

# Biogeochemical Dynamics of Molybdenum in a Crater Lake: Seasonal Impact and Long-Term Removal

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## Abstract

Despite a large variety of processes that can control Mo and its potential to become an environmental tracer of euxinic environment, this element is not often studied in lakes. The aim of this paper is to identify main seasonal biogeochemical processes that involve Mo in a well constrained freshwater system (Lake Pavin water-column) in order to evaluate their respective importance. In Lake Pavin, 4 main processes have been identified: 1) the transitional process represented by Mo assimilation of by phytoplankton in the epilimnion (nitrogen biological fixation and nitrate assimilation); 2) transient process represented by dissolved Mo adsorption onto Fe and Mn metal oxides at oxic/anoxic interface (depth 50 - 60 m); 3) Mo precipitation where apparent sulfide production rate is maximum, and from 80 m depths; 4) release of dissolved Mo due to Mo benthic flux or input from a deep source.

## Keywords

Molybdenum; Biogeochemical Cycles; Diatoms; ICP-MS; Meromictic Lake

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## 1. Introduction

Mo is a trace element which interests both geochemists and biochemists because it plays an important role in natural biogeochemical cycles of elements such as nitrogen and sulphur cycle where they are bound to molybdenum by specific enzymes [1] [2]. Mo is also considered in marine sediment records as a proxy of anoxic paleo-environments where sulphide builds up and precipitate molybdenum [3]-[7]. In spite of molybdenum biological properties and potential reactivity in aquatic systems, there are very few works on lake ecosystem. Particularly, there is a lack of publications that compare to different biogeochemical processes [8].

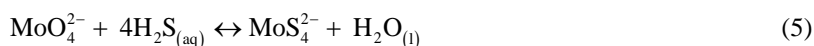
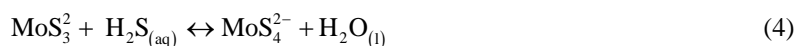
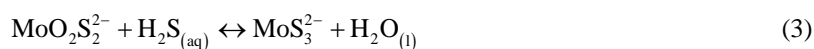
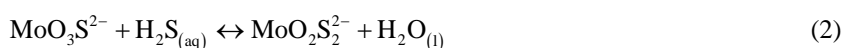
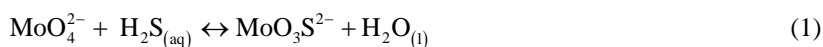
The aim of this research is to identify processes that involve Mo in a well constrained freshwater system in order to evaluate their respective importance. Lake Pavin is the perfect natural laboratory to study dynamic behaviour of Mo in presence both of microalgae, manganese and iron oxides productive layers and sulphidic layers.

## 2. Biogeochemical Background

Mo is a biologically essential trace element [9]-[15]; however, unlike many bioactive elements, variations in ocean are small [16]-[19]. Consistent with its generally conservative ocean distribution, Mo has a high salinity-normalized dissolved concentration (110 nM) [16] [17] and a modern-ocean residence time of approximately 0.8 million years [20] [21]. Rivers serve as the dominant source term for Mo to the ocean; whereas anoxic marine sedimentary systems are believed to be the primary sinks [19]-[32].

Mo is introduced into cells in molybdate ions form and operates in various enzymes where it oscillates between stages MoIV and MoVI. Unlike iron or manganese, molybdenum is not used as a final acceptor of electrons in cells [2]. Different categories of Mo enzymes were revealed by crystallography on cells of model bacteria (*i.e.*, *Escherichia coli*) and can be classified on one hand in two categories linked to nitrogen cycle: nitrogenase (Enzyme multimeric complex) which is irreversibly inhibited by molecular oxygen and molybdoenzymes essentially represented by nitrate reductases [33]. On the other hand, Mo enzymes such as sulfite oxidase, formate dehydrogenase and aldehyde oxidase, were also identified [34]. They play a role in aquatic systems in the oxidation of sulphite to sulphate and dimethyl sulfoxide to dimethyl sulphide.

At the global scale, Mo is a rare metal (0.001% of the earth crust). In natural waters and especially in oxic conditions, Mo is present mainly under the form of molybdate ( $\text{Mo}_{\text{VI}}^{2-}$ ). Its chemical characteristics are a strong chemical inertia, as a result of covalent bonds between Mo and O, and high solubility [31]. In lakes water column depending on oxygen conditions, processes would tend to follow a vertical sequence. Mo is important in biological processes like nitrogen fixation and nitrate assimilation under oxic conditions in lakes epilimnion. In seawater where molybdenum concentration is above 100 nM, the effect of biological uptake on molybdenum vertical distribution is not visible. In continental waters where concentrations are ten times lower, it might be worth checking for this biological signature. In oxygenated waters iron and manganese hydrated oxides are also effective extractors of molybdenum [35]. Molybdates ions can be adsorbed onto oxides manganese authigenic and transported to anoxic compartment (bottom waters or sediment-water interface). This reaction allows a major molybdate redistribution throughout water column however, this observation does not explain molybdenum fixation in sediment [35]-[37]. In anoxic condition molybdenum is strongly associated with natural colloidal organic matter [38], or directly complexed by the natural organic matter [39]. Following the possible transformation of molybdate to thiomolybdates (Equations (1) to (5)), molybdenum can co-precipitate with iron sulfides and organic molecules-rich sulphide participating in the capture and long term sequestration of molybdenum [27] [40] [41].



The equilibrium constant of reaction is:

$$K = \left( \text{MoS}_4^{2-} \right) / \left\{ \left( \text{MoO}_4^{2-} \right) \left( \text{H}_2\text{S} \right)^4 \right\} = 7.4 \times 10^{19}$$

Very recently precipitation of a previously unrecognized, probably nanoscale Fe(II)-Mo(VI) sulfide mineral with predicted formula  $\text{Fe}_5\text{Mo}_3\text{S}_{14}$  is postulated for sulfidic anoxic water column of Rogoznica Lake [42].

