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Biogeochemical sulfur cycling in the water column of a shallow stratified sea-water lake: Speciation and quadruple sulfur isotope composition

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ABSTRACT

Concentrations of sulfate, sulfide and intermediate sulfur species as well as quadruple sulfur isotope compositions of sulfate, sulfide and zero-valent sulfur (ZVS) were analyzed in the water column of Lake Rogoznica (Croatia), a stratified marine euxinic lake. The chemocline in the lake, which was located at 8.5–9.5 m depth, supports a dense population of purple phototrophic sulfide oxidizing bacteria from the genus *Chromatium*. The highest ZVS (5.42 μmol L^{-1}) and sulfite (1.13 μmol L^{-1}) concentrations were detected at the chemocline. Thiocyanate concentrations up to 288 nmol L^{-1} were detected near the bottom of the lake. The thiocyanate profile suggests that it diffuses up from the sediment, where it may be produced by the reaction of cyanide with sulfide oxidation intermediates. Multiple sulfur isotope fractionations between sulfate and sulfide were consistent with a model finding that disproportionation is not a dominant process below the chemocline. Microbial sulfide oxidation was found to be the dominant process of the reoxidative part of the sulfur cycle. Despite the absence of a clear signal for sulfur disproportionation in multiple sulfur isotope values, $\delta^{34}S$ fractionations between sulfate and sulfide were in the range of 43.8–45.2‰, is relatively large in comparison to most laboratory culturing studies. Our results suggest that such fractionation is achieved by microbial sulfate reduction alone, which is in agreement with metabolic models and recent laboratory studies.

1. Introduction

The formation and reduction of sulfate is one of the most significant biogeochemical processes regulating the redox state of the oceans both presently and over Earth history. In modern seawater and near-surface sediment porewaters, sulfate is the most abundant soluble electron acceptor, with concentrations of 28.24 mmol L^{-1} at salinity of 35.00. Reduction of sulfate in the absence of dissolved oxygen is an important energy source for microorganisms (Eq. (1)).

$$SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow H_2S + 2CO_2 + 2H_2O \quad (1)$$

A complicated web of sulfide oxidation reactions partially replenishes the pool of available sulfate, and maintains sulfate reducing activity. This oxidative part of the sulfur cycle proceeds, in part, through the formation of various intermediate sulfur compounds (inorganic polysulfides and their protonated forms, particulate and dissolved elemental sulfur, thiosulfate, polythionates and sulfite) utilizing different electron acceptors (oxygen, nitrate, iron(III), manganese(III), manganese(IV)) (Zopfi et al., 2004, and references therein).

In stratified water columns hydrogen sulfide can be oxidized to zero-valent sulfur (ZVS) and other intermediate sulfur compounds by phototrophic sulfur oxidizing bacteria (Eq. (2)) (e.g., Overmann et al., 1991; Canfield et al., 2005)

$$2H_2S + CO_2 \rightarrow CH_2O + H_2O + 2S^0 \quad (2)$$

These organisms (primarily green and purple sulfur bacteria) can also reoxidize ZVS and a number of other reduced sulfur compounds (including thiosulfate) to sulfate.

Bacteria can also mediate the disproportionation of elemental sulfur (Bak and Cypionka, 1987; Thamdrup et al., 1993; Canfield and Thamdrup, 1994) (Eq. (3)) as well as thiosulfate and sulfite (Bak and Cypionka, 1987; Cypionka et al., 1998; Jørgensen, 1990; Habicht et al., 1998) (Eqs. (4) and (5)). At sulfide concentrations of >1 mmol L^{-1}, the bacterial disproportionation of elemental sulfur (Eq. (3)) only

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occurs in the presence of an external sulfide sink (Thamdrup et al., 1993).

$$4S^0 + 4H_2O \rightarrow 3H_2S + SO_4^{2-} + 2H^+ \quad (3)$$

$$S_2O_3^{2-} + H_2O \rightarrow H_2S + SO_4^{2-} \quad (4)$$

$$4SO_3^{2} + 2H^+ \rightarrow H_2S + 3SO_4^{2-} \quad (5)$$

In sulfide-rich waters polluted by cyanide, formation of thiocyanate occurs by reaction of cyanide with sulfide oxidation intermediates such as colloidal sulfur (Kamyshny, 2009a), polysulfides (Luthy and Bruce, 1979; Kamyshny et al., 2009), thiosulfate and tetrathionate (Szekeres, 1974; Dzombak et al., 2006; Kamyshny et al., 2011a) (Eqs. (6)–(9)) via reactions such as:

$$S_n^{2-} + (n-1)CN^- + H^+ \rightarrow (n-1)SCN^- + HS^- \quad (6)$$

$$S_2O_3^{2-} + CN^- \rightarrow SO_3^{2-} + SCN^- \quad (7)$$

$$S_nO_6^{2-} + (n-3)CN^- + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ + (n-3)SCN^- \quad (8)$$

$$S_{8(colloidal)} + 8CN^- \rightarrow 8SCN^- \quad (9)$$

Formation of thiocyanate has never been previously documented in stratified non-polluted aquatic systems.

