

# Sulphate Sources in the Sava and Ljubljana Rivers, Slovenia, Inferred from Sulphur and Oxygen Isotope Compositions

BARBARA VOKAL-NEMEC<sup>1</sup>, JANINA SZARAN<sup>2,\*</sup>, ANDRZEJ TREMBACZOWSKI<sup>2</sup>, STANISLAW HALAS<sup>2</sup>, TADEJ DOLENEC<sup>3</sup> and SONJA LOJEN<sup>4</sup>

<sup>1</sup>*Slovenian Nuclear Safety Administration, Zelezna cesta 16, 1000, Ljubljana, Slovenia;* <sup>2</sup>*Institute of Physics, Maria Curie-Sklodowska University, Plac M. Curie-Sklodowskiej 1, 20-031, Lublin, Poland;* <sup>3</sup>*Department of Geology, Faculty of Natural Sciences and Engineering, Aškerčeva 12, 1000, Ljubljana, Slovenia;* <sup>4</sup>*Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, 1000, Ljubljana, Slovenia*

(Received: 31 January 2005; accepted 5 December 2005)

**Abstract.** Measurements were made of sulphur and oxygen isotope ratios of sulphate in some Slovenian rivers, lakes and tap waters.  $\delta^{34}\text{S}$  ranged from  $-0.2$  to  $+13.3\text{‰}$ ,  $\delta^{18}\text{O}$  ranged from  $+4.9$  to  $+13.6\text{‰}$ , and the sulphate content varied from  $0.8$  to  $41.4$  mg/L. Rivers flowing from the Julian Alps contain a very low amount of sulphate that is leached from a thin horizon of soil by rain. As confirmed by their low  $\delta^{18}\text{O}$  values, these sulphates do not enter the rivers directly in rain, but arise from biochemical cycling in the soil. The low  $\delta^{34}\text{S}$  of this sulphate indicates that it originates from the oxidation of sedimentary sulphides. The evolution of sulphates along the river course was investigated for the Sava and Ljubljana rivers. The variations observed in sulphate from the waters studied result from variations in the contribution of sulphates of different origin. Downstream the Sava River sulphate is depleted in the heavy isotopes of both sulphur and oxygen, with  $\delta$ -values gradually tending toward the  $\delta$ -values of groundwater sulphates in the watershed. In contrast, the  $\delta$ -values of sulphate in the Ljubljana River are almost constant and similar to those of sulphate in local groundwater. Introduction of water from Italian and Slovenian mines was recorded in the Soča River, where the lowest  $\delta^{34}\text{S}$  value of sulphate sulphur ( $-0.2\text{‰}$ ) was observed. In addition, the influence of sulphate from the oxidation of sedimentary sulphides was recorded in the Sotla River. No evidence was found for introduction of sulphate from factories.

**Key words:** Ljubljana River, oxygen isotopes, Sava River, sulphates, sulphur isotopes

## 1. Introduction

Sulphate in rivers and groundwater has various origins. It can come from dissolution of soluble sulphate minerals in sedimentary rocks, oxidation and

---

\*Author for correspondence: E-mail: jszaran@tytan.umcs.lublin.pl

leaching of sedimentary sulphides (mostly pyrite), directly from the atmosphere and soil, or from anthropogenic sources like acid rains and organically-bound sulphur (e.g., Moncaster et al., 2000). All of these sulphates are mixed in rivers, and may be partly absorbed by plants, partly reduced by anaerobic bacteria in the bottoms of stagnant waters and reformed by oxidation processes. These different sulphate-forming processes will become active at different times according to varying conditions during the year (e.g., Krouse, 1980; Krouse and Grinenko, 1991; Krouse and Mayer, 2000). They are very well known and discussed in detail elsewhere (Böttcher and Thamdrup, 2001; Böttcher et al., 2001; Canfield, 2001; Dold and Spangenberg, 2005). Most aqueous sulphate is formed by biochemical processes such as dissimilatory reduction which enriches them in the heavy isotopes of both sulphur and oxygen. Assimilation of sulphate by plants or by soil micro-organisms does not change its isotopic composition (Van Stempvoort et al., 1990; Krouse and Grinenko, 1991).

Generally isotopic exchange between sulphate and  $\text{H}_2\text{S}$  or  $\text{H}_2\text{O}$  may be ignored, because these exchange processes are very slow in comparison to the rate rapid sulphur cycling. Different sources of sulphate can be distinguished by their isotopic signatures.

Sulphate derived from dissolved evaporites always has positive  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values, from +10 to +30‰ and from +12 to +20‰, respectively (Claypool et al., 1980), whereas sulphates from oxidation of sulphides or from biogenic emissions may have strongly negative  $\delta^{34}\text{S}$  values (Yang et al., 1997). Sulphate released during the weathering of igneous rocks and hydrothermal deposits is characterised by  $\delta^{34}\text{S}$  values near zero. Oxidation processes produce sulphates with sulphur isotope compositions similar to those encountered in oxidized organic or inorganic material, while their  $\delta^{18}\text{O}$  is low ( $< +10\%$ ) because oxygen comes from the water (Lloyd, 1968; Taylor et al., 1984; Toran and Harris, 1989).

Other fluxes of  $\text{SO}_4^{2-}$  discharged into the river system may come from anthropogenic sources such as municipal and industrial waste, mining activity, and coal power plants.

Acid rains in Central Europe predominantly contain air borne sulphate from combustion of fuels. Mean  $\delta^{34}\text{S}$  values of atmospheric sulphate range from +2.1 to +3.5‰ in southern Germany and Austria (Mayer, 1998), from +1.4 to +6.8‰, with a mean value +3.8‰ in Poland (Trembaczowski, 1991), while the mean values for Central Europe range from about +10 to +12‰ (Krouse and Mayer, 2000). Sulphate aerosol in a heavily industrialised part of the northern Czech Republic at the border with Germany was characterised by average  $\delta^{34}\text{S}$  values of +7.5‰ while atmospheric  $\text{SO}_2$  was isotopically lighter with a mean  $\delta^{34}\text{S}$  of +4.7‰ (Novák et al., 2000).

Sulphates coming from fertilisers. The  $\delta^{34}\text{S}$  values of sludge and effluent particulates from the Deer Island Treatment Facility range from +4.5 to

+8.4‰ (Hunt et al., 1995). The fertilisers have slightly more negative  $\delta^{34}\text{S}$  values of  $-1.1\text{‰}$  for ammonium sulphate and  $+7\text{‰}$  for NPK 5:7:10 (Otero and Soler, 2002).

The concentration of sulphate varies along the river course as sulphates from different natural and anthropogenic sources are added. Sulphur and oxygen isotope compositions of river water sulphates were first studied in Italy by Longinelli and Cortecchi (1970). They observed small seasonal variations and significant variations along the river course. They also found correlation between  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$ . They concluded that the isotopic composition of these sulphates were not established entirely in the river environment as they had also observed similar  $\delta$ -variations in well waters. Hitchon and Krouse (1972) investigated rivers and streams in the McKenzie River system of north-western Canada and found a relation between the isotopic composition of the river sulphate and the geology of the basin. Schwarcz and Cortecchi (1974) made a similar study of the sulphates of spring and stream water from the Italian Alps and the Apennines. Chukhrov et al. (1975) investigated sulphates in rivers flowing throughout the U.S.S.R. They observed  $\delta^{34}\text{S}$  variations along the course the Kuma River that were caused by the changes in the origin of the sulphates discharged into it.

