF membranes) on site, stored in acid-cleaned Teflon bottles following ultra-clean techniques. Samples were collected at 10m-intervals and at < 5m-intervals near the oxycline.


Quantification at ultra-trace levels (pM) were performed on site for DGM and at the laboratory for THg and MeHg using atomic fluorescence spectrometers (Tekran 2500) following US-EPA standard method 1631 [1] for THg and a derivatization method for MeHg [2].

Samples below 55m depth underwent HCl acidification to 15% (v/v) and 1 min of stirring prior to MeHg analyses to minimize analytical bias due to high sulfidic water. Acid Volatile Sulfide (AVS) were performed on site on unfiltrated waters within few hours after sampling: samples were kept under anoxia until analysis following a purge and trap technological innovation designed at ISTerre.

## Results and Discussion

Major elements ($Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$) analysis shows the stratification of the lake with increasing concentrations downward the oxycline starting at around 55m depth (Fig.2A). $THg_F$ and $THg_{UNF}$ ranged from 0.5 to 11.8 pM (Fig.2B), DGM ranged from 0.02 to 1.10 pM (Fig.2C). $MeHg_F$ and $MeHg_{UNF}$ ranged from < LD to 3.2 pM (Fig.2D). MeHg represented up to 44% of THg on filtrated waters at 60m depth, which is high compared to other studies [3, 4, 5]. Both THg and MeHg maxima were located below the maximum turbidity.

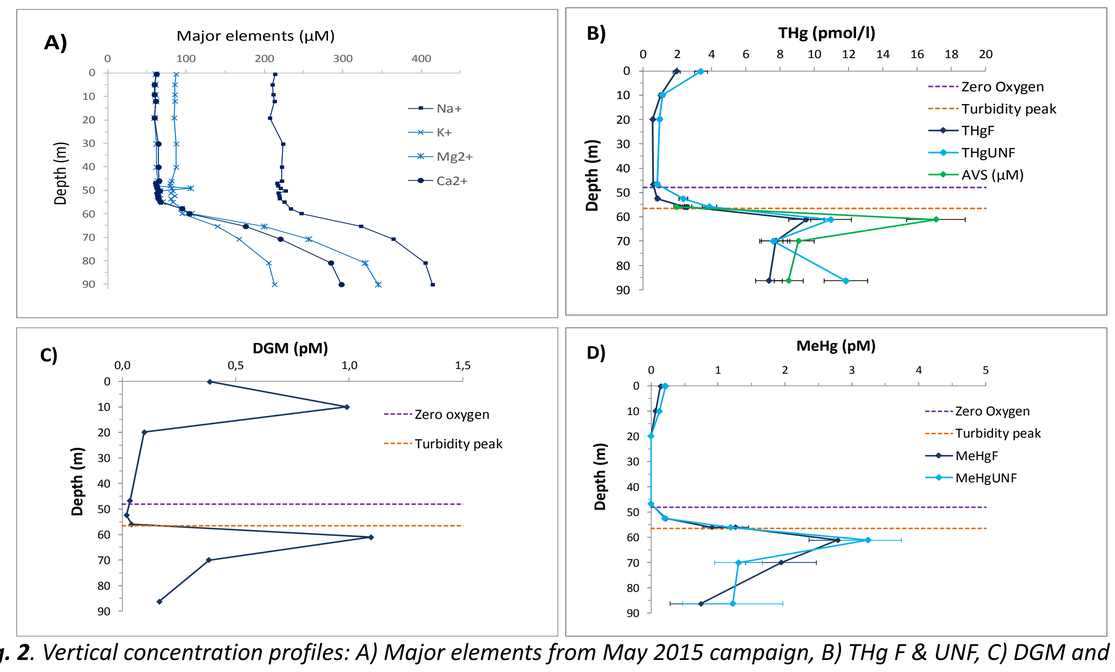
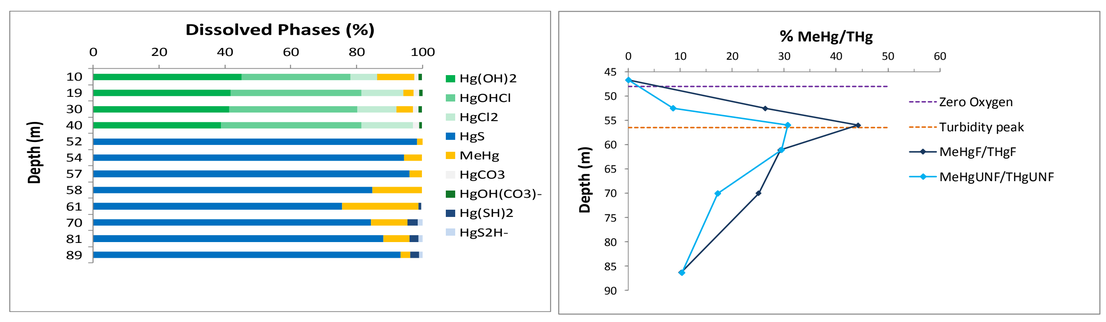