Typically, speciation and isotope composition analyses alone are not sufficient to understand the relative importance of various processes in element cycling. The chemical and microbial transformations of sulfur species lead to measurable fractionations of sulfur isotopes between reactants and reaction products, and these fractionations provide insight into reductive and oxidative sulfur pathways, considered in the context of chemical speciation. Sulfide produced in experiments with cultures and natural populations of sulfate reducers has been found to be up to 70‰ depleted in ^{34}S with respect to sulfate (Harrison and Thode, 1958; Bolliger et al., 2001; Canfield et al., 2010; Sim et al., 2011). Li et al. (2010) recently argued that the differences between sulfate and sulfide $\delta^{34}S$ (~54‰) in the Cariaco Basin water column were consistent with the activity of sulfate reduction alone, based on multiple sulfur isotope fractionation.

The magnitude of sulfur isotope fractionation by sulfate reduction is known to depend on substrate type and substrate concentrations. Oxidation of hydrogen as well as incomplete oxidation of lactate, propionate, or pyruvate to acetate leads to relatively small fractionation (Kaplan and Rittenberg, 1964; Brüchert et al., 2001). Oxidation of acetate to CO_2 leads to larger sulfur isotope fractionations, possibly due to lower cell specific sulfate reduction rates (Brüchert et al., 2001). The largest fractionations were observed during oxidation of complex substrates, such as crude oil (Bolliger et al., 2001). Lower, but still non-limiting electron donor concentrations lead to larger fractionations (Chambers et al., 1975; Canfield, 2001).

In some natural aquatic systems, large fractionations between sulfide and sulfate greater than 48‰ (Fry et al., 1991; Canfield and Teske, 1996; Neretin et al., 2003) have been explained by repeated step-wise fractionations imparted during oxidative sulfur cycling, including sulfide oxidation and the disproportionation of product sulfur intermediates (especially ZVS) to produce more ^{34}S-depleted sulfide and ^{34}S-enriched sulfate (e.g., Canfield and Thamdrup, 1994). Unidirectional sulfate reduction in sediments, however, was also argued to create sulfur isotope fractionation exceeding 65‰ (Wortmann et al., 2001; Rudnicki et al., 2001) as has been shown in recent experiments (Sim et al., 2011).

Nevertheless, even analysis of ^{34}S to ^{32}S ratios is often insufficient to quantify the oxidative part of the sulfur cycle, since the majority of the fractionation is imparted during sulfate reduction (e.g. Brunner and Bernasconi, 2005). Analysis of multiple sulfur isotope values is an emerging tool for the study of biogeochemical sulfur cycling in modern aquatic (Canfield et al., 2010; Li et al., 2010; Zerkle et al., 2010) and ancient sedimentary (Johnston et al., 2005a; Philippot et al., 2007; Shen et al., 2009; Wacey et al., 2010) systems. Small variations in mass dependent fractionation of ^{33}S and ^{36}S isotopes were shown to have a diagnostic pattern for biogeochemical transformations of sulfur compounds, such as sulfate reduction (Farquhar et al., 2003, 2007; Ono et al., 2006), sulfide oxidation (Zerkle et al., 2009, 2010) and sulfur compound disproportionation (Johnston et al., 2005b). Although a limited amount of data for quadruple sulfur isotope fractionation by various biological and chemical processes is available, this approach has already been successfully applied to determine the origin of sulfide (sulfate reduction alone vs. sulfide oxidation and sulfur disproportionation), elemental sulfur (chemical vs. microbial sulfide oxidation) and sulfate (consumption by sulfate reduction vs. production by sulfur disproportionation and/or sulfide oxidation) in natural aquatic systems (Canfield et al., 2010; Li et al., 2010; Zerkle et al., 2010). Patterns in minor sulfur isotopes (^{33}S in particular) have revealed that very large fractionations between sulfate and sulfide may be produced via sulfate reduction in natural systems, both with and without the additional overlay of oxidative sulfur cycling (Li et al., 2010; Zerkle et al., 2010).