Several investigations have been made of sulphur and oxygen isotopes variations of river sulphates in Poland (Trembaczowski, 1991; Trembaczowski and Halas, 1993; Trembaczowski et al., 2004). These variations are caused by processes occurring in local groundwater and reflect sulphur cycling processes in the environment.

The investigations of the sulphate origin in rivers by means of isotopic techniques are widely documented (Morrison et al., 1999; Soler et al., 1999; Bottrell et al., 2000; Haubrich and Tichomirowa, 2002; Otero and Soler, 2002; Soler et al., 2002). This paper presents the results of the first extensive stable isotope study of soluble sulphate in the major rivers of Slovenia.

## 2. The Study Area

The study area is shown in Figure 1. The sampling sites, according to numbers shown in Figure 1, are given in Table I.

### 2.1. THE SAVA RIVER

The Sava River is the longest river in Slovenia and is fed by two springs; one in Zelenci discharging the Sava Dolinka (the main river) and the other discharging the Sava Bohinjka, which is treated as a confluent. The main river in Zelenci spews out of the bottom in the form of little geysers. The Sava Bohinjka spring yields the Savica waterfall, which after a few hundred meters

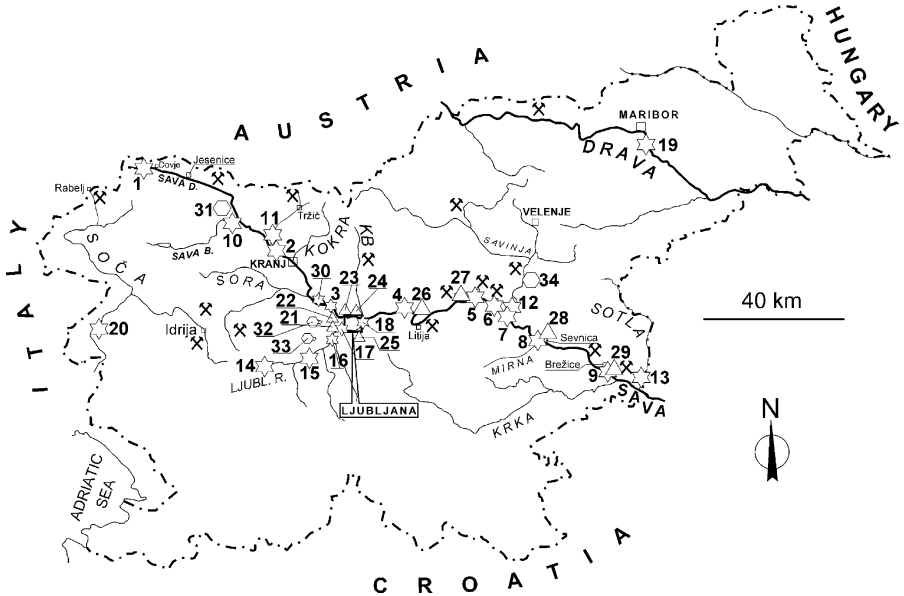


Figure 1. Map of the river system in Slovenia (sampling sites – see Table I). Crossed hammers denote locations of mines, abandoned mines and outcrops, which may discharge sulphur into the river system.

flows into Lake Bohinj. From there it proceeds its course as the Sava Bohinjka and finally flows into the Sava River near the village of Radovljica, from which point the river is called the Sava. It has a length of 219 km from the spring in Zelenci in the foothills of the Julian Alps on one side and the Karavanke Mountains on the other, to the border with Croatia. The Sava River joins the Danube River in Belgrad, Serbia.

In the study area, from Zelenci to Brežice, the Sava River flows through villages and towns of different touristic and industrial importance (e.g., Kranjska Gora, Dovje, Jesenice, Radovljica, Kranj, Ljubljana, Litija, Zagorje, Trbovlje, Hrastnik, Radeče, Sevnica and Brežice) with populations ranging from a hundred to several hundred thousand (Ljubljana), respectively, as well as through the agricultural areas of the SE Slovenia. The Sava water balance is chiefly controlled by its tributaries. The most important tributaries from Dovje to the sampling points in Brežice are: the Sava Bohinjka, the Tržiška Bistrica, the Kokra, the Sora, the Kamniška Bistrica, the Ljubljanica (the Ljubljanica River will be treated separately in this paper) the Savinja and the Mirna (Figure 1). These tributaries also control the chemical and isotopic characteristics of the Sava River.

The geology of watershed area of the Sava River at its spring in Zelenci is dominated by Mesozoic sediments, mostly carbonate rocks and to a minor extent by Paleozoic carbonates and siliciclastites. In the middle part, from

Table I. Sampling sites according to numbers shown in Figure 1.

---

☆ Rivers	
1	Sava Dovje
2	Sava Okroglo
3	Sava Črnuče
4	Sava Kresnice
5	Sava Trbovlje
6	Sava Hrastnik
7	Sava Radeče
8	Sava Sevnica
9	Sava Brežice
10	Sava Bohinjka
11	Tržiska Bistrica
12	Savinja
13	Sotla
14	Ljubljana Močilnik
15	Ljubljana Podpeč
16	Ljubljana Livada
17	Ljubljana Vevče
18	Ljubljana Podgrad
19	Drava
20	Soča
△ Tap water	
21	Vič
22	Šiška
23	Bežigrad
24	Beričevo
25	Moste
26	Kresnice
27	Trbovlje
28	Sevnica
29	Brežice
○ Lakes	
30	Lake of Zbilje
31	Lake of Bled
32	Koseški Bajer
33	Podpeca Lake
34	Slivnica Lake

---

Okroglo to Vevče, the Sava River drains Quaternary beds, while in its lower part, from Vevče to Brežice Paleozoic, Mesozoic and Cenozoic sedimentary rocks. In the wider area between Ljubljana and Radeče, in Late Paleozoic

and Triassic sediments, called Sava Folds, copper, iron and lead ores were mined. The most important mining centre at the beginning of the last century was Litija. The drainage basins of most tributaries such as the Sava Bohinjka, the Tržiška Bistrica, the Kokra, the Sora, and the Kamniška Bistrica are also dominated by sedimentary, mostly carbonate lithologies.

The watershed geology of the Savinja River is dominated by volcanic rocks (andesite, spilite and keratophyre) of Smrekovec Mountain and the Savinian Alps, as well as by Mesozoic carbonates and Tertiary sediments (carbonates, sandstones, conglomerates, clays). A Pliocene lignite-bearing succession in the Šalek area (Velenje coal mine) comprises exclusively non-marine deposits that were laid down in lacustrine and various fluvial systems (Pleničar, 1956). The lower part of the Savinja drainage system is dominated by the Carboniferous, Permian and Triassic beds, containing mostly Pb–Zn sulphide minerals, as well as a Oligocene to Pliocene coal-bearing succession. It is important to note that some small tributaries on the left side of the Sava River in the vicinity of the Zagorje, Trbovlje and Hrastnik area also drain coal mine waters from the adjacent coal mines into the Sava River.

Taking into account the geologic features of the main tributaries of the Sava River, except the Savinja, are similar to those of the main river, any large deviation of the chemical and isotopic composition can be interpreted as resulting from an anthropogenic impact, since domestic or industrial wastes are discharged more-or-less directly into the Sava River and its tributaries.

## 2.2. THE LJUBLJANICA RIVER

The Ljubljanica River is one of the most important tributaries of the Sava River. The watershed area of the Ljubljanica River extends about 25 km west and southwest of the city of Ljubljana. The Ljubljanica River is fed by the well-known Močilnik spring as well as two other nearby springs the Malo and Veliko Okence. The main tributaries of the Ljubljanica River are the Ljubija, the Bistra, the Iška, the Iščica, the Horjulščica and the Gradaščica. In Podgrad, about 46 km from its spring, the Ljubljanica River spills into the Sava River.