### 3. Study Site: Lake Pavin

Scientific literature about lake Pavin biogeochemistry is quantitatively important: [38] [43]-[69]. Lake Pavin is a small ( $0.44 \text{ km}^2$ ), but deep (92 m), nearly circular lake located at an altitude of 1197 m in the French Massif Central ( $45^\circ 30' \text{N}$ ,  $2^\circ 54' \text{E}$ ). It occupies a maar crater which was formed 6900 years ago [54]. It represents the most recent period of volcanic activity in the Massif Central. Its geological setting is similar to that of other maar lakes such as Lake Nyos (Cameroon) or Laacher See (Germany). Lake Pavin is meromictic. It is characterized by the presence of permanent stratified layers: the upper layer called mixolimnion (0 to 60 m depth) is affected by seasonal mixing; an intermediate layer called mesolimnion (60 to 70 m depth); the deepest layer called monimolimnion (about 70 to 92 m depth). Mesolimnion and monimolimnion are anoxic and progressively enriched with depth in reduced compounds (ions  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{NH}_4^+$  ...) and gases such as  $\text{CO}_2$  and  $\text{CH}_4$  [54,70], as well as of many trace element [60] [61]. Molybdenum showed strong removal in the mesolimnion and a strong association with natural dissolved organic matter in the monimolimnion [38]. The monimolimnion is often considered to have reached a geochemical steady state [58]. Dissolved molybdenum in the water column comes from 16 surface streams (Figure 1) and sublacustrine inputs.

Subsurface inputs at about 45 m and 85 m are discussed in [60] [61] and [71]. Basically, the 45 m depth input has a composition close to surface running waters with an average flow rate close to the average visible surface input [71]. The 85 m depth input has a composition influenced by mineral springs emerging in the area. The best surrogate is Fontaine Goyon a mineral spring located 1.5 km from Lake Pavin crater. Regular visual observations indicate that the water level of the lake has been stable, within an uncertainty of 50 cm, for at least several decades. Dissolved molybdenum in rain is  $<1 \text{ nM}$  [61].

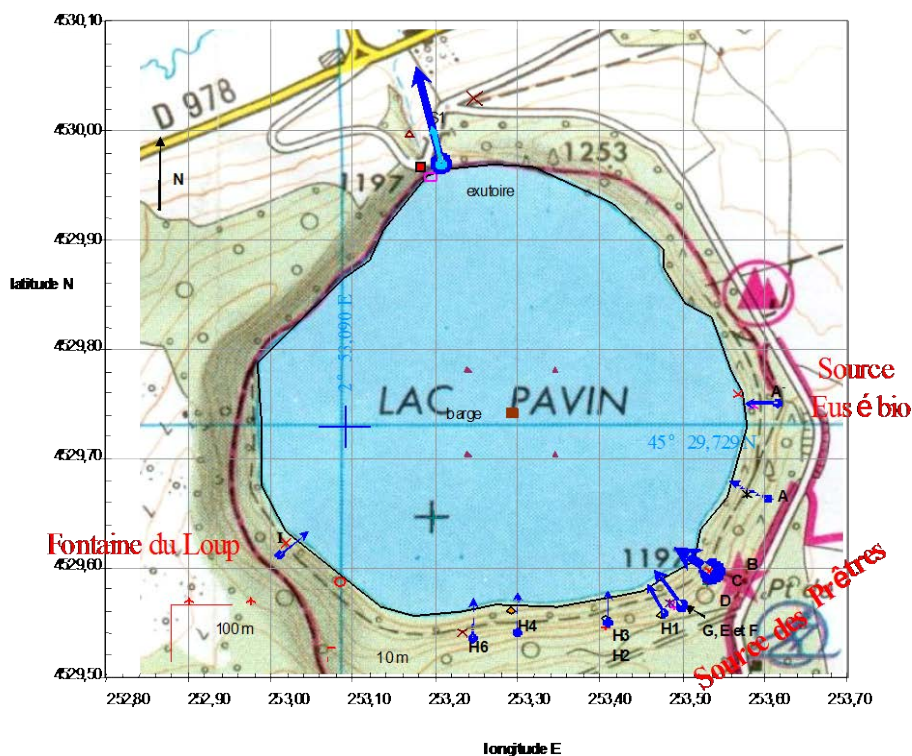


Figure 1. Tributaries location (France) and Lake Pavin.

## 4. Methods

Water column and rivers sampled were collected and analyzed during METANOX multidisciplinary project (Biodiversity and Metabolism in Anoxic Aquatic Systems). During this project, 17 monthly campaigns from May 2006 to August 2007 were carried out.

### 4.1. Water Column Monitoring

During first campaigns, samples were collected from a platform (45°29.740N, 2°53.280E) at depth by a 50 ml syringe sampler. For other campaigns we used a syringe of 1 liter. This latter syringe sampler is a lab-made prototype designed for an accurate sampling depth and to avoid gas bubble formation during retrieval. Small tributaries are sampled for various analyses directly with a 50 mL Polypropylene syringe. Filtration is done with a Sartorius Luer membrane support rinsed with the sample immediately after retrieving the syringes. Filtered samples for trace element analyses (*i.e.*, molybdenum) are acidified with Merck Suprapur nitric acid. In addition tests of chemical entity sizing were done using ultrafiltration in the monimolimnion [38], for operational details. Separative membrane allowed the following cut off sizes: 1 kDa, 5 kDa, 10 kDa, 0.45  $\mu\text{m}$ .

### 4.2. Settling Particles

Settling particles in Lake Pavin were collected at 4 strategic depths according to physical and biogeochemical stratification: 23 m (below biological production), 58 m (above the mesolimnion), 70 m (below the mesolimnion), and 88 m (above sediment). For June, July, August and September 2006 campaigns, 4 lab-made sediment traps deployed on individual lines [61] were maintained in position by a 15 kg weight at the lake bottom and a buoy at the lake surface. Concerning the remaining campaigns 4 Uwitec® sediment traps have been used on a single vertical line attached to a platform in the center of the lake. Two cylinders per depth were available. Sodium azide was used as a poison to prevent particles degradation by microorganism. Immediately after sampling, settled samples are filtered under nitrogen atmosphere on GFF membrane with average size of 0.6  $\mu\text{m}$ .

### 4.3. Diatoms Culture

In order to estimate independently the potential impact of molybdenum uptake by algae on the lake water column, Diatoms *Aulacoseira italica* (phytoplankton dominant species, 80% of microalgae species in February-March 2007) was grown in the lab from a known quantity of molybdenum. Diatoms originated from LMGE collection at University of Clermont-Ferrand. 100 nM of molybdenum were added in Synura growth medium [72] (Table 1). The culture was carried out in one control and 3 replicates. Control (250 ml) is equivalent of synura medium while each replicats consists of 250 ml synura medium and 50 ml of homogenized diatoms strains. The culture has been carried out on a regular workbench at 25°C with alternating outdoor daylight and outdoor darkness. Samples were taken daily to measure absorbance at 670 nm in order to estimate algal biomass growth.

All visible spectroscopic measurements were carried out on an ICP-MS by using an internal standard  $^{115}\text{In}$  (1  $\mu\text{g/L}$ ) to correct matrix effects and derivatives.

