Pathways of redox processes in a seasonally anoxic lake, Aydat lake, France

G. Michard   Laboratoire de Géochimie des Eaux, Groupe de l'UPRESA 7074, Université Paris 7 et I.P.G. Paris, France

P. Albéric   Laboratoire de Géologie de la Matière Organique, UMR, 6531 & FR09, Université d'Orléans, France

D. Jézéquel   Laboratoire de Géochimie des Eaux, Groupe de l'UPRESA 7074,
G. Sarazin   Université Paris 7 et I.P.G. Paris, France
E. Viollier

The classical sequence of successive « thermodynamically » favourable electron acceptors (O_2, NO_3^-, MnO_x, $FeOOH$, SO_4^{2-}), utilized by microorganisms to decompose organic matter (primary redox reactions), in lacustrine or coastal marine sediments (Froelich *et al*, 1979), occurs also in water column. However, the interpretation of the distribution of reactions by-products is not straight forward. Though, this sequence at a first glance would appear with depth, species distribution can alternatively be related to the interplay between transport processes and secondary inorganic redox reactions (Van Cappellen and Wang, 1996). In this paper, we discuss the seasonal distribution of redox species, the location and pathways of redox processes in a eutrophic lake studied by biologists and geochemists for more than 10 years (Sarazin *et al.*, 1995).

Aydat lake located in the French Massif Central, 25 km SW from Clermont Ferrand originates from the damming of the Veyre river by a basaltic flow which occurred 7500 years ago. The lake surface is 6×10^5 m^2, its volume 5×10^6 m^3, its maximum depth 15 m. The water residence time is about 7 months. The lake is typically eutrophic and develops an anoxic hypolimnion from May to November.

Experimental

From January 1994 to November 1994 and from September 1995 to September 1996, the water column was sampled each month along a vertical profile close to the center of the lake. Waters were sampled with an *in situ* filtration (0.45 μm cellulose acetate membranes) device designed and built in our lab (Jézéquel *et al.*, in prep.). Samples were collected within one meter above the sediment-water interface with a dialyser (cells height: 7 cm) derived from pore waters 'peepers' (Hesslein, 1976). Nitrate and

sulphate were analysed by ionic chromatography, Fe(II) and total dissolved Fe by 1–10 phenanthroline colorimetric technique or by GFAAS, dissolved Mn by GFAAS.

Particles were collected by in-line pumping of water through 0.45 μm PVDF membrane (Durapore). The latter were attacked by a HF-HCl mixture at ambient temperature for 24 h. Boric acid was then added to remove HF interference. Analyses were subsequently made by GFAAS.

Results

In Winter, O_2, NO_3^- and SO_4^{2-} concentrations are constant along the profile including the sediment-water interface respectively at 400, 45 and 27 μmol/L. Dissolved iron is less than 0,5 μmol/L, dissolved Mn is about 5–10 nmol/L.

In April, O_2 disappears near the bottom and the oxic-anoxic boundary rises up to 5 m depth in July, then goes slowly down until mid-October. This boundary then goes down more abruptly until the overturn in November. As soon as April, dissolved Mn concentration increase at the bottom of the lake and, from April to June, Mn profiles are similar to the ones calculated by a simple diffusion model with constant flux from the sediment-water interface. Nitrate concentration, high in inlet waters (> 100 μmol/L), starts to decrease in May both at the surface and at the bottom of the lake. In June, NO_3^- concentrations are close to 0 both at the surface and at the bottom of the lake. In August, NO_3^- concentrations are close to the detection limit in the whole lake. Dissolved Fe concentration begins to increase near the bottom of the lake in May. However, increase in the layers above 60 cm from the bottom starts only in July. Particulate Fe concentration increase strongly in the anoxic zone

in June and July. Particulate form of other elements (Al, Mn,..) do not exhibit the same behaviour. Sulphate concentration decreases in July and remains higher than 10 µmol/L until the overturn.

From August to November, when the oxic-anoxic boundary goes down, observations are focused on the compartment just below the redox transition. In this layer, dissolved Mn concentration is higher and Fe concentration is lower than in the same layer one month before.

Discussion

Between March and May, a mean flux of 40 mmol.m^{-2}.month^{-1} of dissolved Mn from the sediment water interface can be derived from changes in the stock of Mn below the redox interface. This value, incorporated to a reactive transport model including a dissolution reaction on the bottom of the lake, allows to reproduce accurately manganese profiles from April to June.