The watershed area of Ljubljanica and its tributaries comprises Mesozoic carbonates and Upper Paleozoic sedimentary rocks. The Ljubljanica River drains the so-called Ljubljansko barje, which is a semi-dried marsh pan consisting of alluvial sediments, lenses and delta-type clastic sediments like gravel, sand and clay (Pezdič, 1998). Most of the water of the Ljubljanica River at its springs is derived from the surrounding karst area.

The composition of rocks in the watershed area of the Ljubljanica River and its tributaries should control the downstream evolution of the Ljubljanica River chemistry. Nonetheless, the natural pattern can be disturbed by

anthropogenic influences due to introduction of wastes from domestic and urban usage as well as sources in the highly industrialised and partly agriculturally developed area in the vicinity of Ljubljana.

### 3. Analytical Methods

In September, 2000 we sampled Sava River water at seven locations spread over 210 km along its course (Figure 1, Table I). Ljubljana River water was also sampled that same month at five locations spread over 46 km. Sava River water was also sampled in November, 2002 at three locations. In addition, four major tributaries were sampled close to their confluence with the Sava River. In order to characterise the sulphur isotope signature in Slovenian natural waters, water samples were also collected from some other rivers and lakes as well as tap waters.

Water samples were placed in 1.5 L plastic vessels and transported immediately to the laboratory. The volumes of the water samples were measured (with accuracy of 10 mL), after which the waters were filtered and acidified with HCl to pH=1. With this treatment any microbiological activity which could possibly affect the sulphate was excluded. Then BaCl<sub>2</sub> solution was added to the solution and the sulphate was precipitated as BaSO<sub>4</sub>. The precipitate was recovered by filtering, washed with distilled water to remove Cl<sup>-</sup> anion, and dried. The pure BaSO<sub>4</sub> was then weighed, and the SO<sub>4</sub><sup>2-</sup> concentration was determined.

For sulphur isotope analysis barium sulphate samples were converted to SO<sub>2</sub> in a vacuum line at 800 °C in Cu-boat where BaSO<sub>4</sub> was loaded with appropriate reagents (Halas and Szaran, 2001; 2004). For δ<sup>18</sup>O analysis the BaSO<sub>4</sub> was reduced with graphite at 1000 °C to BaS and CO which was quantitatively converted to CO<sub>2</sub> by glow discharge (Mizutani, 1971). The isotopic compositions of SO<sub>2</sub> and CO<sub>2</sub> were measured with a dual-inlet, triple-collector mass spectrometer (Halas, 1979).

The standard uncertainty of δ<sup>34</sup>S and δ<sup>18</sup>O values is 0.05‰. The results were normalised to the international sulphur standard V-CDT (Vienna–Canyon Diablo Troilite) by comparison of delta values with that of the NBS-127 standard (Ding et al., 2001; Halas and Szaran, 2001) and to V-SMOW (Vienna–Standard Mean Ocean Water). Sulphate extracted from a water sample taken in Adriatic Sea (Portorož) had δ<sup>34</sup>S = +21.1‰.

### 4. Results and Discussion

The results are summarised in Table II and presented in Figures 2–5. The data are limited and the discussion emphasizes biochemical processes that occur in surface water. However, dissolved sulphate has the advantage of

being labelled isotopically in nature by the action of two biogeochemical systems.

#### 4.1. RAINWATER

Sulphate in three samples of rainwater had  $\delta^{34}\text{S}$  values of +4.7‰, +5.2‰ and +5.8‰ and  $\delta^{18}\text{O}$  values of +18.0‰ and +11.7‰ (Table II). These values are typical for sulphates in atmospheric precipitation. The concentration of sulphate in rain collected in September 2000, in Ljubljana was 0.2 mg/L. The relatively low  $\delta^{34}\text{S}$  value of rainwater indicates that in the continental part of Slovenia the precipitation contains a very small fraction of sea spray  $\text{SO}_4^{2-}$  with a  $\delta^{34}\text{S}$  value close to +21.1‰ (measured in Portorož). Although marine biogenic sulphur with mean  $\delta^{34}\text{S}$  values close to 0‰ can constitute a significant component of sulphate in atmospheric aerosols due to oxidation of dimethyl sulphide and  $\text{H}_2\text{S}$  (Mitzutani and Rafter, 1969; Wakshal and Nielsen, 1982; Turner et al., 1988), the  $\text{SO}_4^{2-}$  in the Kozina rainwater seems to originate predominantly from continental sources of sulphur, with  $\delta^{34}\text{S}$  values closer to +5‰.

The isotopic composition of sulphur in Slovenian rainwater is similar to that in atmospheric  $\text{SO}_2$  of the northern Czech Republic at the border with Germany (Novák et al., 2000). Because mean annual precipitation in the watershed areas of the Sava River and its tributaries is generally between 1200 and 2000 mm and the sulphate concentration is below 1.5 mg/L, the input of sulphate from rainwater seems negligible.

#### 4.2. THE SAVA RIVER

The water of the Sava-Bohinjska has a very low sulphate concentration of 0.8 mg/L. The down river evolution of  $\text{SO}_4^{2-}$  concentration and variations of sulphate  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values are plotted in Figure 2 (see also Table II).

Sulphur and oxygen isotope compositions of sulphate have generally similar downstream trends.  $\delta^{18}\text{O}$  values rise from +10.9 to +11.8‰ while  $\delta^{34}\text{S}$  values rise from +10.6 to +10.9‰ in the first 60 km from Dovje to Okroglo. An inverse trend is observed in the Okroglo–Brežice section, where there is a downstream depletion in the heavy isotopes of sulphur and oxygen. The lowest  $\delta^{34}\text{S}$  (+6.6‰) and  $\delta^{18}\text{O}$  (+5.8‰) of river sulphate were measured at Brežice. However, the only exception in this section represents the sampling point near Trbovlje where the  $\delta^{34}\text{S}$  value was slightly higher at +8.3‰.

The sulphate concentration is low at the spring, but from Dovje village to Okroglo village it increases to double the initial value (Figure 2). In that sector the  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values increase up to +11.9‰ and +10.9‰, respectively. These shifts are due to a significant admixture of sulphates from



Table II. Oxygen and sulphur isotope compositions of sulphates in Slovenian rivers, tap water, rains and lakes.

River, sampling place	SO <sub>4</sub> <sup>2-</sup> concentration [mg/L]	δ <sup>18</sup> O <sub>V-SMOW</sub> [‰]	δ <sup>34</sup> S <sub>V-CDT</sub> [‰]
Rivers			
<i>Samples collected in September 2000 (if not indicated)</i>			
The Sava, Dovje	8.7	10.64	10.90
The Sava, Okroglo	15.5	10.89	11.85
The Sava, Črnuče	13.2	9.08	9.86
The Sava, Kresnice	7.6	8.20	7.63
The Sava, Kresnice (sampling – November 2002)	7.4	8.34	7.69
The Sava, Trbovlje	14.0	7.59	8.25
The Sava, Hrastnik (sampling – November 2002)	11.9	7.45	7.31
The Sava, Radeče (sampling – November 2002)	12.3	7.35	6.21
The Sava, Sevnica	17.3	7.29	6.71
The Sava, Brežice	20.0	5.82	6.61
The Ljubljana, Močilnik	4.8	7.35	6.60
The Ljubljana, Podpeč	12.6	7.08	6.48
The Ljubljana, Livada	14.7	7.84	7.59
The Ljubljana, Vevče	11.8	8.47	7.52
The Ljubljana, Podgrad	14.4	7.37	6.55
<i>Confluents of the Sava River</i>			
The Sava Bohinjska (sampling in 2000)	0.8	5.38	0.49
The Tržiška Bistrica (sampling in 2001)	41.4	13.57	13.33
The Savinja (sampling in 2001)		7.21	4.13
The Savinja, Zidani Most (sampling – November 2002)	27.7	7.59	4.06
<i>Other rivers (2001)</i>			
The Drava		8.37	7.65
The Soča		5.47	-0.15
The Sotla		4.85	1.41
Tap water			
<i>Tap water samples collected along the Sava River in November 2002</i>			
Brežice	Very small amount of sulphates		
Sevnica	29.5	5.31	5.54
Trbovlje	9.0	4.13	6.95

Table II. Continued.