Analytical quality was made by a SLR4, certified standard. Mo was determined in filtered and acidified samples by ICP-MS.

**Table 1.** Growth media for diatoms culture.

Synura Media (Mignot-Brugerolle, 1982) in 1 L			
Chemical formula	m (g)	M (g·mol <sup>-1</sup> )	C (mol·L <sup>-1</sup> )
CaCl <sub>2</sub> ·2H <sub>2</sub> O	0.03676	147	2.50E-04
MgSO <sub>4</sub> ·7H <sub>2</sub> O	0.03697	246	1.50E-04
NaHCO <sub>3</sub>	0.0126	84	1.50E-04
K <sub>2</sub> HPO <sub>4</sub>	0.00403	174.18	2.31E-05
NaNO <sub>3</sub>	0.8501	85	1.00E-02
Na <sub>2</sub> SiO <sub>3</sub> ·5H <sub>2</sub> O	0.02842	212	1.34E-04

+5 ml of oligo-nutrients solution, 1 ml of Thiamine HCl, 5 ml of biotine, 0.5 ml of B12 vitamin, pH adjusted at  $7.5 \pm 0.2$  with Suprapur HCl.

## 4.4. Laboratory and Field Analyses

### 4.4.1. Auxiliary Parameters

In order to locate physico-chemical gradients, vertical CTD profiles are done with a Seacat Seabird CTD profiler (pressure/depth, temperature, conductivity, dissolved oxygen, pH). It has resulted in situ vertical profiles of main physical and chemical parameters over the entire water column of the lake.

### 4.4.2. Iron and Manganese

Dissolved iron (II) is measured by colorimetry at 565 nm by the ferrozine method [61]. Dissolved manganese concentration is determined by ICP-AES (Optima 3000, Perkin Elmer).

### 4.4.3. Nitrate, Sulphate and Total Sulphide

Volatile and oxidizable sulfide is trapped after filtration at the time of sampling by precipitation in the form of insoluble zinc sulfide. These solid/colloids are maintained in suspension with the addition of gelatin. Sulfide is measured colorimetrically at 665 nm. Nitrate and sulfate are determined with ion chromatography after addition of cadmium acetate to prevent sulfide oxidation to sulfate.

### 4.4.4. Molybdenum

Samples stored in the dark at 5°C in Polypropylen tubes were analyzed by ICP-MS (X7 series Thermo Scientific). ICP-MS analyses were calibrated with an external standardization. Internal standard technique using  $^{115}\text{In}$  at 1 µg/L was used in order to correct matrix and drift effect. Particles samples obtained from sediment traps were analysed at CRPG (Nancy, France) for C, H, N and S. For molybdenum, only two samples were analysed at CRPG (58 m and 70 m) by ICP-MS after complete sample dissolution.

## 5. Results

### 5.1. Mixolimnion Stratification

**Figure 2** shows vertical profiles of temperature in Lake Pavin. During 2006, surface temperature increases until July before decreasing by nearly 5°C in August. At this time the metalimnion moves down allowing surface water to mix partly with hypolimnion waters. Cooling down goes on until autumn when the lake surface starts to freeze. From melting ice in March 2007 to June 2007, temperature goes up.

**Figure 3** presents dissolved oxygen concentrations evolution in Lake Pavin. Residual peak of oxygen is almost always visible at metalimnion depth (excluding December when no significant peak is observed). During high photosynthesis activity (*supersaturation is often observed in the epilimnion*), oxygen accumulates in the less dynamic zone (metalimnion) where exchange with the atmosphere or with the hypolimnion is limited. From May to September the oxycline rises up in the water column from 58 to 52 m. When the oxycline rises upward in the water column the chemocline (shown through the iron profile in **Figure 4** does not undergo such vertical shift (nearly 10 meters).

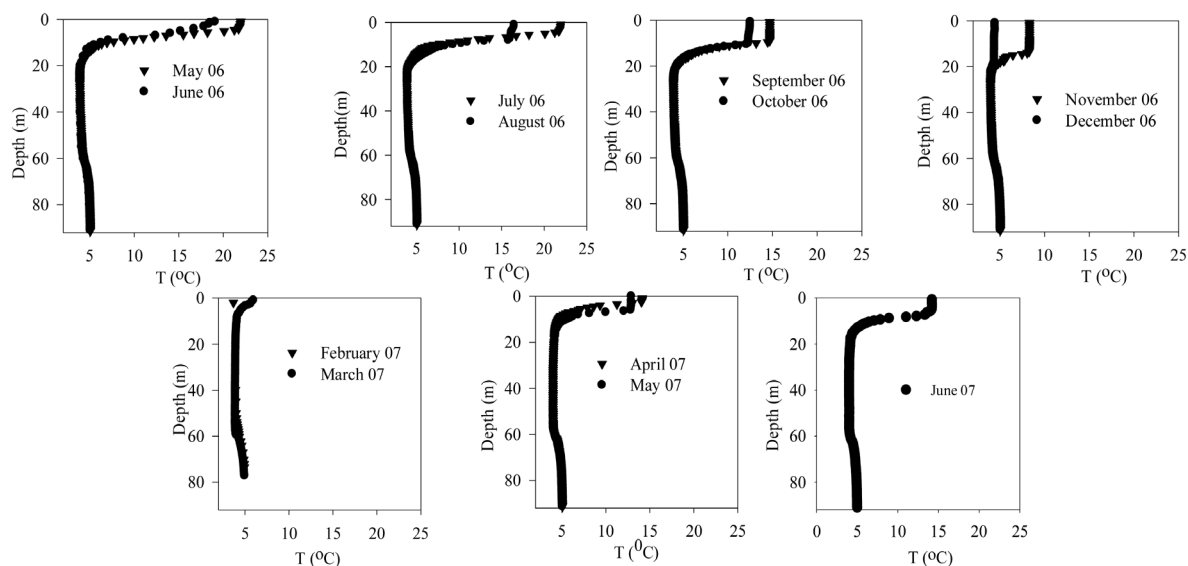
### 5.2. Redox Biogeochemical Cycles

Nitrate, spite of input surface concentration  $>20 \mu\text{mol}\cdot\text{L}^{-1}$ , shows almost constantly concentrations  $<5 \mu\text{mol}\cdot\text{L}^{-1}$  in the epilimnion (**Figure 5**) mostly due to uptake by growing phytoplankton. Nitrification of large concentrations of ammonium ( $>1 \text{ mmol}\cdot\text{L}^{-1}$ ) can explain the presence of a nearly constant nitrate peak above the mesolimnion.

