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

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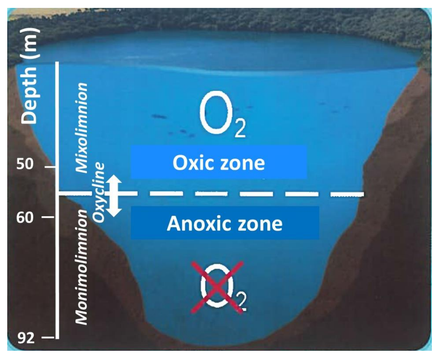
Introduction

Context: Lake Pavin (France) is a 92m-deep maar lake divided in an oxic mixolimnion overlying an anoxic monimolimnion. The oxycline (50-60m) is also characterized by chemical changes (chemocline) and a turbidity peak. **Objective:** Document the speciation and the partitioning of Hg in the water column in order to understand the biogeochemical cycle of Hg in relation with Fe, S and organic matter (O.M.) chemistry by performing high resolution profiles in the chemocline.



Lake Pavin, a permanently stratified lake.

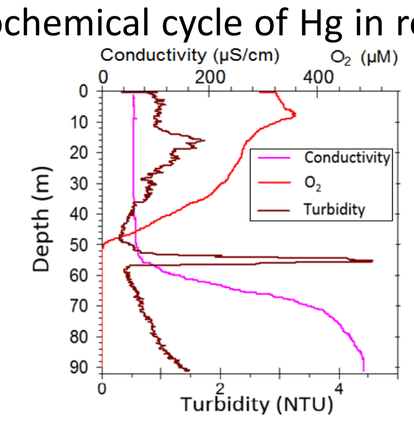


Fig. 1. *Conductivity, dissolved oxygen (O_2) and turbidity in Lake Pavin waters in May 2014.*

Methods

- Water column sampling (July 2018) was performed using a Teflon setup (pumping system, vials), following ultra-clean techniques [1]. Samples were collected at 10m-intervals from the top to the bottom of the lake and at 1m-intervals from 52 to 65m depth.
- Fe was quantified by ICP-MS, Fe^{II} and H_2S by colorimetry, SO_4 by IC, Fe_P and P_P by ICP-AES after acid-digestion and dissolved organic carbon (DOC) by IR absorption.
- Hg analyses were performed by CV-AFS (Tekran 2500) following US-EPA standard method 1631 [2].

Hg analyses and partitioning

Unfiltered sample (UNF), Filtration (F) at 0.45µm (hydrophilic PTFE)
Ultrafiltration (UF) at 2-3 Da (PES or cellulose)
Total mercury ($THg_{UNF,}THg_F$, THg_{UF})
Dissolved gaseous Hg (DGM)
Total particulate mercury (THg_P) after acid-digestion of filters

- Crossed modeling using WHAM 7 and PHREEQC 2.0 allowed to determine dissolved and colloidal Hg speciation and mineral phase equilibrium accounting for redox gradient and dissolved O.M. complexation [3]. Fulvic acids (FA) and humic acids (HA) were defined at a ratio of 9:1 [3].

