

# **Sulphur speciation in the Late Glacial and Holocene sediments of the Lac du Bouchet (Haute Loire, France).**

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**Key-words-** *carbon bounded sulphur, sulphate-esters, pyritic sulphur, PO<sub>4</sub>-exchangeable sulphur, lacustrine sediment.*

**Abstract-** Four main sulphur forms have been identified and quantified in sediments of the Lac du Bouchet. These forms and, obviously, the total sulphur, present variations that follow those of the organic carbon. At the end of the Würm and during the Late Glacial which were periods of low productivity, sediments have low sulphur contents (<1000 µg/g) and the predominant form is the sulphate-ester fraction. During the Holocene, when the lacustrine and terrestrial biomass had developed, higher sulphur (up to 5500 µg/g) and carbon contents vary concomitantly. In Holocene sediments, the carbon bonded sulphur fraction increases to levels equal to or slightly higher than the sulphate-ester fraction. The mineral forms, identified as adsorbed sulphate and pyrite, represent a minor part of the total sulphur.

## **Introduction-**

Sulphur dynamics have been studied for a long time in marine environments in which the microbial transformation of sulphate into sulphide leads to the formation of pyrite and to the sulphuration of organic matter. In freshwater environments and especially for lake sediments, research has been encouraged by the recent increase of the acidity of atmospheric deposition in which sulphate is a major anionic component (Cook and Schindler, 1983; Nriagu and Soon, 1985; Rudd *et al.*, 1986).

The Lac du Bouchet is a crater lake situated at the middle of a small watershed. As the lake surface represents 31% of the watershed surface (Decobert and Bonifay, 1991), the lake acts as a pluviometer (Viollier *et al.*, this volume) and collects organic and mineral particles transported over very short distances. Presently, the forest environment is composed of spruce plantings and mixed fir and beech open forests. The mean annual rainfall is 870 mm (Truze, 1990) and the concentration of sulphate in rainwater is probably close to 3 mg/l with slight interannual variations around this value. Nevertheless, it is also probable that sulphate concentrations in rainwater have varied strongly in the past due to intense volcanic activity that occurred in the closed area of the Chaîne des Puys, mainly around 8,300 yrs BP and from 6,600 to 5,700 yrs BP (Brousse *et al.*, 1969). This research deals with the forms and the distribution of sulphur in the lake sediments. Four main forms have been easily quantified on the basis of parallel and sequential extractions of sulphur fractions.

## Sampling-

The Lac du Bouchet (elevation : 1205m) is a sub-circular crater lake, 28 m water depth (Viollier *et al.*; Jézéquel *et al.*, this volume) located in the Massif Central (France) at the Devès Plateau (Sifeddine *et al.*, this volume). Sediments were sampled from the LDB.X core which was recovered from the center of the lake in September 1990. The 2.80 m long core was kept cool at 4°C before the selection of samples (5 cm thick) used for this study. The samples were freeze-dried and finely ground.