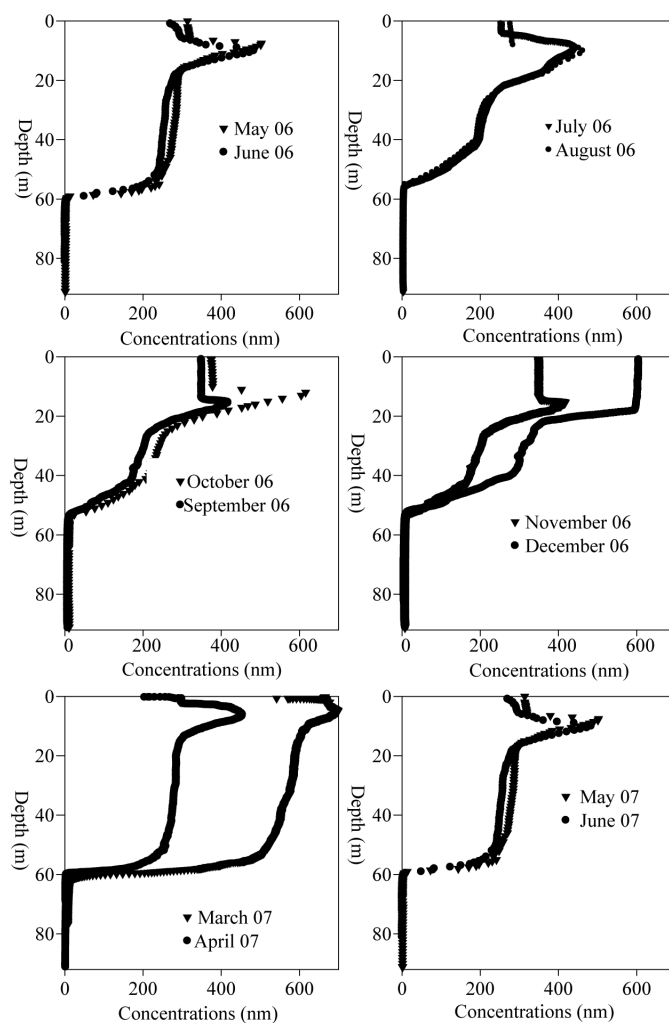
Iron (II) (**Figure 4**) and manganese (**Figure 6**) in very low concentration in the mixolimnion show significant accumulations in the meso-monimolimnion layers; especially dissolved iron for which concentrations reach  $1 \text{ mmol}\cdot\text{L}^{-1}$ . Consequently, metal oxides formed in the oxycline zone are likely to be present [62] and might follow the oxycline when rising up. Sulfate reduction within the mesolimnion causes the production of sulfide (**Figure 7**), sulfide oxidation by-products (S(0)) and colloidal iron sulfide [68] [69]. Sulfide results are very close to those published by [58].

### 5.3. Molybdenum

Roughly, dissolved molybdenum in tributaries ranges from 5 to  $15 \text{ nmol}\cdot\text{L}^{-1}$  (**Figure 8(a)**) depending on tributary



**Figure 2.** Lake pavin—Temperature data.



**Figure 3.** Lake pavin—Oxygen data.

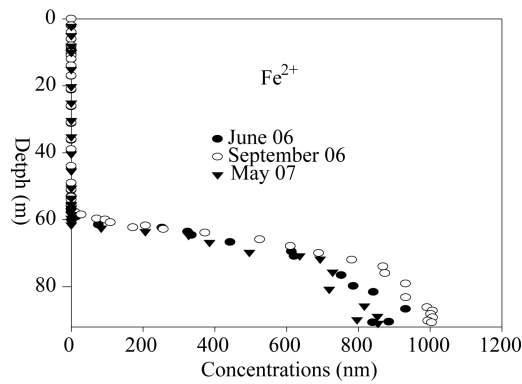


Figure 4. Iron (II) in deep layers of Lake Pavin.

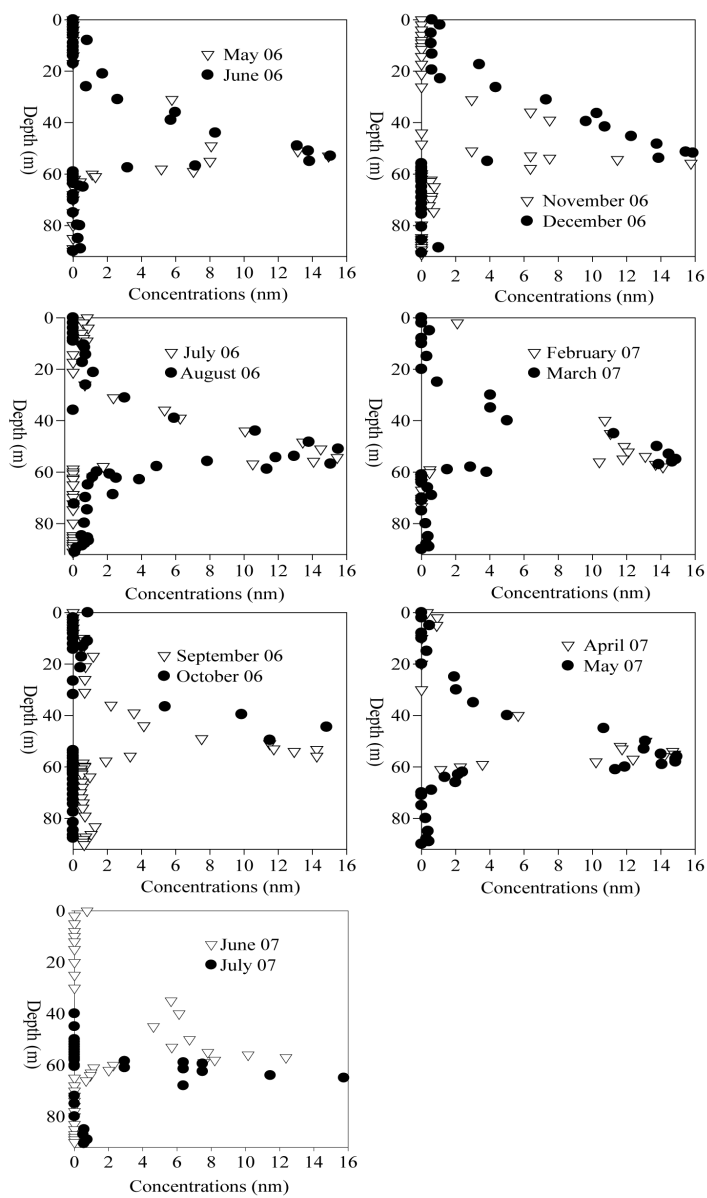
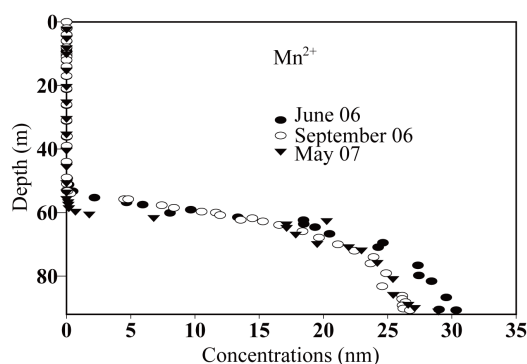
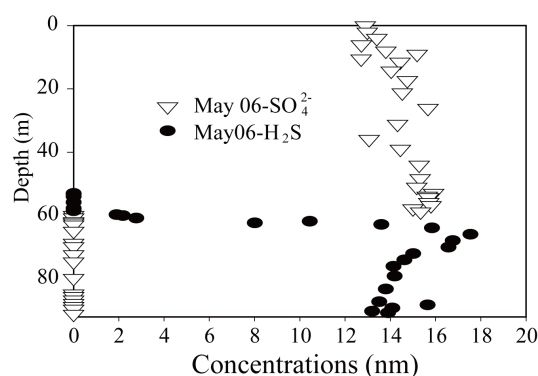