In this paper we studied the sulfur cycle in the stratified water column of seasonally anoxic seawater Lake Rogoznica, Croatia, a unique marine anoxic environment on the Adriatic coast (Fig. 1). Lake Rogoznica provides the opportunity to study sulfur dynamics in a stratified anoxic basin where the deep basin is sulfidic, and discernible rates of sulfur cycling dominate at the chemocline, in an otherwise normal seawater environment. We were especially interested to see how such a close to marine situation compares with other well-studied sulfidic lakes such as Green Lake or Lago di Cadagno. Here we present concentrations of sulfur species, including sulfur intermediates such as thiocyanate, sulfite, thiosulfate, and ZVS in the lake. Moreover, we present data on the distribution of quadruple sulfur isotopes in a stratified sea-water lake, in order to understand the processes which control isotopic fractionation between sulfur species.

2. Materials and methods

2.1. Study site

Lake Rogoznica is a seawater lake located on the Gradina Peninsula (43°32′N, 15°58′E) approximately 100 m from the open Adriatic Sea, close to village Rogoznica on the Dalmatian coast (Fig. 1). The lake has a circular shape with an area of 10,276 m^2, maximum length of 143 m, and a maximum depth of 15 m. It is sheltered from the wind by 4–23 m high cliffs that prevent wind-shear mixing. Lake Rogoznica can be characterized as a typical euxinic environment (Ciglenečki et al., 2006). Very limited water exchange with the open sea through porous karsts leads to a visible push-and-pull water movement associated with Adriatic Sea tidal cycle (Žic and Branica, 2006 and references therein). Compared with the open Adriatic Sea, Lake Rogoznica is eutrophic. Nitrate, phosphate and silicate concentrations are up to 19 μmol L^{-1}, 22 μmol L^{-1}, 400 μmol L^{-1} respectively (Ciglenečki et al., 2005). Lake Rogoznica is thermo-haline stratified from spring to autumn (Ciglenečki et al., 1998, 2005). In years with cold and dry autumn and winter, mixing of the lake water layers takes place (Ciglenečki et al., 1998, 2005).

We can define three geochemically-distinct water layers in the lake. The epilimnion is the upper, oxic water layer. At the chemocline the hydrogen sulfide concentration is below 1 μmol L^{-1} and oxygen concentration is below 5 μmol L^{-1}. In Lake Rogoznica this layer is c.a. 50 cm thick. The chemocline of the lake hosts a dense population of purple phototrophic sulfur bacteria (up to 4.3×10^8 cells mL^{-1} in July 1997) *Chromatium* that comprises up to 51% of total bacteria

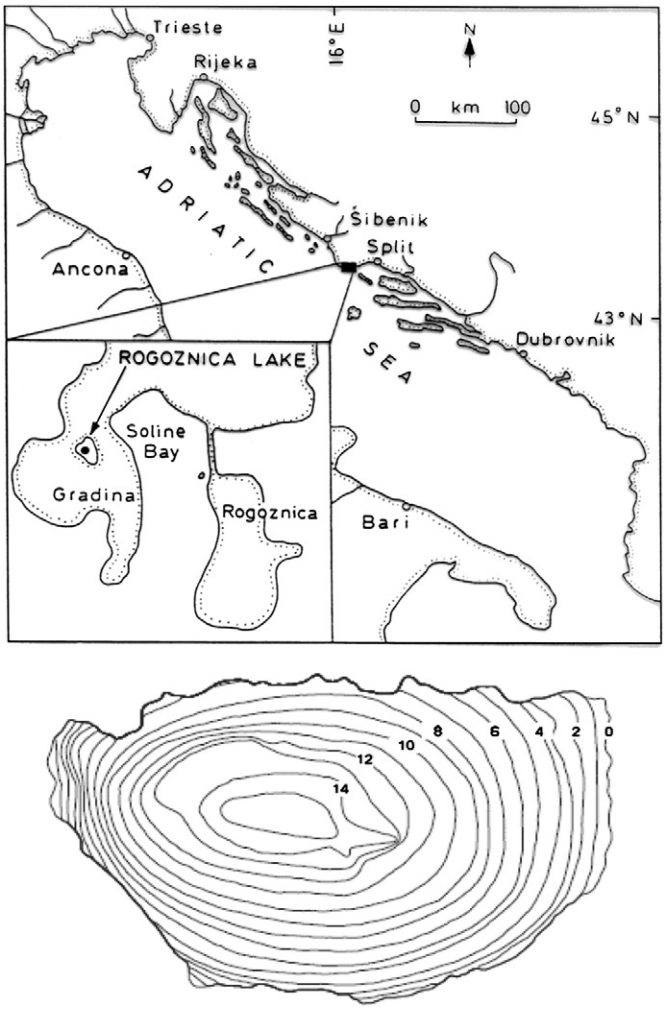

Fig. 1. Location and bathymetry map of Rogoznica Lake, modified from Žic and Branica (2006) and Ciglenečki et al. (2006). The contours in the bathymetry map refer to the depth in meters.