River, sampling place	SO <sub>4</sub> <sup>2-</sup> concentration [mg/L]	δ <sup>18</sup> O <sub>V-SMOW</sub> [‰]	δ <sup>34</sup> S <sub>V-CDT</sub> [‰]
Kresnice	7.9	2.36	3.40
<i>Tap water samples collected in Ljubljana</i>			
Beričevo (sampling in 2000)	14.9	5.27	3.00
Bežigrad (sampling in 2002)	11.9	6.16	6.75
Moste (sampling in 2002)	17.6	5.85	6.54
Šiška (sampling in 2002)	5.3	5.99	
Vič (sampling in 2002)	3.0	4.59	
Rainwater			
Ljubljana–Beričevo (September 2000)	0.15		5.83
Ljubljana 2001		11.69	5.19
Kozina 2001		18.04	4.71
Lakes			
Zbiljsko Jezero	9.6	10.45	10.27
Blejsko Jezero	10.2	6.07	9.34
Koseški Bajer	14.3	6.17	7.42
Podpeško Jezero	4.9	3.86	4.25
Slivniško Jezero	18.9	3.75	9.29

the left side confluent, the Tržiška Bistrica River, which is rich in isotopically heavy sulphate (concentration 41.4 mg/L, δ<sup>34</sup>S = +13.3‰ and δ<sup>18</sup>O = +13.6‰). Although the delta values suggest an evaporitic origin, it cannot be excluded that at least part of the sulphate came from industrial wastes (iron industry in Jesenice, power plant in Moste, food production in Lesce and a shoe factory in Tržič).

A relatively low sulphate concentration and high δ<sup>34</sup>S values of sulphate in the Sava River at Dovje (8.7 mg/L and +10.9‰) indicate dissolution of structurally substituted sulphate and to a minor degree evaporites in the Mesozoic carbonates of the watershed area of the Sava River in the Julian Alps. The very low sulphate concentration and δ<sup>34</sup>S = +0.5‰ encountered in its tributary, the Sava Bohinjka River, can be attributed to oxidation and dissolution of reduced sulphur minerals. A possible SO<sub>4</sub><sup>2-</sup> reduction in the anaerobic environment of Lake Bohinj does not appreciably modify the sulphur isotope composition of the sulphate. However, the inflow of the

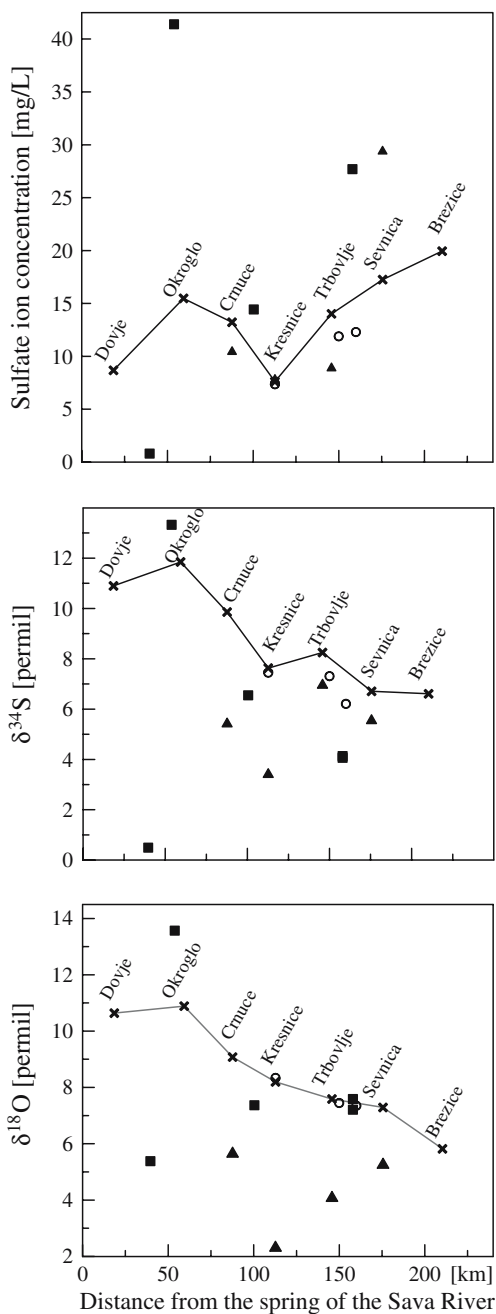


Figure 2. Sulphate concentration and sulphur and oxygen isotope compositions along the course of the Sava River. Open circles refer to sampling repeated after 2 years, squares refer to confluents and triangles refer to tap water.

Tržiška Bistrica tributary at Okroglo considerably changes the chemical and isotopic composition of the main river. The higher sulphate concentration, as well as higher  $\delta^{34}\text{S}$  values of river sulphate, can be interpreted as resulting from dissolution of evaporitic sulphates during weathering of evaporite sequences in the watershed area of the Tržiška Bistrica River in the Karavanke Mountains. Evaporitic sulphates and structurally substituted sulphates of the Upper Permian and Triassic sedimentary sequences in the Karavanke Mountains and in western Slovenia have  $\delta^{34}\text{S}$  values between  $+12\text{‰}$  and  $+24\text{‰}$  (Dolenec et al., unpublished). Gypsum samples near Idrija mine had  $\delta^{34}\text{S}$  values of  $+12.3\text{‰}$  and  $+16.4\text{‰}$ , within the range of Permian to Middle Triassic marine evaporites (Lavrič and Spangenberg, 2003). So the sulphur isotopic composition suggests that the sulphate in the Tržiška Bistrica tributary is derived mostly from the dissolution of marine sulphates in the exposed sediments of its watershed area. The main anthropogenic source of sulphates in the Tržiška Bistrica tributary is admixture of domestic and urban wastes, as well as the industrial influents from the textile industry, shoe factory and paper industry. However, these sulphate sources did not significantly change the primary evaporitic isotope signature.

From Okroglo to Kresnice the concentration of  $\text{SO}_4^{2-}$  decreases from 15.5 to 7.5 mg/L, and then returns to higher values (up to 20 mg/L) in the Kresnice–Brežice section. A steady depletion in  $^{34}\text{S}$  and  $^{18}\text{O}$  was observed along the river course. This isotopically light sulphate may come from tap water as well as from the groundwater, which is similar to the water supplying the springs of the Ljubljana River.