Figure 5. Nitrate seasonal dynamics in Lake Pavin.



**Figure 6.** Manganese in deep layers of Lake Pavin.



**Figure 7.** Sulphate and sulphide in Lake Pavin.

or period of the year. From measured flow rates (**Figure 8(b)**), one can calculate a weighted average concentration entering the lake annually of  $11 \text{ nmol} \cdot \text{L}^{-1}$ . In deep layers, ultrafiltration results (**Figure 9(a)**) point out the presence of molybdenum in rather large molecules  $>10 \text{ kDa}$ . Organic molecules (**Figure 9(b)**) are the best candidates to carry molybdenum in the monimolimnion through binary or ternary association however association with iron sulfide species cannot be ruled out [42].

From May 2006 to October 2006, slight dissolved molybdenum depletion is observable in the epilimnion (**Figure 10**). This feature disappears in autumn when the mixolimnion becomes homogeneous. More permanent is the removal feature observable in the oxycline zone (about 50 m depth). Also permanent but more consequent is the removal feature that is observed within the mesolimnion and already described in [61]. The maximum removal leading to concentrations  $<5 \text{ nmol} \cdot \text{L}^{-1}$  occurs in the zone of maximum sulfide production (**Figure 10**).

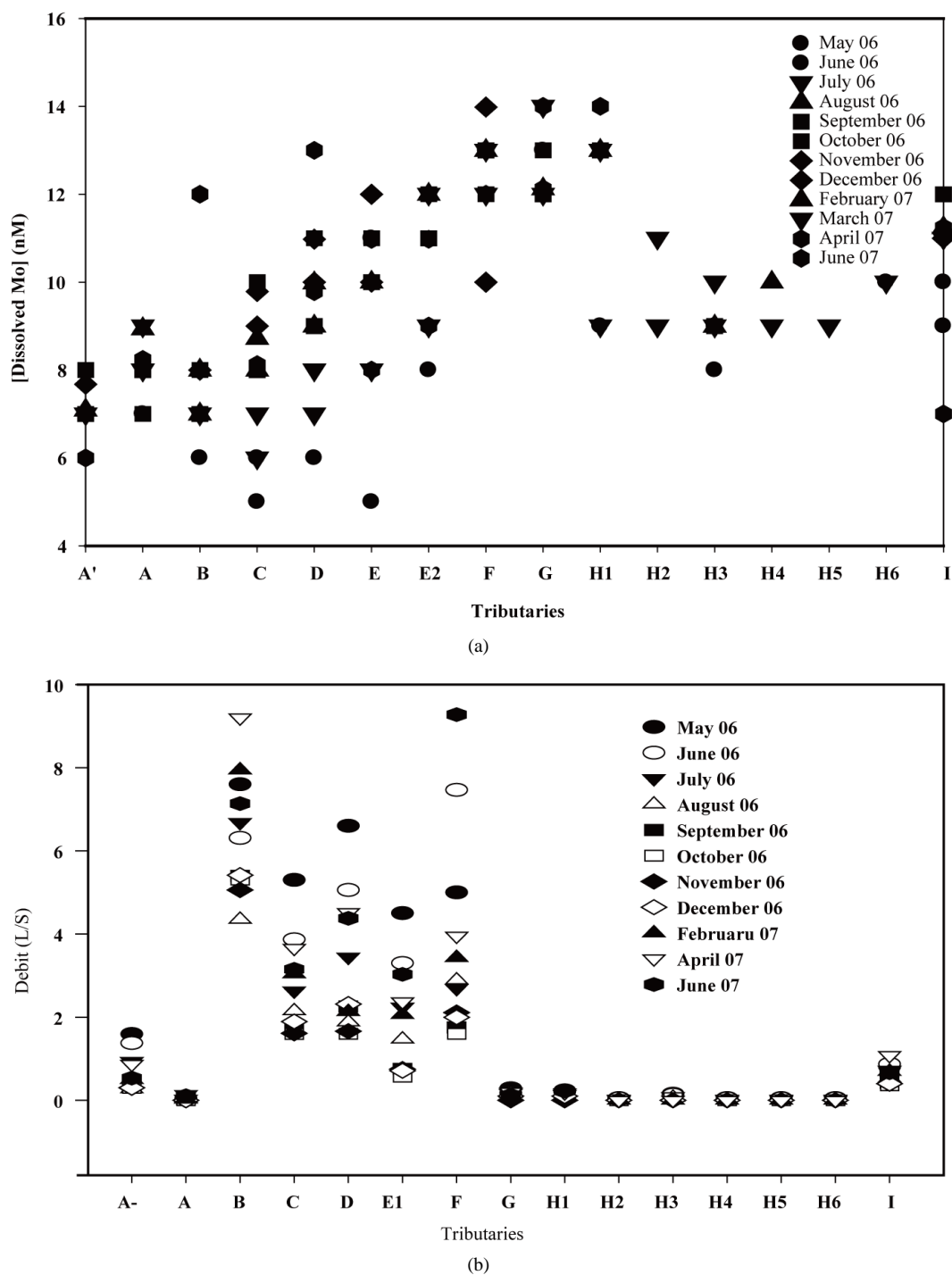
#### 5.4. CHNS

**Table 2** presents the results obtained on settling particles from sediments traps. Their average carbon content is close to 12% (**Table 2**). The highest value (19%) is found in the hypolimnion whereas the lowest value is found in the monimolimnion (7.5%) corresponding likely to partly degraded material. This can also be observed in nitrogen content which varies from 2 in the mixolimnion to 1% in the monimolimnion. Degradation by-products are likely to be the source of organic macromolecules detected in the monimolimnion.