(Ciglenečki et al., 1998; Ciglenečki, unpubl.). The hypolimnion, the deepest water layer, is anoxic and hydrogen sulfide rich (up to 5 mmol L^{-1}; Bura-Nakić et al., 2009). Iodide concentrations in the hypolimnion are as high as 2.27 μmol L^{-1} (Žic and Branica, 2006), indicating rapid remineralization of organic matter in the sediment (Ullman and Aller, 1983; Ullman et al., 1988).

2.2. Sampling

Lake Rogoznica depth profiles were sampled on the 16 and 19 September 2009. Water was sampled with a peristaltic environmental pump (Masterflex E/S Variable Speed Water Pump, EnviroTech, CA). Temperature, pH (during the second sampling only), redox potential, and dissolved oxygen concentration were recorded by CTD probe (Hach Lange HQ40D). Salinity was measured by hand-held refractometer (Atago, Japan) during the first sampling only.

2.3. Sample preservation and analysis: Speciation

Samples for analysis of sulfate, sulfide and total ZVS concentrations were preserved by addition of 49 mL sample to 50 mL falcon tubes pre-filled with 1 mL of 200 g L^{-1} zinc acetate solution, frozen within 12 h and stored frozen until analysis. Samples for the analysis of sulfide and total ZVS concentrations, and some samples for the analysis of sulfate concentrations, were taken in triplicates.

Sulfide was measured spectrophotometrically according to Cline (1969). Total ZVS was analyzed by chloroform extraction followed by HPLC-UV analysis according to Kamyshny et al. (2009). During the second sampling some samples were filtered through 1.2 μm pore size Minisart filters before preservation for total ZVS analysis. Inorganic polysulfides were assayed by fast single-phase derivatization with methyl trifluoromethanesulfonate, followed by HPLC-UV analysis according to Kamyshny et al. (2006). Samples for thiosulfate and sulfite analysis (0.5 mL) were derivatized by monobromobimane and analyzed by HPLC using a fluorescence detector according to the method of Zopfi et al. (2004), with modification by using a 250 mm Prevail C18 Alltech column and longer (95 min) gradient program for separation. An Agilent Technologies 1200 HPLC system with multiple wavelength UV–vis and fluorescence detectors was used for these chromatographic analyses. Sulfate concentrations were measured by ion-chromatography. A 761 Compakt Metrohm Ion Chromatograph with Metrosep A Supp 5 Metrohm column and 3.2 mmol L^{-1} Na_2CO_3/1 mmol L^{-1} $NaHCO_3$ mobile phase with flow rate 0.7 mL min^{-1} was used for sulfate concentration measurements.

2.4. Sample preservation and analysis: Quadruple sulfur isotope composition

Ten liter samples were collected from each depth for sulfur isotope analyses of sulfate, acid volatile sulfide (AVS) and total ZVS, and preserved in a similar manner. Samples were pumped straight into zinc acetate solution (250 mL of 200 g L^{-1} zinc acetate per sample). In the laboratory, the samples were homogenized by vigorous shaking, and 5 to 9.5 L of sample was extracted thrice by 30 mL chloroform per liter of sample. The rest of the sample (0.5 to 5 L, depending on the hydrogen sulfide concentration) was filtered through Whatman glass fiber filters with 0.2 μm pore size and 47 mm diameter. Filters were immediately frozen. Filtrate (10–20 mL) was treated by 2 mL of 1 mol L^{-1} $BaCl_2$ solution to precipitate sulfate. $BaSO_4$ was collected on 0.2 μm filter and immediately frozen.

Zinc sulfide was converted to silver sulfide by boiling for 3 h with 5 mol L^{-1} HCl under slow flow of nitrogen. Evolving hydrogen sulfide was trapped in silver nitrate–nitric acid solution containing 2 mL of 0.3 mol L^{-1} $AgNO_3$, 2 mL of 1.55 mol L^{-1} HNO_3 and 15 mL Milli Q water.

Barium sulfate was reduced to hydrogen sulfide by boiling for 3 h with 25 mL of solution prepared from 500 mL 47% HI, 820 mL 12 mol L^{-1} HCl and 242 mL 50% H_3PO_2 under slow flow of nitrogen according to Forrest and Newman (1977). Hydrogen sulfide was trapped in silver nitrate–nitric acid solution.