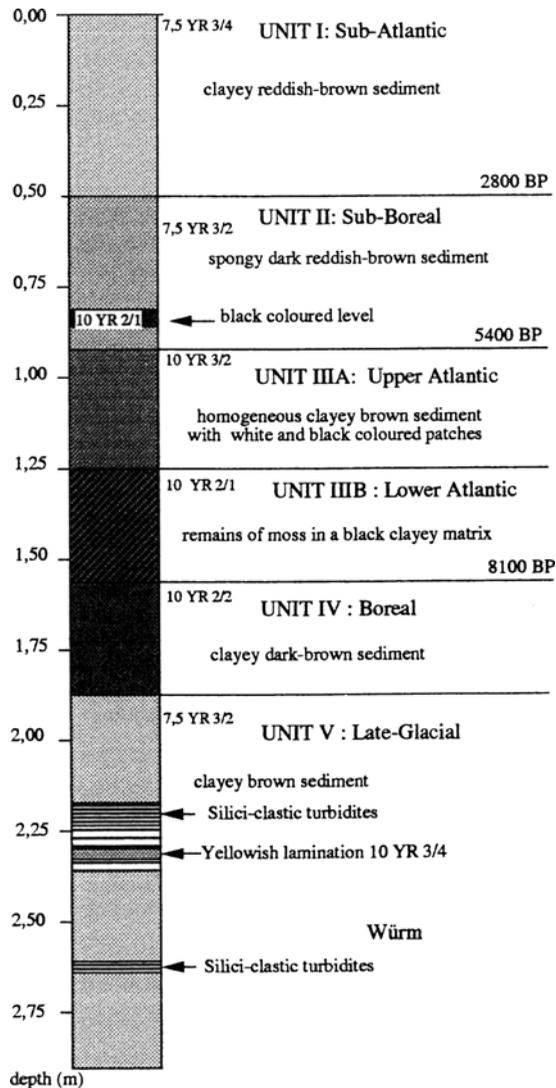


Figure 1: Description of the core LDB X. (after Lallier-Vergès *et al.* 1993)

Five main sedimentary units were distinguished from the color and texture of the sediment, and from analyses of palynofacies and organic matter types. The biostratigraphic chronosequence of these units was presented by Lallier-Vergès *et al.*, (1993) on the basis of the pollen analyses of the sediments. All periods of the Holocene have been recognised, except for the Preboreal. Figure 1 presents the chronosequence and the characteristics of the sediments. 18 samples were selected, namely 5, 3, 5, 2 and 3 samples for the Sub-Atlantic, Sub-Boreal, Atlantic, Boreal and Late-Glacial periods respectively.

## **Methods-**

The chemical procedures performed for the determination and the quantification of various sulphur forms derive from the methods described by Johnson and Nishita, (1952), Zhabina and Volkov (1978) and Wieder *et al.*, (1985).

### *Methods of sulphur determination-*

Two methods were used for sulphur determination according to the status of the material in which sulphur has to be determined. Sulphur in liquid extracts was determined in ICP atomic emission spectrometry (ICP AES) whereas sulphur in solid samples must be transformed into a volatile form ( $H_2S$ ) before its determination by the method of Johnson and Nishita (J-N).

For the latter method, a sample was introduced in the boiling flask of the J-N distillation device in the presence of a reducing solution of hydriodic acid (HI) and Na-hypophosphite ( $NaH_2PO_2$ ). The reaction is generated under reflux in a nitrogen flow. The released hydrogen sulphur is trapped in a solution of zinc acetate. Then, the formation of methylene blue is developed from the reaction of the zinc sulphur with a p.amino-dimethylanilin solution in the presence of  $Fe^{(III)}-NH_4$  sulphate. The sulphur dosage is run by colorimetry at 670 nm.

### *Total sulphur and sulphur forms-*

To determine total sulphur, the oxidation method using Na-hypobromide (Tabatabai, 1982) was preferred to others owing to its good repeatability.

The identified and quantified forms are presented in figure 2. It is assumed that oxidised forms such as adsorbed sulphate ( $\text{SO}_4^{2-}$ ) and sulphate-esters ( $\text{Est-SO}_4^{2-}$ ) may coexist with reduced forms. The latter could be mineral such as elemental sulphur ( $\text{S}^\circ$ ), metastable sulphur minerals called "acid volatile sulphur" in this paper (AVS) and pyrite (Py.S.). Organic sulphur forms in which sulphur atoms are bonded to carbon atoms (S-C) can also be present. A series of reagents used on various sediment assays allowed the evaluation of the amounts of sulphur attributable to the various forms.

*a - Determination of the sulphur forms directly reducible by HI mixture.*

As shown in figure 2, the reagent reduces inorganic and organic sulphate as well as elemental sulphur and dissociates labile sulphur forms (Wieder *et al.*, 1985). Samples (50 mg) were treated under reflux in the J-N distillation device for 20 minutes. Results are means of duplicate runs.