A strong lowering of sulphate concentration was observed in the Sava River below Črnuče to Kresnice. Such a low sulphate concentration in Kresnice (about 7.5 mg/L) was observed in September, 2000 as well as in November, 2002. The decrease of the sulphate concentration from Okroglo to Kresnice, accompanied by a simultaneous decrease of  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values (Figure 2), is most likely due to the input of relatively unpolluted tributaries, including the Kokra, the Sora and the Kamniška Bistrica, which carries weakly mineralised water. The waters of these tributaries contain only trace amounts of isotopically light sulphate, which probably originate from oxidation of sedimentary sulphides. The inflow of the tributary in Dolsko, which is located about 500 m east from the Vevče sampling point, has no influence on the sulphate concentration, nor on the sulphur isotope composition of sulphate. The sulphate concentration and sulphur isotope composition of sulphate in the Ljubljana River in Vevče are very similar to those of the Sava River in Kresnice (Table II).

From Kresnice to Brežice the concentration of sulphate gradually increases, while the  $\delta^{18}\text{O}$  value decreases. A small, but noticeable increase of  $\delta^{34}\text{S}$  in river sulphate was recorded from Kresnice to Trbovlje. The increase

of sulphate concentration from Kresnice to Brežice is followed by a general decrease of both delta values.

The following four contributions can control the chemistry of water in this section of the Sava River and its downstream evolution. (1) The input of sulphates with relatively low  $\delta^{34}\text{S}$  values from the oxidation of sulphide ores and minerals in the old Pb–Zn mines that which occur in the Sava Folds in the broad area around Kresnice,  $\delta^{34}\text{S}_{\text{sulphides}} = -3$  to  $-10\text{‰}$ , and  $\delta^{34}\text{S}_{\text{sulphates}} = +16$  to  $+18\text{‰}$  in the Litija-Sitarjevec mine (Drovenik et al., 1976) and the late oxidized minerals gypsum and greenockite have  $\delta^{34}\text{S}$  values of  $-19.5$  to  $-16.1\text{‰}$  (median  $-17.0\text{‰}$ ) and  $-19.2$  to  $-7.8\text{‰}$  (median  $-12.2\text{‰}$ ), respectively, in the Mežica Pb–Zn deposit (Spangenberg et al., 2001). (2) The water draining the coal mine from Trbovlje–Zagorje–Hrastnik area. The  $\delta^{34}\text{S}$  of sulphate from coal mine waters in the Trbovlje–Zagorje–Hrastnik area varies between  $+1.4$  and  $+44.6\text{‰}$  (Dolenec et al., 1989). Thus the  $^{34}\text{S}$  enrichment of sulphate in Trbovlje could be explained by addition of waters that drain the coal mines in this area. (3) The tributary to the Sotla which leaches sulphides from magmatic and hydrothermal rocks and from Tertiary coal-bearing sediments in the Šalek area (Velenje coal mine). (4) Domestic and industrial wastes (cement factory, coal power plant), discharging into the Sava River and its tributaries.

Down the course of the Sava River the sulphates become depleted in  $^{34}\text{S}$  and  $^{18}\text{O}$ , towards  $\delta$ -values characteristic of sulphates in the local tap water. Although there are some factories near this section of the Sava River, significant variations of isotopic composition have not been observed. The influence of industrial pollution does not change the isotopic composition of either sulphur or oxygen in this section.

A further increase in the sulphate content and decrease in  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values of sulphate from Trbovlje to Sevnica reflect the influence of the Savinja River, whose water has almost twice the concentration of sulphate as the Sava River (Figure 2, Table II). These sulphates have significantly lower  $\delta^{34}\text{S}$ , while  $\delta^{18}\text{O}$  values are very similar. The Sava River passes the paper factory and coal mines in this section.

The Sevnica–Brežice section is more industrialised; there are paper factories, food production factories and pharmaceutical factories. All of them use tap water, so they discharge the sulphates of groundwater origin into the Sava River, which obviously results in a decrease of delta values. No further changes of isotopic composition were observed in this section. The sulphur isotope composition of wastes is unknown.

#### 4.3. THE LJUBLJANICA RIVER

The lowest sulphate concentration observed in the Ljubljana River system was in the spring water at Močilnik (Table II and Figure 3). Sulphate

concentrations generally increase downstream (up to Podpeč) from 4.8 to 12.6 mg/L, while the sulphur and oxygen isotope compositions remain relatively unchanged at about  $\delta^{34}\text{S} = +6.5\text{‰}$ ,  $\delta^{18}\text{O} = +7.3\text{‰}$  (Figure 3). The increase in sulphate concentration may reflect discharge of urban and industrial wastes into the Ljubljanica River and its tributaries, as well as the agricultural activity in this area.

The constancy of the isotopic compositions strongly suggests a common origin for the sulphate, most probably leached from rocks or soil. The relatively low  $\delta^{34}\text{S}$  values of sulphate (from +6.6 to +7.6‰, Table II) could also be attributed to anthropogenic and agricultural sources.

Another source of sulphate in the Ljubljanica River seems to be sedimentary sulphides in the exposed rocks in the watershed area and in semi-dry marsh pan sediments. Oxidation of these sulphides can take place in soil or in the river water. No changes were observed in the isotopic compositions of sulphate which could be caused by activity of the leather factory in Vrhnika. The S and O the isotope composition of sulphates would probably be constant along the whole course of the Ljubljanica River, if no anthropogenic sulphates were introduced. Municipal sewage and industrial waste are sources of sulphate enriched in heavy isotopes, but this pollution is carried by tap whose sulphate is isotopically lighter and less concentrated than sulphate in the river. Thus introduction of tap water causes a lowering of both the sulphate concentration and the  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values. This effect makes it difficult to quantify the contribution of anthropogenic sources to the Ljubljanica River system.

In the section of the river from Livada to Vevče we recorded a distinct decrease of sulphate concentration while  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values shifted towards higher values (Figure 3). About 10 km below Ljubljana, in Podgrad, the concentration of sulphate in the river and the S and O isotope compositions return to the values that were observed upstream of the town. The observed shift of  $\delta$ -values in the vicinity of Ljubljana is caused by the admixture of tap water.

#### 4.4. OTHER RIVERS

The sulphur isotope composition of sulphate in other rivers under investigation (Table I) depends primarily on the geology of the respective watershed areas, and anthropogenic impacts that arise mainly from mine water pollution. Inflow of mine waters draining Pb–Zn ores in the Raibl mine (Italy) and from the mercury mine Idrija (Slovenia) is the most common source of pollution of the Soča River, where the lowest  $\delta^{34}\text{S}$  value of sulphate ( $-0.2\text{‰}$ ) was recorded.  $\delta^{34}\text{S}$  values of pyrites from the Idrija mine are  $-22.4$  to  $+13.2\text{‰}$  (Lavrič and Spangenberg, 2003). Similarly, a low  $\delta^{34}\text{S}$  value of sulphate was encountered in the Sotla River, which is the tributary of the

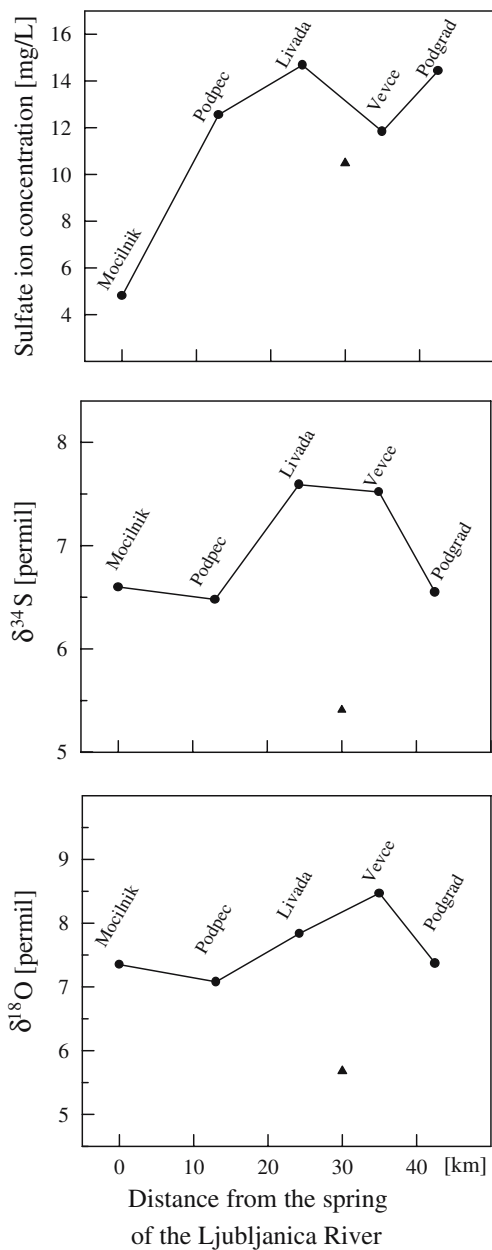


Figure 3. Sulphate concentration and sulphur and oxygen isotope compositions along the course of the Ljubljana River. Triangle refers to tap water.