***Fig. 2****. Vertical concentration profiles: A) Major elements from May 2015 campaign, B) THg F & UNF, C) DGM and D) MeHg F & UNF and AVS concentrations sampled in October 2016.*

- Calculations using PhreeqC (without organic species), reveal that in oxic conditions, $Hg(OH)_2$ and HgOHCl are the dominant aqueous species, whereas in sulfidic and anoxic waters, aqueous HgS is the major specie (Fig.3) that could play an important role for methylation [6, 7].
- Highest $MeHg_F/THg_F$ and $MeHg_{UNF}/THg_{UNF}$ ratios are reached at the turbidity peak (Fig.4), whereas maximum concentrations are located below. This suggests that methylation is favored by Fe (oxy)hydroxides reduction (*via* iron reducing bacteria, IRB). Below 60m, precise MeHg quantification is disturbed by matrix effect and thus results in high error bars that can get to 61% (Fig.2D).
- In anoxic waters, AVS exist as free sulfides ($H_2S/HS^-$) and disordered FeS [8]. AVS concentrations measured on unfiltrated waters follow the same tendency as THg with a maximum reached at 61m depth. The correlation between AVS and THg and the maximum of DGM at 61m suggest (1) a link between FeS and Hg [9] and (2) that bacteria (possibly Sulfate Reducing Bacteria, SRB, highlighted in the lake [10]) or Fe2+ could be involved in the reduction of inorganic $Hg^{II}$ to $Hg^0$ (DGM) [11, 12].
- THg and MeHg were mainly present in the filtered phase indicating that these species are either totally dissolved or could be hosted by sulphide filter passing nanoparticles present in the lake [13,14]. $THg_F$ and $THg_{UNF}$ evolve in parallel except at the bottom of the lake where much higher $THg_{UNF}$ suggests that Hg could be hosted by particles bigger than 0.45µm.
- MeHg and Hg maxima suggest that MeHg production depends of the simultaneous presence of methylation agents (IRB/SRB) and $Hg^{II}$ availability [11,15].




***Figs. 3, 4.*** *Calculations from PhreeqC for Hg speciation within the aqueous phase and MeHg/THg ratios.*

The perspective of this study is to develop a more reliable analytical method to quantify MeHg in pM range in high sulfidic zone in order to delete the bias encountered with the derivatization method. Secondly, we will determine what is the Hg partitioning between aqueous and solid mineral phases with the identification of particles that host Hg. A third question is to determine which solid species favor or restrict the availability of Hg for methylation/demethylation at the interface and in the anoxic zone.

## References

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## Ackowlegments

This work was founded by Geochemistry group, which is part of Labex OSUG@2020.

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*Presented at Lake Pavin internship– April 2018*