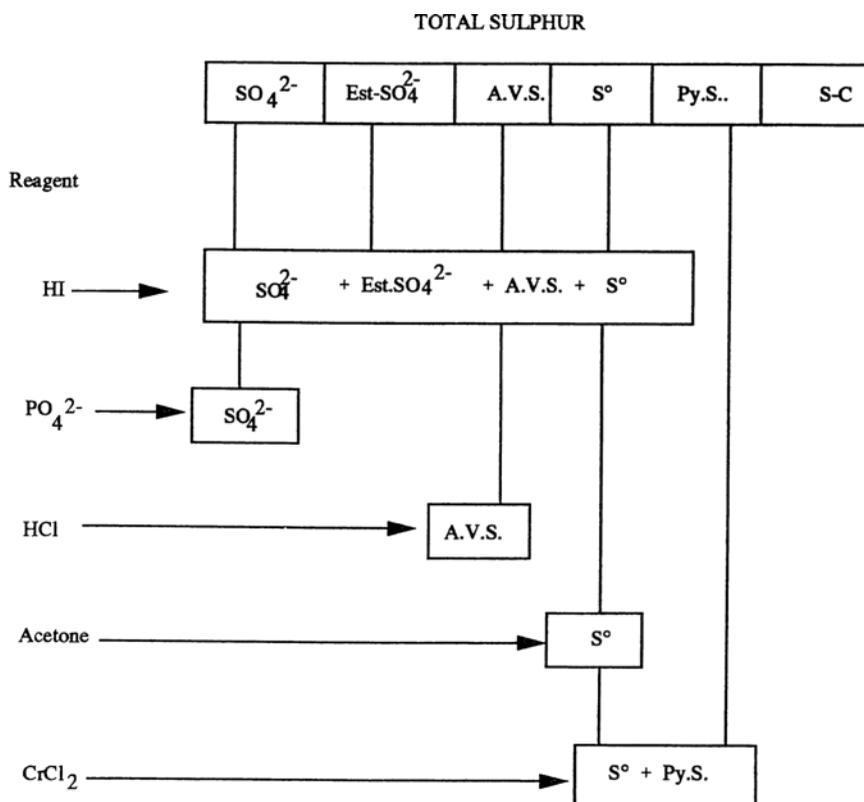


Figure 2: Flow chart of sulphur speciation analysis

*b - Determination of adsorbed sulphate.*

This form was extracted by a phosphate solution buffered at pH 6 ( $\text{KH}_2\text{PO}_4$  0.1M, NaOH 0.1M and water in proportions of 50/5.6/44.4) because this reagent has been used successfully in various kinds of soils exposed to atmospheric sulphur pollution (Vannier *et al.*, 1993). The sample (500 mg) was agitated by rotation (40 r/min.) for one hour in the presence of 2.5 ml of the buffer solution. After centrifugation and filtration, sulphur of the filtrate was determined by ICP AES.

*c - Determination of elemental sulphur.*

The extraction procedure is similar to that described by Wieder *et al.*, (1985) using acetone as extractant. The sample (150 mg) was agitated for 16 hours with 10 ml of acetone in a hermetic flask. After filtration, 2 ml of the filtrate was introduced in the boiling flask of the J-N distillation device and the reduction of elemental sulphur was done with the HI reagent.

*d - Determination of acid-volatile sulphur.*

This form was determined by introducing 150 mg of sample in the boiling flask of the J-N distillation device and 15 ml of 6N HCl. The material was kept at boiling point for 30 mn. Unstable metallic sulphide compounds were decomposed and the evolved  $\text{H}_2\text{S}$  was trapped in the zinc acetate solution. After cooling, the whole suspension of the boiling flask was centrifuged. The solid residual fraction was kept as aqueous suspension in a vial under  $\text{N}_2$  and was used for the determination of the elemental sulphur together with the pyritic sulphur.

