The origin of S and O isotope ratios in lakewater sulphate

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Introduction

Sulphur is an important bioelement and the main form of sulphur in water is the dissolved sulphate. The dissolved sulphate, in turn, is the major substrate for microbial sequestration of organic compounds and inhibitor of methane ebullitive flux from freshwater sediments. This paper reports systematic study of sulphate ion dissolved in water and bubble methane from sediments of 30 freshwater aquifers (lakes, ponds, rivers) from Poland.

Results

The highest concentration of sulphate has been detected in rivers (85.47 SO_4^{2-} mg/l) and in an artificial lake (70.3 SO_4^{2-} mg/l) located in the E margin of the extremely SO_4^{2-}-polluted region, in SW Poland, called Black Triangle (Jedrysek 2000). The lowest concentration of sulphate has been detected in dystrophic and mountain lakes (from 0.5 to about 3.0 SO_4^{2-} mg/l). The lowest $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values have been detected in unpolluted lakes in Eastern Poland (-0.94 and 1.38 ‰, respectively). The highest $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values have been detected in polluted lakes in western Poland and dystrophic lakes (12.95 16.15 ‰, respectively).
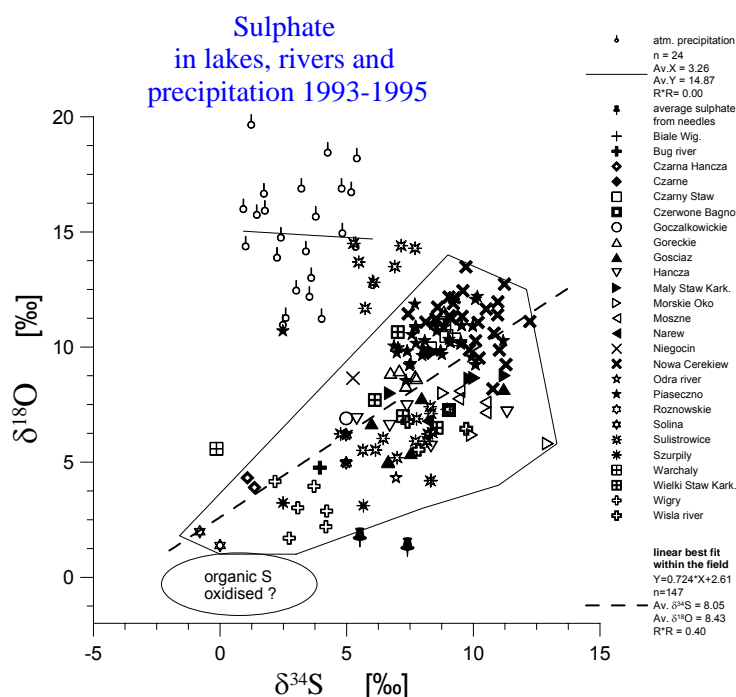
Fig. 1. Sulphur and oxygen isotope ratios in sulphate dissolved in lake water. Sulphur and oxygen isotope variations in lake water may results from some ongoing processes. The points behind the field represents rain from Wroclaw downtown (SW Poland, see Jedrysek 2000), surficial lakewater collected during/after heavy rains or spruce needles sulphate.

Discussion

In the region under study, the anthropogenic sulphate has about 10 ‰ higher $\delta^{18}O$ value than its natural analogue (Jedrysek 2000). The isotopic composition of sulphate in the rain in Wroclaw downtown shows no correlation in the oxygen and sulphur isotope system and the R^2 coefficient is 0.00 (Fig. 2). Therefore, the $R^2 = 0.4$ found in lakewater sulphate cannot be ignored and should be elucidated.

The isotope signature of sulphate dissolved in lakewater can isotopically evolve due to microbial reduction, mixing with its natural analogues (geogenic, oceanic) or formation of sulphate (oxidation). Therefore, the mixing ratio of these three main sources of sulphate together with reduction of sulphate are the main factors controlling concentration and isotopic signature of the sulphate in lakes. The lake-born sulphate in lakes (aquatic sulphate) is the sulphate formed form oxidation of reduced sulphur compounds in lakes. In contrast to clean lakes, an increase of the $\delta^{13}C(CH_4)$ value with increasing depth of the water column in strongly SO_4^{2-} contaminated lake has been observed (Jedrysek 1998). It may resulted from exceeding of the biological buffering potential of the lake reflected by an active oxidation of methane and methane precursors.

Two biogenic sources of sulphate in lakes, (i) allochtonous or terrestrial that formed by terrestrial organisms (macrophytes, oxidation in soil *etc*.) and (ii) autochtonous aquatic -

that formed by aquatic organisms (*e.g.* Krouse *et al.,* 1991). The $\delta^{18}O$ value of the atmospheric oxygen is rather stable and isotopically heavy, but $\delta^{18}O(H_2O)$ value in precipitation varies seasonally. Likewise, evaporation from lakes causes a significant enrichment of the lakewater, while lakes at higher elevations or at higher latitudes shows lower $\delta^{18}O(H_2O)$ value accordingly to decreasing $\delta^{18}O(H_2O)$ value in meteoric precipitation (*e.g.* Różański *et al.,* 1993). In fact, it has been shown that in precipitation annual variations in the $\delta^{18}O(SO_4^{2-})$ value roughly corresponds to the annual variations in $\delta^{18}O(H_2O)$ (*e.g.* Lloyd 1968; Longinelli and Cortecci 1970; Trembaczowski 1991, 1994).