Results and Discussion

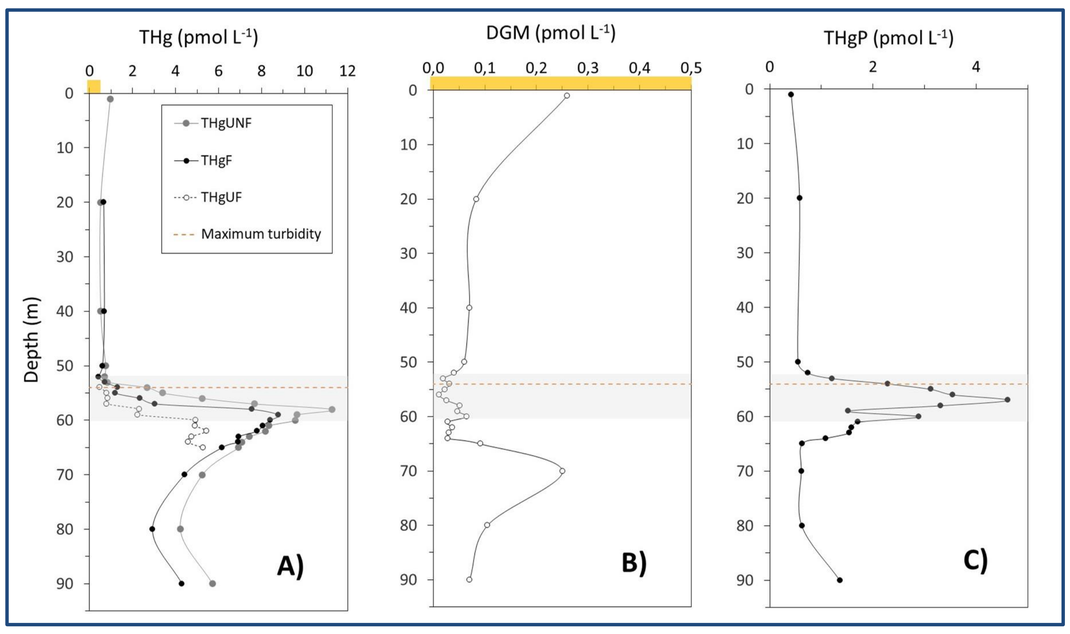


Fig. 2. *Measured vertical Hg concentration profiles: (A) THg_{UNF}, THg_F & THg_{UF}, (B) DGM, (C) THg_P. The grey shaded area represents the oxycline. At the bottom of the oxycline, $THg_{UNF,F,P}$ reach maximum concentrations (Fig. 2A, 2C) Up to 74% of Hg is colloidal (<0.45µm) (Fig. 2A), DGM is low (<0.7%) (Fig. 2B). Below the interface, $THg_{UNF,F,P}$ decrease until 80m then slightly increase, while DGM peaks at 70m.*

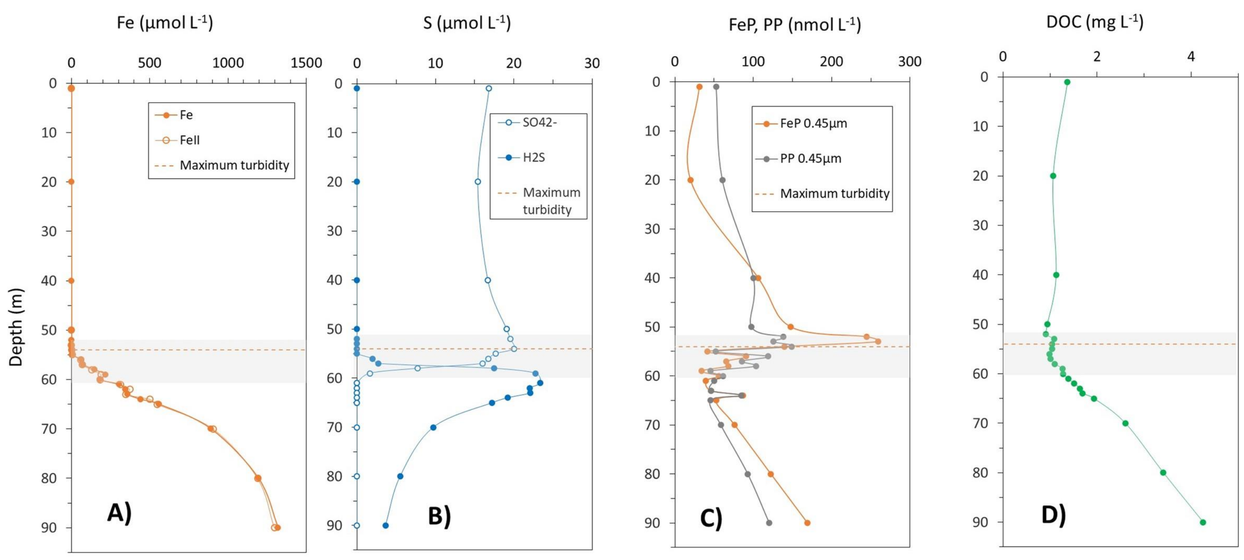


Fig. 3. *Measured vertical concentration profiles: (A) Fe, (B) SO_4 & H_2S, (C) Fe_P & P_P, (D) DOC. The grey shaded area represents the oxycline. SO_4, Fe_P and P_P are maximum in the mixolimnion whereas from the interface, Fe^{II}, H_2S and DOC increase.*

Fig. 4. *Modelled Hg speciation in the total dissolved (true dissolved + colloïdal) and saturation indexes. In the oxic part, Hg is mainly complexed to colloidal O.M. (FA and HA) and Fe_2O_3 saturates. From the interface to the bottom, dissolved Hg is linked to sulfur complexes, $Fe_3(PO_4)_2.8H_2O$ is over-saturated and FeS is saturated near the equilibrium.*