*e - Determination of pyritic sulphur.*

The entire solid residue resulting from the HCl attack was immersed in the boiling flask of the N-J distillation device. Before adding 15 ml of a chromium(II) solution and 4 ml of 12N HCl, it was necessary to evacuate oxygen from the device by means of a nitrogen flow. Heat was applied after 5 minutes and the reaction time was fixed at 45 minutes. The evolved  $\text{H}_2\text{S}$  was trapped in zinc acetate solution and the dosage of sulphur was performed with the methylene blue method. The use of the chromium(II) solution has been recommended by Zhabina and Volkov (1978) and Howarth and Jorgensen (1984). This reagent was prepared from an acid solution of chromium(III) percolating through a Jones reductor following the method described in Skoog and West (1966).

## Results-

### *Distribution of organic carbon, organic nitrogen and total sulphur-*

The total organic carbon (TOC) contents vary from 6.4 to 255.0 mg.g<sup>-1</sup> (Table 1), with the lowest values observed in Würmian and Late-Glacial sediments (Unit V) and a peak (Unit III) corresponding to a large layer of moss stalks of *Fontinalis* (255.0 mg.g<sup>-1</sup>). Unit I at the top of the core has TOC values of about 75 mg.g<sup>-1</sup>.

The profile of organic nitrogen is the exact copy of TOC distribution (figure 3). In the Holocene sediment, the C/N ranges from 12 to 14 except for the level where *Fontinalis* is abundant (C/N = 19.1). An analysis of selected stalks of *Fontinalis* yields a TOC content of 358.4 mg.g<sup>-1</sup> and a C/N ratio of 42 which indicates that this aquatic moss is an important component of the sediment at certain levels of Unit III.

	Depth (cm)	Org. C (mg.g-1)	Org. N (mg.g-1)	Total S. (mg.g-1)	C/N atm.	N/S atm.
<b>Sediment samples</b>						
11211	5-15	83.40	8.10	1.87	21.0	9.9
11214	20-25	74.00	7.40	1.61	11.7	10.5
11216	30-35	76.40	7.30	1.73	12.2	9.6
11218	41-50	78.10	6.80	1.60	13.4	9.7
11220	50-55	85.50	7.40	1.77	13.5	9.6
11222	60-65	131.00	10.70	3.00	14.3	8.2
11225	75-80	162.20	n.d	3.87	n.d	n.d
11228	90-95	117.90	n.d	2.31	n.d	n.d
11230	100-105	114.00	8.50	2.03	15.7	9.6
11233	115-120	126.40	n.d	2.70	n.d	n.d
11238	140-145	255.00	15.60	4.62	19.1	7.7
11239	145-150	234.40	nd	4.70	n.d	n.d
11240	150-155	177.60	nd	5.54	n.d	n.d
11243	165-170	91.30	8.20	2.70	13.0	6.9
11247	185-190	33.30	n.d	1.30	n.d	n.d
11250	200-205	10.50	n.d	0.77	n.d	n.d
11255	225-230	7.20	1.00	0.74	8.4	3.1
11264	270-275	6.40	0.90	0.59	8.3	3.5
<b>Fontinalis</b>		359.10	33.70	2.99	12.4	25.7

Table 1: Organic carbon, organic nitrogen and total sulphur contents.

The total sulphur contents vary from 590 to 5535  $\text{mg.g}^{-1}$  the highest values being observed at the levels where *Fontinalis* is abundant (specially 150-155 in Unit III). A sample of *Fontinalis* collected in a mesotrophic river provided atomic C/N and N/S values of respectively 12.4 and 25.7 ( $\text{TOC} = 359.1 \text{ mg.g}^{-1}$ ). This N/S value appears to be lower than the atomic ratio value of higher plants having a modal composition in proteins and amino-acids ( $\text{N/S} = 34$ ; cf. Mitchell *et al.*, 1992). As is shown in table 1, the N/S ratios of sediments are considerably lower, suggesting that sulphur forms other than proteic sulphur are present.