Sava River, south of the sampling point in Brežice. Its low  $\delta^{34}\text{S}$  value is probably related to the oxidation of sedimentary sulphides in the Tertiary beds exposed in the watershed area as well as along the river course.

Sulphate in the Drava River has  $\delta^{34}\text{S} = +7.7\text{‰}$  and  $\delta^{18}\text{O} = +8.4\text{‰}$ , values that are very similar to those measured in the Sava River in Kresnice.

#### 4.5. TAP WATERS

One of the objectives of the present study was the determination of some geochemical characteristics of tap waters, which could provide insights in the recharge and storage of groundwater in the vicinity of Ljubljana, Trbovlje, Sevnica and Brežice.

Tap water in Ljubljana was investigated at five sampling points: Beričevo, Bežigrad, Moste, Šiška and Vič regions (Table II). Sulphate concentrations range from 3.0 mg/L (Vič) to 17.6 mg/L (Moste) with the mean value of 10.5 mg/L.  $\delta^{18}\text{O}$  values varied over a narrow range from +4.6 to +6.2‰, with a weighted mean of +5.7‰. Sulphur isotope compositions were measured at three locations where sulphate concentrations were above 6 mg/L. These  $\delta^{34}\text{S}$  values ranged from +3.0 to +6.8‰, with a weighted mean value of +5.4‰.

Tap water in Brežice has a very low concentration of sulphates (below 3 mg/L), and for this reason the isotopic compositions were not measured. The concentrations and  $\delta$ -values of oxygen and sulphur of sulphate in tap water in Kresnice, Trbovlje and Sevnica range from 7.9 to 29.5 mg/L, from +2.4 to +5.3‰ and from +3.4 to +6.9‰, respectively (Table II).

In the southern part of Ljubljana city the drinking water is supplied into the pumping station from Tertiary aquifers charged mainly by karst water. The sulphate contents as well as the isotopic compositions reflect the individual conditions present in the water-bearing layers, that consist mainly of various granulated and permeable alluvial clastic sediments (Pezdič, 1998). Tap waters from Moste and Beričevo have a sulphate concentration similar to that in the Ljubljanica River, but the  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values are lower. Tap waters from Vič and Šiška have very low concentrations of sulphate, while tap water in Bežigrad has an isotopic composition similar to that of the Sava River in Črnuče. These data most probably indicate a variable influence of river water (from the Ljubljanica River and the Sava River) into aquifers being recharged and stored in the Ljubljana area.

The geochemical characteristics of tap water in Sevnica can be explained by an inflow of relatively polluted Sava River water to the aquifer, as well as by the infiltration of precipitation, flushing oxidised Pb–Zn sulphides into the aquifers. These sulphides come from nearby SE parts of Sava Fold. The tap water data at Trbovlje indicate only limited infiltration from the Sava River beds. Most of the water in this aquifer is supposed to be supplied from local precipitations. Tap water at Kresnice probably originates in the Sava River.

Sulphates in the tap waters investigated have lower concentrations and lower delta values than those in the Ljubljanica and the Sava rivers.



#### 4.6. LAKE WATERS

A preliminary investigation of Slovenian lakes (Table II and Figure 5) exhibit rather uniform concentrations of sulphate and sulphur isotope compositions that are similar to those in river water. The isotopic composition of sulphate observed in lakes also reflects the isotopic composition of sulphur compounds existing in the watershed areas. The artificial Lake Zbiljsko Jezero, has a sulphate content and isotopic signature that is similar to those in the Sava River. This is not surprising, as the lake formed from damming the Sava River in Medvode.

#### 4.7. THE CORRELATION BETWEEN $\delta^{34}\text{S}$ AND $\delta^{18}\text{O}$

A good linear correlation ( $R^2=0.78$ ,  $n=5$ ) was observed between  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values of sulphates in the Ljubljana River and an even better correlation ( $R^2=0.90$ ,  $n=7$ ) was found for the Sava River. The regression line for all the river sulphate data (black dots) is plotted ( $R^2=0.79$ ,  $n=22$ ) in Figure 4. No such correlation is observed for sulphates in tap water or in lakes. The  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  correlation observed in sulphate along the river course may result from gradual evolution of river sulphates that is caused by the admixture of sulphates from numerous sources: tributaries, groundwater and anthropogenic waste.

### 5. Concluding Remarks

1. Sulphur and oxygen isotope compositions of sulphate in Slovenian rain are the same as those of sulphates in precipitation falling in other regions of Europe. They originate mainly from combustion of fossil fuels. The oxygen isotope composition of such sulphate varies seasonally.

2. Tap waters have low concentrations of sulphate. Sulphate coming from Tertiary aquifers was observed in the southern part of Ljubljana city. The influence of water coming from the Ljubljana and Sava rivers into the local groundwater aquifers was observed in Bežigrad, Kresnice, Trbovlje and Sevnica.

The presence of sulphate from oxidation of sulphide minerals could not be excluded by analyses of tap waters in Sevnica and Kresnice. The low  $\delta^{34}\text{S}$  values of sulphate most likely indicate the oxidation of sulphide from surrounding old Pb–Zn mines.

3. Sulphates in lakes are characterised by a rather narrow ranges of  $\delta$ -values. This may be result from mixing of sulphates of different origin. The sulphur isotope composition of sulphate in lakes reflects the isotopic composition of sulphur compounds existing in the adjacent watershed.

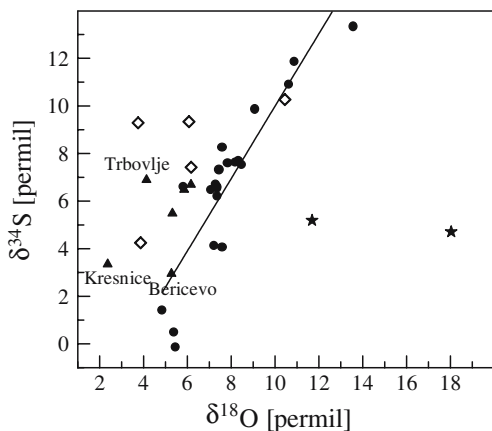


Figure 4. Correlation between sulphur and oxygen isotope compositions of sulphates in the rivers (black dots), in lakes (diamonds), in tap water (triangles) and in rains (asterisks). Straight line is the linear fitting for rivers sulphate only ( $\delta^{34}\text{S} = 1.52 \cdot \delta^{18}\text{O} - 5.21$ ,  $R^2 = 0.79$ ,  $n = 22$ ).