Mass fluxes show higher values during March and April. This period corresponds to the bloom of diatoms (**Table 3**). In this period, analyses show that Mo concentrations are varying between 9.304 and 13.53 ppm

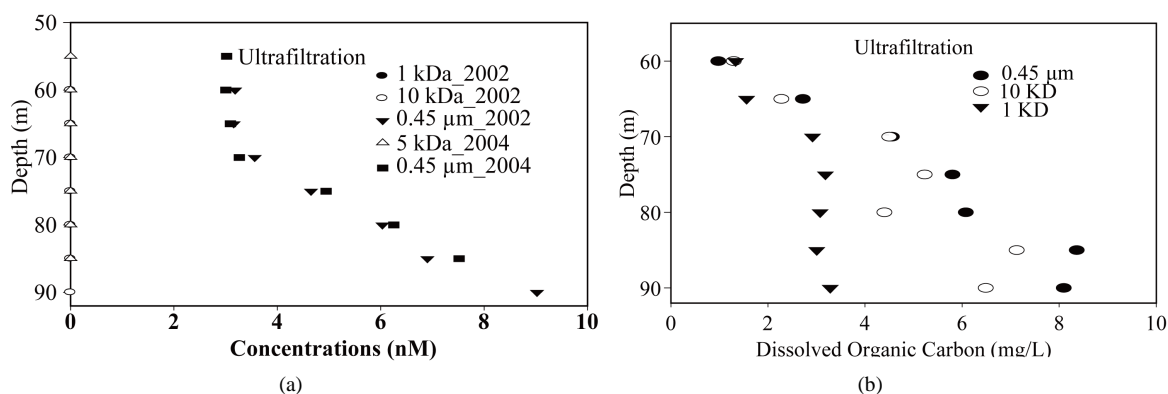
#### 5.5. Diatoms Culture

Absorbance measurements for control and replicates show (**Figure 11(a)**) a lag phase until day 6, followed by a nearly exponential growth until a stationar activity which is recorded in the last day of the experiment. Corres-

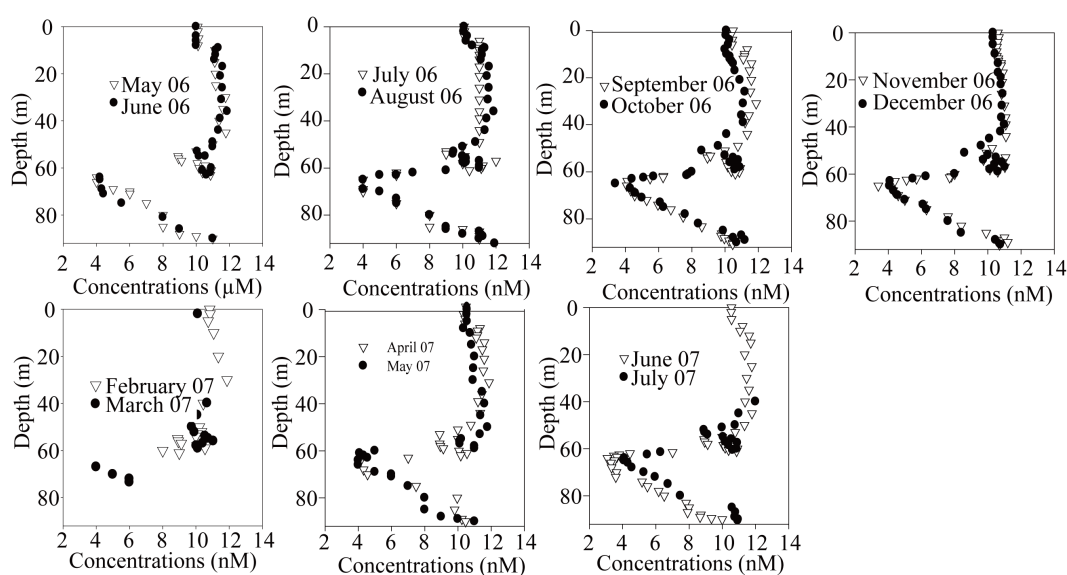


**Figure 8.** (a) Molybdenum seasonal dynamics in tributaries; (b) Mo flow rate dynamics of tributaries.

ponding molybdenum uptake shows (Figure 11(b)) the same lag period but followed by a constant removal rate until reaching the stationary phase. Direct (filament) cell counting with an optic microscope from an aliquot is rather difficult and lead to less smoothed data (Figure 11(c)); cell·L<sup>-1</sup>). If one presume that molybdenum uptake in the experiment is related to assimilation alone and not adsorption at cell surface (which remains to be proven), it is possible to calculate a first order estimate of molybdenum growth requirement (in this experiment) per cell unit. Such estimation leads to  $5 \times 10^{-6}$  nmol·cell<sup>-1</sup>.



**Figure 9.** (a) Molybdenum size; (b) DOC size.



**Figure 10.** Dissolved molybdenum seasonal dynamics.

**Table 2.** Mass % of C, H, N and S measured on settling particles.

Mass %				
Samples Identification	N	C	H	S
February-2007-(with NaN <sub>3</sub> ) (23 m)	1.41	10.46	2.38	0.24
March-2007-(with NaN <sub>3</sub> ) (23 m)	1.81	14.43	2.91	0.17
April-2007-(with NaN <sub>3</sub> ) (23 m)	2.10	19.25	2.91	❖
May-June-2007-(with NaN <sub>3</sub> ) (23 m)	1.69	12.76	2.80	0.11
February-2007-(with NaN <sub>3</sub> ) (58 m)	1.33	9.19	2.47	0.12
March 2007-(with NaN <sub>3</sub> ) (58 m)	1.43	10.78	2.79	0.11
February-07-(with NaN <sub>3</sub> ) (70 m)	1.70	14.69	2.73	❖
March-2007-(with NaN <sub>3</sub> ) (70 m)	1.13	7.98	2.29	0.17
February-2007-(with NaN <sub>3</sub> ) (88 m)	1.38	9.76	2.74	0.19
March-2007-(with NaN <sub>3</sub> ) (88 m)	1.06	7.53	2.1	0.16

❖ Any chemical analyses.