Lakes are often surrounded by coniferous forests which, in much larger rates than deciduous trees, assimilate SO_2 from the atmosphere and store it in their needles in the form of organic sulphur compounds and sulphate. The sulphate in needles is usually about 3.5 ‰ enriched in ^{34}S isotope compared to organic sulphur. Moreover, in SO_2-contaminated regions, conifers remove excessive sulphur in the form of H_2S, which results in additional ^{34}S and ^{18}O enrichment of the retained needle sulphate (Jedrysek *et al.,* 2002). Sulphate from shedded needles is easy mobilized by rainwater and transported through streamwater and groundwater to the neighbouring lakes. Consequently, the lakes receive additional input of sulphate from coniferous forested catchments. Besides, evaporation of lakes also slightly increases concentration of sulphate, however this is probably less important than the terrestrial biosphere input. In fact, in most mountainous lakes, surrounded dominantly by dwarf mountain pine (*Pinis mughus*) and spruce (*Picea abies*), concentration of the sulphate in lakewater was found to be higher than in the local precipitation (Jedrysek – in preparation). This can be explained from rough calculations. Namely, average concentration of sulphate on the surface of needles, inside needles and organic sulphur is 0.03, 0.01 and 0.1%, respectively (Jedrysek *et al.,* 2002). On the other hand, the total quantity of the litter from coniferous vegetation amounts from about 0.8 to 3.0 t/ha/year (*e.g.* Schall 1991; Oleksyn – oral information) and the total quantity of the litter from, the comparable to the mountain lakes studied, shrub *Pinus mugo Turra* high mountain and subalpine belt of the Romanian Carpathians (1500-2200 m) amounts to 2.6 t/ha/year (Coldea and Plamada 1978). When 20 % of organic S is oxidised to sulphate and when practically all sulphate is removed from shedded needles, the total output of SO_4^{2-} from these needles to the ecosystem is more than 1 t/ha/year. That means that in a typical mountainous lake (small watershed, deep) surrounded by coniferous vegetation, the total input of SO_4^{2-} can be estimated to vary between 10 to 100 mg/l of lakewater per year. Hence, the

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SO_4^{2-} is dominantly of allochtonous biogenic origin and from isotopic mass balance point of view the SO_4^{2-} from precipitation is negligible, because concentration of SO_4^{2-} in precipitation is usually between much less than 1 and not higher than 10 mg/l. Consequently, coniferous areas may determine concentration of sulphate in freshwater systems (including groundwaters) thus control oxidation of organic compounds in freshwater sediments and the water column in freshwater systems.

Although, sulphur isotope ratios in the needles (sulphate and organic sulphur) are generally similar to that in precipitation, the $\delta^{18}O(SO_4^{2-})$ value in needles is significantly lower than that in precipitation (Fig. 2). This is due to the fact, and in contrast to atmospheric sulphate (see above), that the needle sulphate forms within the needles and the oxygen in it comes from isotopically depleted water (in average $\delta^{18}O$ during vegetation season is about –12 ‰). In addition, the low $\delta^{18}O(SO_4^{2-})$ value in needles is due to the fact that a large part of sulphate is formed in needles during winter when the assimilation is active and local precipitation show lowest values in the annual cycle. Likewise, it can be expected that sulphate, formed due to oxidation of shedded needles organic sulphur, may show slightly lower $\delta^{18}O(SO_4^{2-})$ value than the needle sulphate when the latter experience advanced reduction resulting in ^{34}S and ^{18}O isotope enrichment of the residual sulphate. Therefore, the allochtnonus sulphate can be largely responsible for the $\delta^{34}S(SO_4^{2-})$-$\delta^{18}O(SO_4^{2-})$ correlation in lakes.

Conclusions

1. Most lakes shows an individual $\delta^{34}S$ and $\delta^{18}O$ signal and relatively little variations in its $\delta^{34}S$ and $\delta^{18}O$ system

2. $\delta^{18}O(SO_4^{2-})$ and $\delta^{34}S(SO_4^{2-})$ values, in many of the lakes, is controlled by mixing ratio between sulphate from precipitation and that of biogenic (allo- and autochtonous) origin and microbial reduction of sulphate. Biogenic sulphate of terrestrial origin can be the main source of sulphate on lakes with watershed dominated by coniferous vegetation.

3. Degraded eutrophic lakes show high $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2})$ values while clean or oligotrophic lakes show low $\delta^{34}S(SO_4^{2})$ and $\delta^{18}O(SO_4^{2})$ values.

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