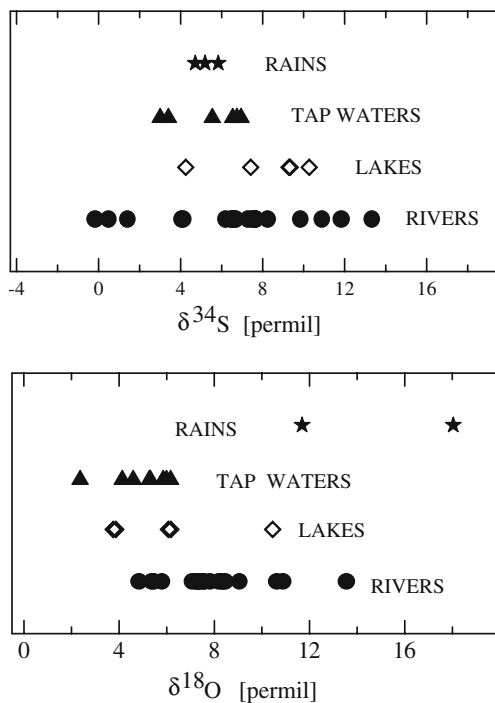


Figure 5. Sulphur and oxygen isotope compositions of sampled sulphates.

4. Rivers contain sulphates of different origin, derived from their watershed. Rivers flowing from Julian Alps (the Kokra, the Sora and the Kamniška Bistrica) contain very low amounts of sulphate that is leached

from a thin stratum of soil by rainwater. These clean, weakly mineralised waters of tributaries dilute the water of the main rivers. The oxygen isotope compositions of these sulphates confirm that they do not originate directly from rain, and the sulphur isotope compositions suggest that the sulphate gets into rivers after biochemical cycling in the soil. The isotopically light sulphur probably originates from the dissolution and oxidation of sedimentary sulphides.

The anthropogenic impact in the form of an inflow of mine waters draining the Pb–Zn ores from the Raibl mine (Italy) and from the mercury Idrija mine (Slovenia) was recorded in the Soča River, where the lowermost  $\delta^{34}\text{S}$  value ( $-0.2\text{‰}$ ) was observed. Similarly a low  $\delta^{34}\text{S}$  value of sulphate was measured in the Sotla River, a tributary to the Sava River. The influence of oxidation of sedimentary sulphides in Tertiary beds was recorded in the Sotla River.

5. The evolution of sulphates along the river course is caused by the delivery of sulphates of different origin by tributaries, wastes and tap water. Some tributaries carrying weakly mineralised water may lower the sulphate content. Our observations can be summarised as follows:

- (1) The relatively low sulphate concentrations and high  $\delta^{34}\text{S}$  values (the Sava River in Dovje) indicate dissolution of structurally substituted sulphate and to a minor degree leaching of evaporites from the Mesozoic carbonates in the watershed of the Sava River in the Julian Alps.
- (2) The high concentrations of sulphate enriched in  $^{34}\text{S}$  result from dissolution of weathered Upper Permian and Triassic evaporites in the watershed area of the Tržiška Bistrica River in the Karavanke Mountains and in western Slovenia.
- (3) Sulphates with relatively low  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values may come from tap water as well as from groundwater.
- (4) Waters that drain coal mines enrich the river sulphate in heavy sulphur.
- (5) Down the course of the Sava River sulphate is gradually enriched in light isotopes, while almost constant  $\delta$ -values are observed in the Ljubljana River. The difference between the two rivers can be explained by significant inflow of heavy sulphates at the beginning of the course of the Sava River. The river water is subsequently diluted by groundwater with low  $\delta$ -values.
- (6) Waste from factories located near the rivers does not cause significant variations in the isotopic compositions of river sulphate. This is because all the factories dispose tap water, so they discharge sulphates of groundwater origin into the rivers.

## Acknowledgments

This research was supported by Slovenian-Polish Project for 2001–2002 No 15 “Sulfur and oxygen isotopic composition investigation of natural sulfate minerals and water”. Authors are grateful to the reviewers Dr A. Soler and Dr J. Spangenberg for constructive comments, which resulted in a great improvement of the manuscript. Authors are also very grateful to Dr Jim O’Neil for his effort of final correcting the English language of the manuscript.

## References

- Böttcher M. E. and Thamdrup B. (2001) Anaerobic sulfide oxidation and stable isotope fractionation associated with bacterial sulfur disproportionation in the presence of MnO<sub>2</sub>. *Geochimica et Cosmochimica Acta* **65**, 1573–1581.
- Böttcher M. E., Thamdrup B. and Vennemann T. W. (2001) Oxygen and sulfur isotope fractionation during anaerobic bacterial disproportionation of elemental sulfur. *Geochimica et Cosmochimica Acta* **65**, 1601–1609.
- Bottrell S. H., Webber N., Gunn J. and Worthington S. R. H. (2000) The geochemistry of sulphur in a mixed allo-genic-autogenic karst catchment, Castleton, Derbyshire, UK. *Earth Surface Processes and Landforms* **25**, 155–165.
- Canfield D. E. (2001) Isotope fractionation by natural populations of sulfate-reducing bacteria. *Geochimica et Cosmochimica Acta* **65**, 1117–1124.
- Chukhrov F. V., Churikov V. S., Yermilova L. P. and Nosik L. P. (1975) On the variation of sulfur isotopic composition in some natural waters. *Geochem Int.* **12**(2) 20–33 (Translation from *Geokhimiya*, 1975, **3**, 343–356).
- Claypool G. E., Holser W. T., Kaplan I. R., Sakai H. and Zak I. (1980) The age curve of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chemical Geology* **28**, 199–260.
- Ding T., Valkiers S., Kipphardt H., De Bievre P., Taylor P. D. P., Gonfiantini R. and Krouse H. R., (2001) Calibrated sulfur isotope abundance ratios of three IAEA sulfur isotope reference materials and V-CDT with a reassessment of the atomic weight of sulfur. *Geochimica et Cosmochimica Acta* **65**, 2433–2437.
- Dold B. and Spangenberg J. E. (2005) Sulfur speciation and stable isotope trends of water-soluble sulfates in mine tailings profiles. *Environmental Science & Technology* **39**, 5650–5656.
- Dolenec T., Pezdič J., Herlec U., Kušcar D. and Mitrevski G. (1989) Determining of origin of waters in collieries with natural isotopes and other geochemical parameters. *Mining and Metallurgy Quarterly* **36**(3), 521–546.
- Drovenik M., Duhovnik J. and Pezdic J. (1976) Isotopska sestava zvelpa v sulfidih rudnih nahajalisc v Sloveniji. *Rudarkso-metalurski zbornik* **2–3**, 193–246.
- Halas S. (1979) An automatic inlet system with pneumatic changeover valves for isotope ratio mass spectrometer. *Journal of Physics E.: Science Instruments* **18**, 417–420.
- Halas S. and Szaran J. (2001) Improved thermal decomposition of sulfates to SO<sub>2</sub> and mass spectrometric determination of δ<sup>34</sup>S of IAEA SO-5, IAEA SO-6 and NBS-127 sulfate standards. *Rapid Communication Mass Spectrometry* **15**, 1618–1620.
- Halas S. and Szaran J. (2004) Use of Cu<sub>2</sub>O–NaPO<sub>3</sub> mixtures for SO<sub>2</sub> extraction from BaSO<sub>4</sub> for sulfur isotope analysis. *Isotopes in Environmental and Health Studies* **40**(3), 229–231.