## 6. Discussions

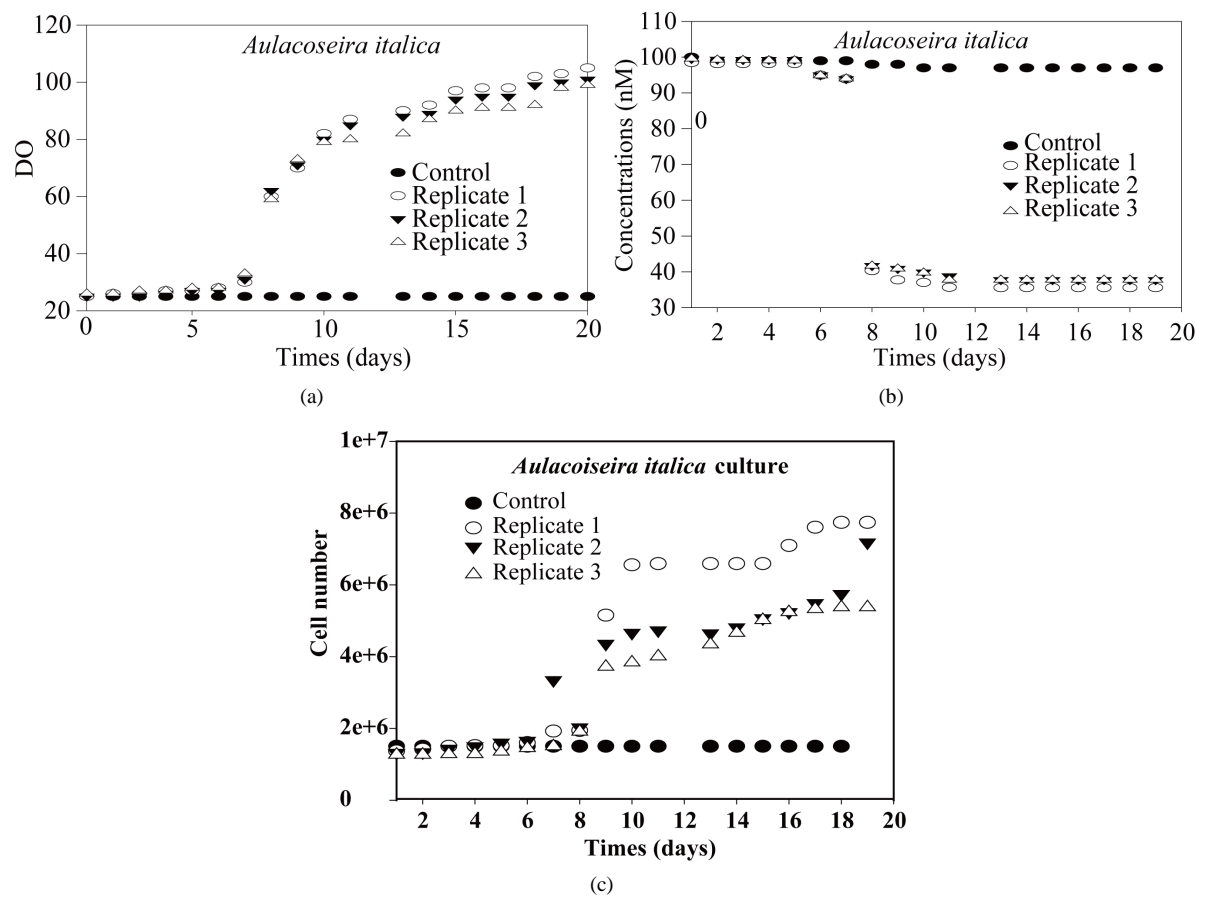
### 6.1. Evidence of Phytoplankton Growth Impact on Dissolved Mo Distribution in the Mixolimnion

Nitrate reductase is an enzyme used both in nitrate assimilation in cells and also during intermediate steps of

**Table 3.** Mass fluxes obtained by traps sediment.

	Flux (g/m <sup>2</sup> /day)							
	23 mm		58 mm		70 mm		88 mm	
Dates of campaigns	without NaN <sub>3</sub>	with NaN <sub>3</sub>	without NaN <sub>3</sub>	with NaN <sub>3</sub>	without NaN <sub>3</sub>	with NaN <sub>3</sub>	without NaN <sub>3</sub>	with NaN <sub>3</sub>
June-06	0.16	*	0.13	*	0.02	*	0.46	*
July-06	0.78	*	0.81	*	0.73	*	1.53	*
August-06	0.13	*	1.99	*	1.12	*	0.34	*
September-06	0.04	*	0.09	*	0.12	*	0.09	*
October-06	0.09	0.2	0.08	0.26	0.22	0.24	0.28	0.3
November-06	0.18	0.21	0.24	0.22	0.3	0.35	0.28	0.41
February-07	0.17	0.19	0.19	0.25	0.11	0.1	0.44	0.65
March-07	3	2.05	0.15	4.01	1.26	1.11	0.67	0.8
April-07	3.49	3.3	5.94	2.53	4.17	2.32	1.34	1.83
May-07	0.38	0.38	2.71	0.312	0.59	0.59	0.67	0.60

\* means traps with single pipe.



**Figure 11.** (a) *Aulacoseira italica* culture: absorbance (DO); (b) *Aulacoseira italica* culture: Molybdenum; (c) *Aulacoseira italica* culture: cell number equivalent.

nitrification. Since both processes are obviously active in Lake Pavin, as well as denitrification as suggested by [70], it would be straightforward to attribute the epilimnion slight depletion in spring and summer to microbiological activity. On one hand, one cannot exclude, tributaries seasonal variations to explain the observation since the average input of  $11 \text{ nmol} \cdot \text{L}^{-1}$  matches closely the winter value of the mixolimnion. On the other hand, during high productivity period for diatoms (late February to late March), it is usual to find more than  $10^7 \text{ cell} \cdot \text{L}^{-1}$ . This would correspond to a growth uptake of  $50 \text{ nmol} \cdot \text{L}^{-1}$  in the right order of magnitude to influence epilimnion

molybdenum concentration. Though the growth dynamics is not completely solved to conclude definitely and the direct transfer from lab pure culture to the field can be strongly biased, this simple approach supports the idea of a visible molybdenum uptake par phytoplankton.