Mn fluxes estimated from pore waters gradient using the gel technique of Davison and Zhang (1994) are comprised between 5 and 7 mmol.m^{-2}.month^{-1} (Jézéquel et al, 1998). These results suggest that the dissolution reaction schematized as:

$$2 MnO_2 + CH_2O + 3 H^+ \rightarrow$$
$$2 Mn^{2+} + HCO_3^- + 2 H_2O \quad (1)$$
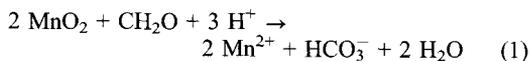
occurs essentially at the sediment-water interface, and neither in the water column nor in the sediment.

Similar pore waters profiles for Fe emphasize the discrepancy between the calculated flux from water column observations, and the calculated diffusion flux resulting from pore waters gradients. Dissolved Fe concentrations increase about two months later than Mn concentrations in the bottom waters and only when nitrate totally vanishes. It can generally be seen that dissolved Fe is never present when NO_3^- concentrations exceed about 3 µmol/L. We suggest that iron reduction occurs mainly at the sediment-water interface and propose that dissolved diffusing Fe(II) is oxidized in the water column by nitrate, following the reaction:

$$NO_3^- + 5 Fe^{2+} + 7 H_2O \rightarrow$$
$$1/2 N_2 + 5 FeOOH + 9 H^+ \quad (2)$$
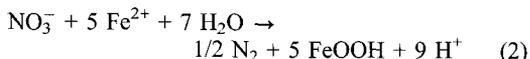
This reaction, which is thermodynamically favoured, can be mediated by bacteria such as Gallionella ferruginea (Gouy et al, 1984). A simplified model associating flux of dissolved ferrous iron from the bottom, in situ oxidation of Fe(II) by nitrates and settling of Fe(III) particles result in profiles similar to those observed. A similar reaction between NO_3^- and

Mn^{2+} can not occur spontaneously and this may explain the different behaviour for the two elements.

We stated above that MnO_x reduction occurs mainly at the sediment-water interface. However, when the redox boundary goes down in the water column, ready accumulation of dissolved Mn just below this zone is observed. This can be explained when an anoxic layer totally mix with epilimnion waters. Dissolved Mn is precipitated as particulate MnO_x. A fraction of these particles settles down the anoxic layer underneath and dissolves. Within this layer, alternatively to the reaction with dissolved oxygen, dissolved Fe(II) can be removed from the solution by the following reaction:

$$MnO_2 + 2 Fe^{2+} + 2 H_2O \rightarrow$$
$$Mn^{2+} + 2 FeOOH + 2 H^+ \quad (3)$$
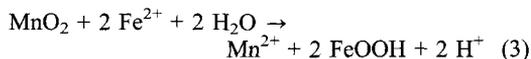
We propose that MnO_x can be reduced within the lake column by dissolved Fe^{2+} present in the hypolimnion. This idea is totally compatible with the location of Fe(II) reaction zone and concentrations time series.

Conclusions

On one hand, seasonal survey of O_2, NO_3^-, SO_4^{2-}, Fe and Mn concentrations in Aydat lake water column and pore waters suggest that reactions between Fe and Mn oxyhydroxides and organic matter occur mainly at the sediment-water interface. On the other hand, secondary redox reactions such as oxidation of Fe(II) by nitrate (or by MnO_2) seem to be important pathways at the redox transition. One of the effects of the redox boundary development in the water column is the progressive separation of primary and secondary redox reactions. Finally, we propose that this separation be controlled by the ratio [Fe(II)]aq/[Mn(II)]aq. The major consequence is the restoration of the by-products spatial distribution like it would be if primary redox reactions play the first role for Mn and Fe cycling in the water column.

References

Davison, W. and Zhang, Y. (1994) Nature, 36, 546–9.

Froelich, P.N., Klinkhammer, G.P., Bender, M., Luedtke N.A., Heath G.R., Cullen, D., Dauphin, P., Hammond D., Hatrmann, P. and Maynard, V. (1979) Geochim. Cosmochim. Acta, 43, 1075–90.

Hesslein, R. (1976) Limnol. Oceanogr., 21, 912–24.

Sarazin, G., Gaillard, J.F., Rabouille, C. and Philippe, L. (1995) Hydrobiol., 1–25.

Van Cappelen, P. and Wang, Y. (1996) Amer. J. Sci., 296, 197–243.