

Chemical Evolution of the Monimolimnion of the Meirama Lake between 2009 and 2013

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INTRODUCTION

The Meirama pit lake is a water mass in the process of controlled flooding that, by the end of November 2013, can be described as a steadily stratified meromictic system. The deepest portion of the lake (monimolimnion) is isolated regarding the annual mixing dynamics (December/January) of the upper water body (mixolimnion), for which the depth of mixing is restricted to a water column of 35-40 m thick. Due to the contrasting flooding history (access of groundwater at the beginning and mixed access of stream/groundwater (being dominant the stream water) the deepest portion of the lake is separated from the upper, non-mixed layer by a marked chemocline. Strictly speaking, the monimolimnion of a meromictic lake extends to the waters located beneath the mixed lake layer. In the case of the Meirama Lake the monimolimnion is internally stratified and made of two major water bodies. From hereafter the deep and upper monimolimnion will be identified as bottom and middle sections of the lake while the mixolimnion is referred to as the surface layer. The general characteristics and evolution of the Meirama Lake have been reported in *Delgado et al. (2011, 2013)*. In this work we focus on a summary description of the chemical evolution of the monimolimnion of the lake based on data gathered between 2009 and 2013 from the still ongoing monitoring survey.

MATERIALS AND METHODS

The characterization of water samples from the lake included the determination of temperature (thermistor), pH (combined glass electrode), O_2 (LED optical sensor), E_H (Pt electrode), K_{25} (T-compensated 4-cell probe), turbidity (optical sensor), chlorophyll-a and phycocyanin (in-vivo fluorometry), DIC and DOC (infrared spectrophotometry with Shimadzu TOC-5000A), TSS

(gravimetry), alkalinity (Gran titration with 0.02 N H_2SO_4 up to pH=4), acidity (NaOH titration), major constituents (Na, K, Mg, Ca, Mn, Fe, SiO_2 (ICP-MS with VG Elemental Quadropolar PlasmaQuad II S-option), Fe^{+2} , Fe^{+3} (1-10 phenanthroline spectrophotometric method with Hach DR2800), NH_4 (spectrophotometry with Aquakem 250), F, Cl, Br, SO_4 , NO_3 , NO_2 , PO_4 (ion chromatography with Metrohm 850 Professional)), trace elements (Ag, Al, As, B, Ba, Cd, Co, Cr, Cu, Hg, Li, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, U, V, Zn (ICP-MS with VG Elemental Quadropolar PlasmaQuad II S-option)), P_{tot} (acid digestion of unfiltered sample and ICP-MS with Thermo Finnigan ELEMENXR) and N_{tot} (acid digestion of unfiltered sample and segmented flow analysis Alliance Futura SFA). For laboratory analysis, water samples are introduced in PTFE bottles previously cleaned, rinsed and conditioned following the specifications of the laboratory and standard methods. Samples for dissolved cation analyses are filtered in the field (0.45 μm cellulose nitrate filter) and acidified with high purity HNO_3 up to pH<2. Multiparameter depth-profiles (1 m step) and water sampling with a Kemmerer-type bottle (Wildlife Supply Co.) have been performed since February 2009 on a monthly basis.

RESULTS AND DISCUSSION

The chemical evolution of the monimolimnion of the lake differs significantly from that of the mixolimnion. In order to simplify the presentation of results and to better illustrate trends figures 1 and 2 depict constant-depth slices of selected parameters corresponding to the bottom (-15 to 0 m a.s.l.), middle (50 to 60 m a.s.l.) and surface (0 to 5 m b.s.) sections of the lake: Bottom and middle sections correspond to the deep and upper monimolimnion while the surface one represents the mixolimnion. Figure 1 depicts the evolution of a number of parameters. Temperature illustrates a

contrasting behavior between the different studied sections.

This is a constant for nearly all the observed parameters. In general, surface

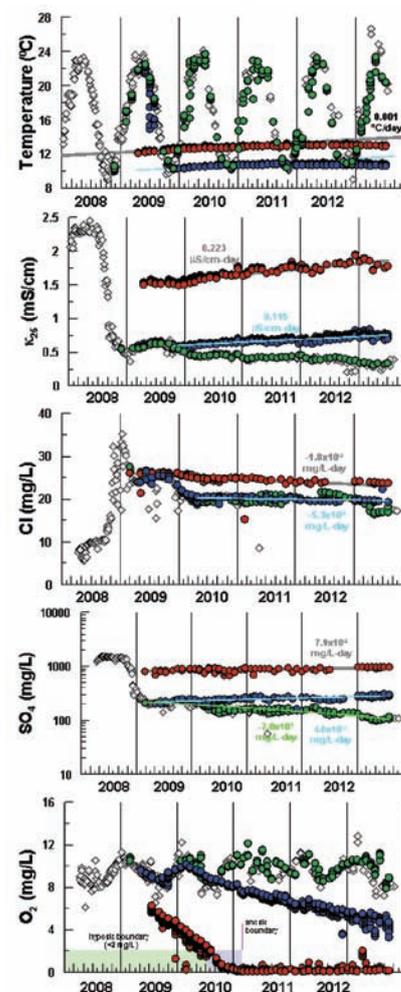


fig 1. Time evolution of selected parameters at different depths in the Meirama Lake: Surface (green/grey), bottom or monimolimnion (red) and middle zone (blue).

water is sensible to seasonal fluctuations due to weather conditions, rainfall and biogeochemical processes. The middle and bottom sections are not sensible, in general, to these effects and their