- Haubrich F. and Tichomirowa M. (2002) Sulfur and oxygen isotope geochemistry of acid mine drainage – the polymetallic sulfide deposit “Himmelfahrt Fundgrube” in Freiberg (Germany). *Isotopes in Environmental and Health Studies* **38**, 121–138.
- Hitchon B. and Krouse H. R. (1972) Hydrogeochemistry of the surface waters of the Mackenzie River drainage basin, Canada, III. Stable isotopes of oxygen, carbon and sulfur. *Geochimica et Cosmochimica Acta* **36**, 1337–1357.
- Hunt C. D., West D. E. and Peven C. S. (1995) Deer Island effluent characterization and pilot treatment plant studies: June 1993–November 1994. *MWRA Technical Report* No. 95-7.
- Krouse H. R. (1980) Sulphur isotopes in our environment, In P. Fritz, and J. Ch. Fontes, (eds.), *Handbook of Environmental Isotope Geochemistry vol. I, The Terrestrial Environment*, A. Amsterdam: Elsevier, pp. 435–471.
- Krouse H. R. and Grinenko V. A. (eds.) In *SCOPE 43, Stable isotopes: Natural and Anthropogenic Sulphur in the Environment*. John Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapore.
- Krouse H. R. and Mayer B. (2000) Sulphur and oxygen isotopes in sulphate. In P. Cook and A. L. Herczeg (eds), *Environmental Tracers in Subsurface Hydrology* Chap. 7, pp. 195–231, Kluwer Academic Publishers.
- Lavrič J. V. and Spangenberg J. E. (2003) Stable isotope (C, O, S) systematics of the mercury mineralization at Idrija, Slovenia: constraints on fluid source and alteration processes. *Mineralium Deposita* **38**, 886–899.
- Lloyd R. M. (1968) Oxygen isotope behavior in the sulfate-water system. *Journal of Geophysical Research* **73**, 6099–6110.
- Longinelli A. and Cortecci G. (1970) Isotope abundance of oxygen and sulfur in sulfate ions from river water. *Earth and Planetary Science Letters* **7**, 376–380.
- Mayer B. (1998) Potential and limitations of using sulfur isotope abundance ratios as an indicator for natural and anthropogenic environmental change. In *Isotope Techniques in the Study of Environmental Change*, pp. 423–435. International Atomic Energy Agency, Vienna.
- Mizutani Y. (1971) An improvement in the carbon-reduction method for the oxygen isotopic analysis of sulphates. *Geochemical Journal* **5**, 69–77.
- Mizutani Y. and Rafter T. A. (1969) Oxygen isotopic composition of sulfates: Part 5, Isotopic value of sulfate in rain water, Gracefield, New Zealand. *New Zealand Journal of Science* **12**, 69–80.
- Moncaster S. J., Bottrell S. H., Tellam J. H., Lloyd J. W. and Konhauser K. O. (2000) Migration and attenuation of agrochemical pollutants: insights from isotopic analysis of ground water sulfate. *Journal of Contaminant Hydrology* **43**, 147–163.
- Morrison J., France-Lanord C. and Pierson-Wickmann A. C. (1999) Oxygen-sulphur-isotopic measurement in continuous flow mode: Application to the origin of dissolved sulphates in Himalayan rivers using elemental analyzer stable isotope ratio mass spectrometry. *Ninth Annual V. M. Goldschmidt Conference, August 22–27, 1999, Cambridge, Massachusetts*, abstract no. 7620.
- Novák M., Kirchner J. W., Groscheová H., Havel M., Černý J., Krejčí R. and Buzek F. (2000) Sulfur isotope dynamics in two Central European watersheds affected by high atmospheric deposition of SO<sub>x</sub>. *Geochimica et Cosmochimica Acta* **64**, 367–383.
- Otero N. and Soler A. (2002) Sulfur isotopes as tracers of the influence of potash mining in groundwater salinisation in the Llobregat Basin (NE Spain). *Water Research* **36**, 3989–4000.
- Pezdič J. (1998) Stable isotopes as natural tracers of the karst recharge to the Tertiary clastic aquifers. A case study of the southern part of Ljubljana marsh (Ljubljansko barje, Slovenia). *Acta Carsologica XXVII/1* **20**, 349–360.

- Pleničar M. (1956) The development of Pliocene in Slovenia. *1st. Geological Congress of FNR Yugoslavia, Bled 1954*, pp. 55–58.
- Schwarz H. P. and Corceci G. (1974) Isotopic analysis of spring and stream water from Italian Alps and Apennines. *Chemical Geology* **13**, 285–294 .
- Soler A., Ginebreda A., Otero N., Canals A., Cardellach E., Antich N., Vitoria L., Godé L. I. and Piniella J. F. (1999) Environmental applications of sulphur isotopic geochemistry to the study of water pollution problems. *9as Jordanas de Analisis Instrumental*, MAP1-55, p. 187.
- Soler A., Canals A., Goldstein S. L., Otero N., Anrtich N. and Spangenberg J. (2002) Sulfur and strontium isotope composition of the Llobregat River (NE Spain): tracers of natural and anthropogenic chemicals in stream waters. *Water, Air and Soil Pollution* **136**, 207–224.
- Spangenberg J. E., Lavrič J. V. and Herlec U. (2001) Sulfur-isotope study of the Mežica Mississippi Valley-type lead–zinc ore deposits, Slovenia: Mineral deposits at the beginning of the 21st century. Proceedings of joint 6th Biennial SGA-SEG Meeting, 26–29 August 2001, Kraków, Poland, pp. 181–184.
- Taylor B. E., Wheeler M. C. and Nordstrom D. K. (1984) Stable isotope geochemistry of acid mine drainage: Experimental oxidation of pyrite. *Geochimica et Cosmochimica Acta* **48**, 2669–2678.
- Toran L. and Harris R. F. (1989) Interpretation of sulfur and oxygen isotopes in biological and abiological sulfide oxidation. *Geochimica et Cosmochimica Acta* **53**, 2341–2348.
- Trembaczowski A. (1991) Sulphur and oxygen isotopes behaviour in sulphates of atmospheric groundwater system, observation and model. *Nordic Hydrology* **22**, 49–66.
- Trembaczowski A. and Hałas S. (1993) Sulphur and oxygen isotopes in sulphates in natural waters (1). Surface waters of relatively unpolluted terrains. *Isotopenpraxis* **28**, 215–228.
- Trembaczowski A., Szaran J. and Niezgoda H. (2004) Investigating the provenance and seasonal variations in the sulphate sulphur and oxygen isotopes of Central Roztocze river water, SE Poland. *Water, Air and Soil Pollution* **157**, 65–84.
- Turner S. M., Malin G., Liss P. S., Harbour D. S. and Holligan P. M. (1988) The seasonal variation of dimethylsulfide and dimethylsulfonio-propionate concentration in near shore waters. *Limnology and Oceanography* **33**, 364–375.
- Van Stempvoort D. R., Reardon E. J. and Fritz P. (1990) Fractionation of sulfur and oxygen isotopes in sulfate by soil sorption. *Geochimica et Cosmochimica Acta* **54**, 2817–2826.
- Wakshal E. and Nielsen H. (1982) Variations of  $\delta^{34}\text{S}$ ,  $\delta^{18}\text{O}$  and Cl/SO<sub>4</sub> rations in rainwater over northern Israel, from the Mediterranean coast to Jordan Rift Valley and Golan Heights. *Earth and Planetary Science Letters* **61**, 272–282.
- Yang W., Spencer R. J. and Krouse H. R. (1997) Stable isotope compositions of waters and sulfate species therein, Death Valley, California, USA; Implications for inflow and sulfate sources, and arid basin climate. *Earth and Planetary Science Letters* **147**, 69–82.