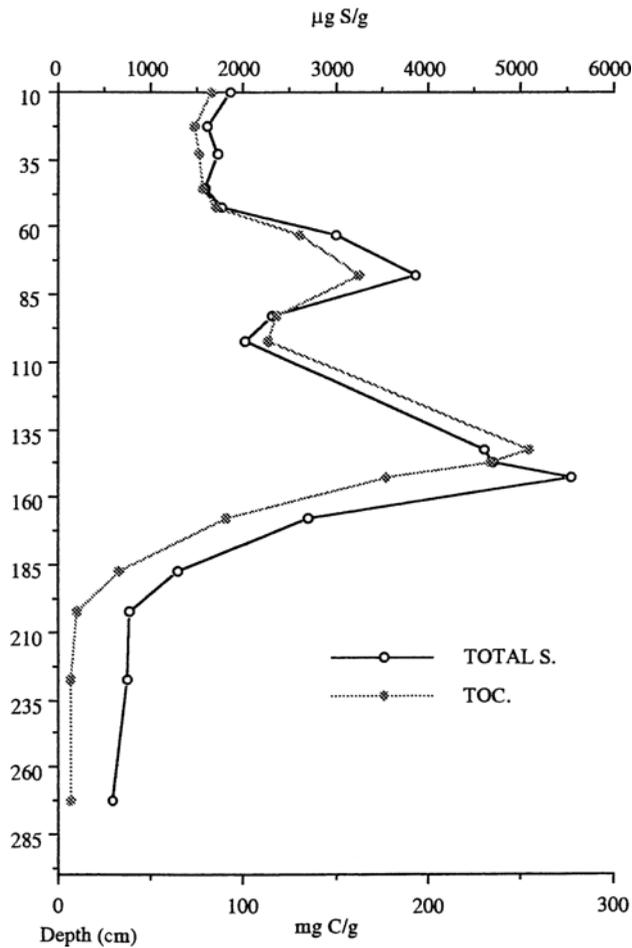


Figure 3: Variation of organic carbon and total sulphur in sediments

*Inventory and quantification of sulphur forms (Table 1)-*

*a - PO<sub>4</sub>-exchangeable sulphate.*

In the Holocene sediment, the content of PO<sub>4</sub>-exchangeable sulphate is relatively constant with an average amount of 150 mg.g<sup>-1</sup> which represents nearly 8% of total sulphur. The levels from 60 to 80 cm and from 140 to 170 cm have higher values which are correlative to larger contents of total sulphur. So the maximum content is observed at the levels where the stalks of *Fontinalis* are abundant. Despite their low values in total sulphur, the Würmian and Late Glacial sediments exhibit the highest percentages of adsorbed sulphate.

Concerning *Fontinalis*, the phosphate buffer dissolved 17% of the total sulphur (510 mg.g<sup>-1</sup>) which probably represents organic sulphur or/and sulphate salts.

*b- Acid-volatile sulphur and elemental sulphur.*

As the optic density of the methylene blue was very close to that of the blank, we concluded that these two sulphur forms have not been identified. In fact, traces of elemental sulphur (S<sup>o</sup>) and acid-volatile sulphur (AVS) might be present at the top and at the bottom of the core respectively.