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evolution obeys to a number of internal processes. In the case of temperature we observe a nearly constant gradient increase (0.001 °C/day) in the middle and deep lake waters up to the beginning of 2012, where it remains constant. The rise in temperature is likely due to the heat provided by groundwater seepage whose temperature is above that of the lake water at the corresponding depth. Likewise, electrical conductance shows a similar constant-rate increasing rate (0.223 and 0.115 µS/cm-day in the bottom and middle sections, respectively) whose origin we also associate with groundwater seepage. Although chloride shows the opposite trend (constant-rate decreasing trend; ~0.02 and ~0.05 µmol/L-day in the bottom and middle sections, respectively) it is worth to mention that the initial lake water has a higher concentration than groundwater so that the progressive seepage will conduct to the dilution of the initial chloride concentration. In the time evolution of SO₄ we observe a slight difference in trend between the surface (-0.72 µmol/L-day) and middle (~0.4 µmol/L-day) lake layers. The decrease in the surface is likely due to stream water dilution while the increase in the middle one must be related with groundwater seepage. At the bottom, SO₄ increases at an average rate of ~0.8 µmol/L-day. That suggests a groundwater seepage reduced by a factor of ~2 compared with that of the middle layer. In addition, the reductive dissolution of earlier deposited minerals (e.g. *schwertmannite*) could also contribute to the observed trend.

Reactive components display a more complex evolution. Oxygen, for instance, shows in the surface water a wavy pattern associated with seasonal phenomena and, more specifically, yearly oversaturation periods in coincidence with the stages of phytoplankton growth. The middle and bottom sections display a constant-rate, oxygen depletion. In the bottom section of the monimolimnion the rate of oxygen consumption was, up to its complete exhaustion, of ~3.4x10⁻⁴ mmol/day while in its middle section the value is about one-half of the previous one (1.84x10⁻⁴ mmol/day). In the case of the deep waters, oxygen consumption is related with a number of oxidation processes (ferrous to ferric iron, organic matter decomposition, seepage of reduced groundwaters, etc.) which have conducted this water mass to an anoxic condition. We conjecture that the oxygen consumption in the middle section is connected to the oxidation of the more or less continuous rain of organic matter

particles falling from the upper layers and seepage of reduced groundwater. We do not expect that the waters located in the middle monimolimnion will be replenished of oxygen. Thus, we conjecture that, on the long term, a new oxygen-depleted stratum will develop in the lake. However, this eventually O₂-depleted (or even anoxic) stratum will be quite different (much more diluted, much less acidic) than the bottom one.

The evolution of ammonium and nitrate illustrated in Figure 2 show a striking contrast. Following the exhaustion of oxygen in the bottom of the lake, nitrate and total nitrogen started a fast decrease trend (0.009 and 0.064 µmol/L-day, respectively) so that NO₃, by mid-2012, was close or below the detection limit. Ammonium shows the opposite trend (0.04 µmol/L-day increase). Total nitrogen becomes also progressively impoverished from the bottom waters. These trends are interpreted to respond to different geochemical processes affecting the N cycle such as NO₃-mediated organic matter oxidation, denitrification and ammonification.

Mn and Al display a similar behavior, with a nearly constant (and low) concentration in the surface and increasing trends with depth (0.02/0.07 µmol Mn/L-day and 0.01/0.04 µmol Al/L-day in the middle/bottom sections, respectively). The >2 factor in the rate of increase of both elements observed in the two portions of the monimolimnion suggests that it is not only groundwater seepage (and the concomitant dilution/concentration effect) what drives the evolution of these constituents. Different phenomena (dissolution/precipitation, ion exchange, surface sorption) may be also relevant, in particular in the case of certain trace elements. Referring to the middle/bottom sections, some examples follow: SiO₂ (0.8/1.5 µmol/L-day), Co (7x10⁻⁴/3.2x10⁻³ µmol/L-day), Li (3x10⁻⁴/6x10⁻⁴ µmol/L-day), Ni (7x10⁻⁴/3.4x10⁻³ µmol/L-day) and Zn (1.7x10⁻³/1.1x10⁻³ µmol/L-day).

We observe that the monimolimnion of the lake, either in its bottom or middle layer is a rather dynamic (transient) geochemical system. The interpretation of the previous information must be performed taking into account the overall behavior of the lake and not as isolated portions.

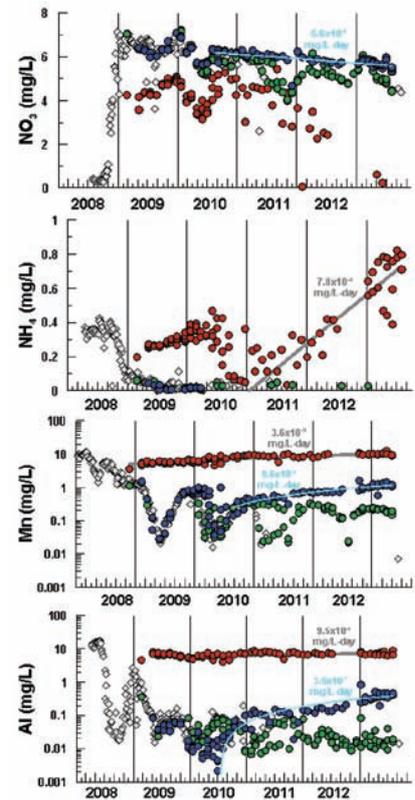


fig 2. Time evolution of the concentrations of Mn, SO₄ and Al in the surface (Green/grey symbols), monimolimnion (red) and middle zone (blue) of the Meirama Lake.

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