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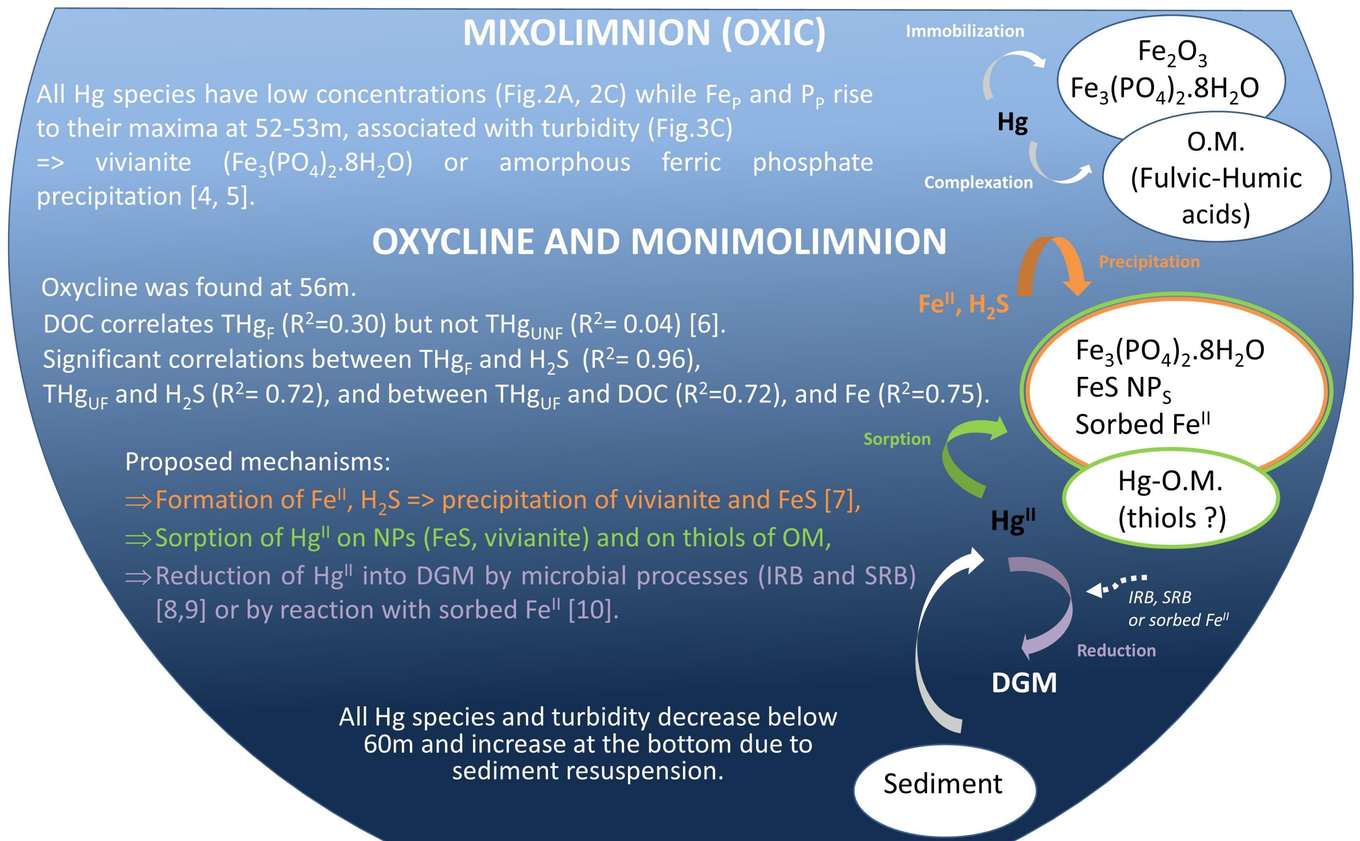

References

[1] Cossa and Gobeil 2000 [3] Rigaud et al., 2013 [5] Viollier et al., 1997 [7] Bura-Nakić et al., 2009 [9] Rolfhus et al., 2004
[2] Telliard et al., 2001 [4] Cosmidis et al., 2014 [6] Lavoie et al., 2019 [8] Hellal et al., 2015 [10] Charlet et al., 2002

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