*c-Sulphur forms reducible by the HI-Phosphite reagent : evaluation of the sulphate-ester fraction.*

The profile of this sulphur compartment has the same design as that of total sulphur. This compartment includes PO<sub>4</sub>-exchangeable sulphate (SO<sub>4</sub><sup>2-</sup>), sulphate-esters (Est-SO<sub>4</sub><sup>2-</sup>), elemental sulphur (S<sup>o</sup>) and acid-volatile sulphur (AVS).

$$(S-HI) = (Est-SO_4^{2-}) + (SO_4^{2-}) + (S^o) + (AVS).$$

As the elemental sulphur (S<sup>o</sup>) and the acid-volatile sulphur (AVS) have not been identified, the sulphate-ester fraction was deduced from the following equation :

$$(Est-SO_4^{2-}) = (S-HI) - (SO_4^{2-})$$

Figure 4 shows that sulphate-esters are a sizeable sulphur fraction, varying from 28 % to 62 % of the total sulphur. The percentage of this fraction is much higher in the Late Glacial and Würmian sediments than in the Holocene sediments.

The aquatic plant *Fontinalis* contained 490 ppm of reducible sulphur by HI. The similarity of results obtained by HI analysis and in the extract of the phosphate buffer (510 ppm) suggests that there is only one compartment of the oxidised sulphur, containing probably sulphated salts. These represented 17% of total sulphur.

*d - Pyritic sulphur.*

The mean content was about  $50 \mu\text{g.g}^{-1}$  except in some levels rich in organic matter where the values can reach several hundred  $\mu\text{g}$  per gram of sediment (table 2 and figure 4). It is well known that the organic matter is an essential constituent in the development of the sulphate reduction and consequently to the genesis of pyrite. However there is no exact relationship between the organic carbon content and the pyrite content of sediment. For example, at the 100-105 cm level, the organic carbon content ( $114 \mu\text{g/g}$ ) is slightly lower than at the 60-65 cm level ( $131 \mu\text{g/g}$ ) whereas the pyritic sulphur content is considerably lower ( $35 \mu\text{g.g}^{-1}$  instead of  $178 \mu\text{g.g}^{-1}$ ). This indicates that the genesis of pyrite is considerably influenced by the nature of the organic matter.