## 6.2. Oxycline Seasonal Change and Molybdenum Adsorption/Release onto/from Metal Oxides

Along with the rise of the oxycline, molybdenum depletion moves also upward in the mixolimnion (*i.e.*, decrease starts shallower), supporting the idea of a removal by adsorption onto authigenic metal oxides. However, the depletion maximum corresponds also roughly to the layers of the “river type” sublacustrine input. The intake of slightly less concentrated water would create the depletion of few  $\text{nmol}\cdot\text{L}^{-1}$ . The use of a dynamic reactive transport model of the lake would probably solve this assumption.

## 6.3. Long Term Control by Iron and Sulfur Species

Removal feature in the mesolimnion has already been observed by [60] [61]. However, the seasonal study allows demonstrating the permanence of this process. Viollier [61] have already published particulate Mo data that demonstrate the strong formation of Mo-bearing particles in the mesolimnion: 2 to 4  $\text{nmol}\cdot\text{L}^{-1}$  were measured. This concentration is very significant in comparison to dissolved molybdenum in the monimolimnion (4 to 10  $\text{nmol}\cdot\text{L}^{-1}$ ). Framboïdal pyrite was also discovered more than a decade ago forming in Lake Pavin [61] while very recent work revealed the presence of  $\text{S}^0$  in micromolar levels and the presence of colloidal FeS which comprises around 70% of total sulfide measured in nonfiltered samples [68] [69].

Thiomolybdates are postulated as key species in sulfidic aquatic systems. However, they are not yet measured in such environments. If thiomolybdates formation is the first step of molybdenum scavenging, these species must be stable in such solution.

Thiomolybdates equilibrium concentrations from the first molybdate sulfuration to monothiomolybdate (0 - 1) until the formation of tetrathiomolybdate (reaction 3 - 4) were calculated by use of MinQL+ (equilibrium calculation software, [73] from Mo and sulfide data measured by colorimetry constants from Erickson and Helz [74] corrected and rearranged according to Lake Pavin ionic strength were used for calculation.

$$\log K_{0-1} = 12.38 \pm 0.03; \log K_{1-2} = 24.5 \pm 0.12; \log K_{2-3} = 36.53 \pm 0.13; \log K_{3-4} = 48.59 \pm 0.28$$

The equilibrium model output is shown on **Figure 12**.

Contrary to the Black Sea [74], there is no total transformation to tetrathiomolybdate due to a lack of free sulfide. At the most, dissolved molybdenum in the monimolimnion is roughly half under the form of molybdate and half under the form of monothiomolybdate, the less reactive form of thiomolybdates. Vorlíček [4] suggest that thiomolybdates adsorbed onto iron sulfide and onto pyrite form Fe-Mo-S cluster stabilized by the reduction of Mo(VI) to Mo(V or IV) in presence of  $\text{H}_2\text{S}$  and S(0)-donors. More recently Helz *et al.* [42] even suggest a mineral's formula that applies in sulfidic anoxic marine environment ( $\text{Fe}_5\text{Mo}_3\text{S}_{14}$ ) however the same model does not fit completely Lake Pavin Mo data. Until now thiomolybdates cannot be measured in the environment directly but Lake Pavin mesolimnion seems to have all necessary conditions to fit the more consensual removal pathway of dissolved molybdenum in sulfidic environment: thermodynamically possible thiomolybdates formation, adsorption onto and co-precipitation with iron sulfide.

The subsistence of stable molybdate in the monimolimnion and its association with natural organic matter [38] would most probably explain the incomplete removal of dissolved molybdenum for the anoxic compartments. Viollier [61] showed that iron oxyhydroxides formed in the mixolimnion of Lake Pavin mainly dissolve at the sediment-water interface. The reductive dissolution of these carrier phases would release molybdenum and contribute to the deep enhancement of its concentration. This statement is highly in accordance with FeS profile previously given in papers [68] [69].

## 7. Conclusion

The seasonal study of dissolved molybdenum allowed the observation of transient phenomenon likely explained by microalgae uptake in the epilimnion. Oscillating feature of dissolved molybdenum depletion at intermediate depth is explained by adsorption onto iron and manganese oxyhydroxides and/or by the injection of a sublacu-

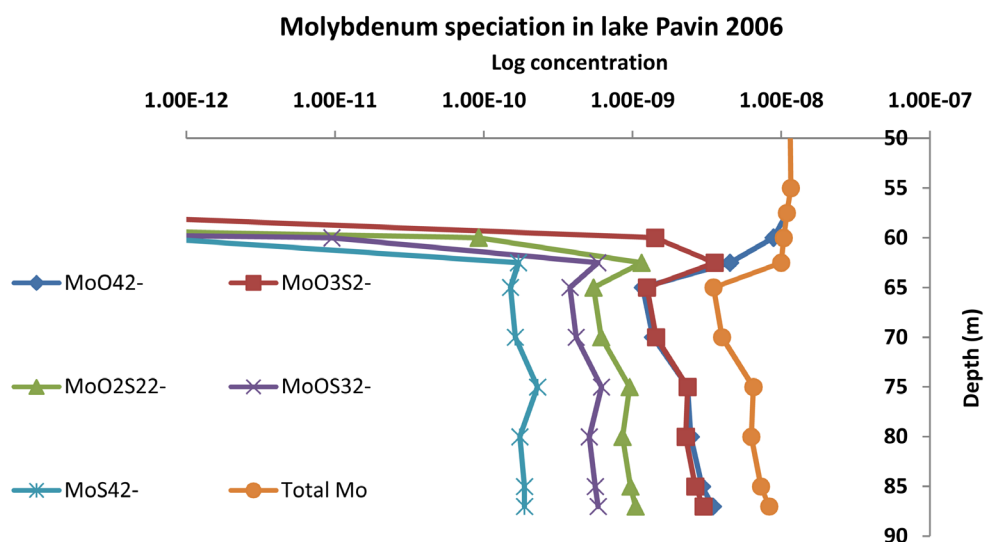


Figure 12. Dissolved molybdenum speciation in Lake Pavin.

strine input containing lower molybdenum concentration. The depletion zone, however, follow more or less the oxycline rise up. This characteristic would argue for the adsorption pathway. In this work, it has also been shown that strong removal in the sulfidic zone is permanent and does not respond significantly to seasonal changes. The most favorable removal pathway involves thiomolybdates formation and reaction with authigenic iron sulfides. At what extent, natural organic matter is involved in long term removal or burial of molybdenum, is still in debate.

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