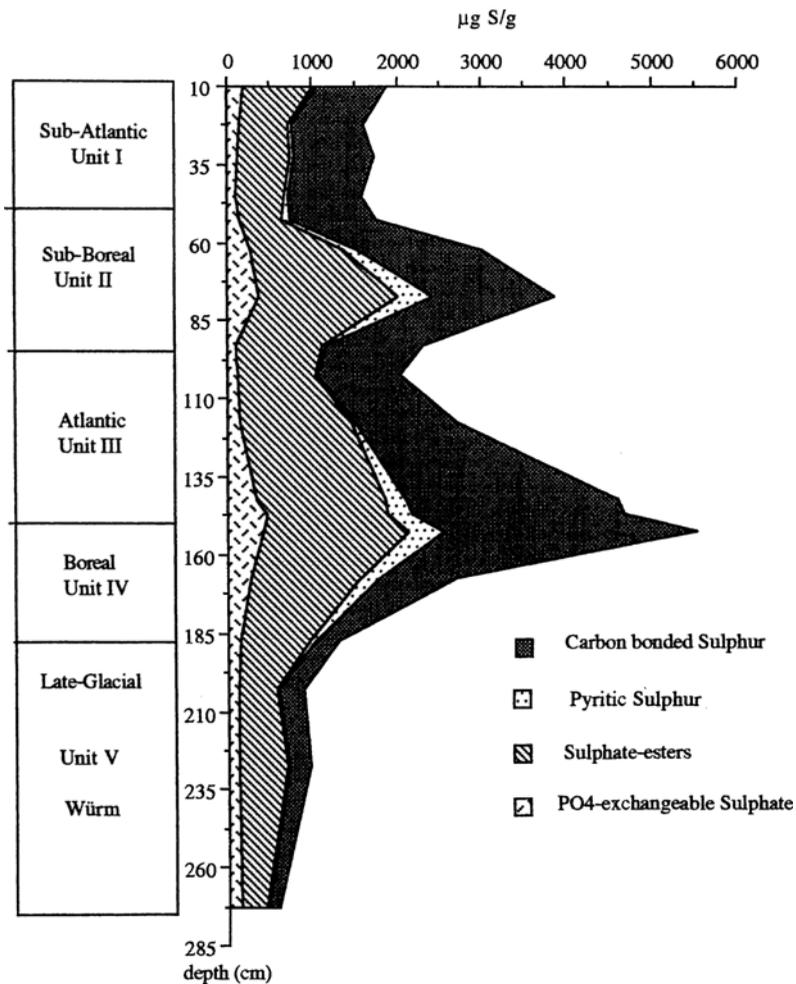


Figure 4: Variation of the Sulphur forms

Sediment samples	Depth (cm)	Total S. ( $\mu\text{g.g}^{-1}$ )	SO <sub>4</sub> ( $\mu\text{g.g}^{-1}$ ) (%)	S - HI ( $\mu\text{g.g}^{-1}$ ) (%)	Est. SO <sub>4</sub> ( $\mu\text{g.g}^{-1}$ ) (%)	Py. S. ( $\mu\text{g.g}^{-1}$ ) (%)	S- C ( $\mu\text{g.g}^{-1}$ ) (%)
11211	5-15	1875	195 10	1010 54	815 44	50 3	815 43
11214	20-25	1610	160 10	730 45	570 35	40 2	840 52
11216	30-35	1735	115 7	755 44	640 37	35 2	945 54
11218	41-50	1595	105 7	675 42	570 35	45 3	875 55
11220	50-55	1770	160 9	650 37	490 28	90 5	1030 58
11222	60-65	2995	275 9	1350 45	1080 36	180 6	1465 49
11225	75-80	3870	365 9	2020 52	1655 43	410 11	1440 37
11228	90-95	2310	110 5	1125 49	1015 44	40 2	1145 50
11230	100-105	2030	115 6	1030 51	915 45	35 2	965 48
11233	115-120	2695	150 6	1455 54	1305 48	45 2	1195 44
11238	140-145	4620	355 8	1870 40	1515 32	230 5	2520 55
11239	145-150	4695	470 10	1895 40	1425 30	275 6	2525 54
11240	150-155	5535	420 8	2135 39	1715 31	420 9	2980 54
11243	165-170	2700	280 10	1560 58	1280 48	215 8	925 34
11247	185-190	1305	160 12	975 75	815 63	70 6	260 20
11250	200-205	885	130 15	565 64	435 49	30 4	290 33
11255	225-230	970	125 13	705 73	580 60	25 2	240 25
11264	270-275	590	140 23	435 74	295 51	25 4	130 22
<i>Fontinalis</i>		2995	510 17	490 16		22 0.7	2505 84

Table 2: The various sulphur forms: contents and percentages of total Sulphur.

In *Fontinalis* samples, traces of sulphur have been identified as pyrite (0.7% of the total sulphur), but this slight amount probably derives from the breakdown of organic sulphur and from the distillation of volatile sulphur.

*e - Carbon bonded sulphur.*

This form results from the difference between the total sulphur and the sum of HI-reducible sulphur and pyritic sulphur. It represents sulphur amounts that are almost equivalent to those reducible by the HI mixture. However, in Würmian and Late Glacial sediments, the S-C forms are slightly less abundant than HI-reducible forms.

Using the N content of *Fontinalis* presented in table 1 and the value of the S-C fraction (2.50 mg/g), one finds a N/S atomic ratio of 31 that is more compatible with the nitrogen- and sulphur-bearing amino acids of plants.

## **Discussion-**

The sulphur variations replicate the organic carbon variations (fig. 3). This parallelism is the result of the productivity and biomass changes that have occurred in the lake itself and in its watershed since the end of the Würm. Whereas the Würmian and Late Glacial sediments have low contents in organic carbon and sulphur, the Holocene sedimentation clearly shows two peaks for each element. The first peak (Unit III) corresponds to the base of Atlantic period which was warmer and more rainy than the present (Reille and de Beaulieu, 1988). The development of a dense mixed-oak forest in the watershed probably led to an important leaching of nutrients from the soils. The consequence was an increase of the primary productivity of aquatic organisms. The high content in organic matter and sulphur, especially in organic sulphur, appears to be related to the abundant presence of plant remains such as the aquatic moss *Fontinalis*. The growth of this moss in the euphotic zone requires support such as immersed rocks or tree trunks, which is unrealistic considering the water-depth at the center of the lake. Thus, its sedimentation is thought to be due to transport mechanisms. The second peak was found in sediments dated of the Sub-Boreal period (Unit II) in which beech forest replaced the oak forest

The organic sulphur forms, including sulphate-esters and carbon bonded sulphur represent the largest part of the total sulphur. The mineral forms identified as  $\text{PO}_4^{2-}$ -exchangeable adsorbed sulphate and pyritic sulphur are minor fractions. This sulphur distribution confirms previous results obtained in various lake sediments (Nriagu and Soon, 1985). However, slight differences appear in the relative distribution of organic and mineral sulphur according to the environmental conditions of sedimentation.

In the Würmian and Late Glacial sediments, the sulphate-esters constitute the most important compartment of organic sulphur and predominate over the carbon bonded sulphur compartment. As sulphate-esters are known to be microbially mediated in soil environment (Fitzgerald, 1976), one can assume that the sulphate-esters are also biosynthesised into lacustrine sediments. The low C/N (8, cf. table 1) of the organic matter is in agreement with the hypothesis of a large proportion of organic matter of microbial origin.

During the Holocene and especially after the Boreal period, the dominating carbon bonded sulphur forms appear in relation with inherited organic matter. The parallel increase in organic carbon and sulphur during the Holocene is to be related to the development of biomass in the watershed as well as in the lake itself and to the transport of partially degraded remains and humified compounds deriving from the soils as assessed by the optical study of the sedimentary organic matter (Lallier-Vergès *et al.*; 1993; Patience *et al.*, this volume). In such humified products, sulphate-esters can be present especially in fulvic acids (Vannier and Guillet, 1994) and linkages between sulphur and carbon atoms may exist under more stable forms than those existing in amino acids. Knowing the low productivity of terrestrial ecosystems in periglacial environments (Gore, 1983), we can assume according to Sifeddine *et al.* (this volume) that during the Late Glacial period, very few humified remains of higher plants were transported towards the bottom of the lake.

Sulphur in oxidised state, as adsorbed sulphate and sulphate-esters, represents 65 to 75% of the total sulphur of Würmian and Late Glacial sediments and 35 to 60 % of total S in Holocene sediments. Given that careful precautions were taken during the sampling and that the oxidation of the material was negligible, these high values of oxidised sulphur preclude the hypothesis of strongly anoxic conditions in the sediments.

However, pyritic sulphur is present in sediments where a large proportion of carbon bonded sulphur forms was found (fig. 4). Pyrite is mainly located inside cells of vegetal remains as has often been observed in sediments of the Lac du Bouchet (Patience *et al.*, this volume). In such microsites, the formation of pyrite was efficient because of the development of local microbial sulphate reduction.

## **Conclusion-**

The organic sulphur forms are considerably more abundant than mineral sulphur forms corresponding to adsorbed sulphate and pyrite. In the Würmian and Late Glacial sediments, sulphate-esters are the main organic sulphur forms, and their formation

appears to be related to the presence of organic matter, probably of microbial and phytoplanktonic origin rather than terrestrial origin. During the Holocene, the influence of the aquatic ecosystems of the lake shore and of the forest ecosystems contributes to the concomitant increase of carbon and sulphur in sediments. The organic forms in which sulphur is linked to carbon notably increase. From a geochemical point of view, the sedimentation conditions do not seem to have been highly anoxic, since the adsorbed sulphate and the sulphate-esters represent almost half of total sulphur in Holocene sediments and even much more in Würmian and Late Glacial sediments.

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