The chloroform extracts were dried with anhydrous calcium chloride, filtered, and evaporated to dryness, first on a rotor evaporator (to 10–20 mL volume) and then in the round-bottom flask of a reduction apparatus under gentle flow of nitrogen. The zero-valent sulfur was reduced to H_2S gas by boiling for 2 h in a solution of 10 mL 12 mol L^{-1} HCl, 40 mL 99.98% ethanol, and 20 mL $CrCl_2$ solution filtered through 0.20 μm filter (Gröger et al., 2009). This method allows quantitative selective reduction of elemental sulfur in the presence of organo-sulfur compounds.

Raney-nickel reduction was performed sequentially on the sample after reduction of chloroform extract for ZVS analysis. This technique reduces organic sulfur to hydrogen sulfide. After ZVS reduction was accomplished, the excess of HCl and ethanol was evaporated by boiling for 2 h, and reaction mixture was cooled to room temperature. Reduction methodology was adopted from Oduro et al. (2011).

Conversion of silver sulfide to sulfur hexafluoride and analysis for quadruple sulfur isotope composition was performed according to Zerkle et al. (2010). Silver sulfide was quantitatively converted to SF_6 by reaction with 10-fold excess of F_2 gas at ~250 °C for ~8 h in Ni bombs. SF_6 was purified cryogenically by distillation in a liquid N_2–ethanol slurry at −115 °C, and by gas chromatography on a 12′

molecular sieve 5 Å/Hasep Q column with thermal conductivity detector. The isotopic abundance of the purified SF_6 was analyzed on a Finnigan MAT 253 dual inlet mass spectrometer at m/e− values of 127, 128, 129, and 131 ($^{32}SF_5^+$, $^{33}SF_5^+$, $^{34}SF_5^+$, and $^{36}SF_5^+$). Analytical uncertainties on sulfur isotope measurements, estimated from long-term reproducibility of Ag_2S fluorinations, are 0.14, 0.008, and 0.20 (1σ) for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$, respectively. Typical standard deviations between analyses of $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$ were 0.02–0.05‰, 0.01–0.02‰, and 0.1–0.2‰, respectively.

Isotopic measurements are reported on a VCDT scale, assuming the composition of IAEA S-1 is $\delta^{34}S = -0.30‰$, $\Delta^{33}S = 0.094‰$, and $\Delta^{36}S = -0.70‰$.

2.5. Reagents

All reagents were purchased from industrial suppliers and used without further purification.

2.6. Isotope notation

We report ^{3X}S isotopic composition of sulfur species in permil (‰) using standard delta (δ) notation:

$$\delta^{3X}S = \left[\left({}^{3X}R_{sample} \Big/ {}^{3X}R_{VCDT}\right) - 1\right] \quad (10)$$

where $^{3X}R_{sample}$ is the isotopic ratio of a sample:

$$^{3X}R = {}^{3X}S/{}^{32}S (\text{for } 3X = 33, 34, \text{or } 36) \quad (11)$$

and $^{3X}R_{VCDT}$ is the isotopic ratio of Vienna-Cañon Diabolo Troilite (VCDT).

We define the fractionation between two sulfur species, A and B, as $\delta^{34}S_A - \delta^{34}S_B$.

The minor isotope compositions of sulfur species are presented using the $\Delta^{3X}S$ notation, which describes the deviation of a sample datum in ^{33}S or ^{36}S (in ‰) from a reference fractionation line:

$$\Delta^{33}S = \delta^{33}S - \left[\left({}^{34}R_{sample} \Big/ {}^{34}R_{VCDT}\right)^{0.515} - 1\right] \quad (12)$$

and

$$\Delta^{36}S = \delta^{36}S - \left[\left({}^{34}R_{sample} \Big/ {}^{34}R_{VCDT}\right)^{1.90} - 1\right] \quad (13)$$

The exponents 0.515 and 1.90 are reference values assigned to approximate mass-dependent fractionations during thermodynamic equilibrium isotope exchange at low temperature (Hulston and Thode, 1965; Farquhar et al., 2003; Johnston et al., 2007). Small deviations from these reference values, which occur in biogeochemical systems due to the redistribution of mass between sulfur pools, by mixing or Rayleigh processes, results in the variation of isotope ratios of sulfur pools in a linear fashion. These deviations differ from that calculated for reference fractionation arrays, which follows an exponential trend. For a more detailed explanation of how these signatures are produced in natural systems see Farquhar et al. (2003, 2007) and Johnston et al. (2007).

The exponent characterizing these deviations, λ, is defined theoretically as:

$$^{3X}\lambda = \frac{\ln^{3X}\alpha}{\ln^{34}\alpha} \quad (14)$$

for $^{33}\lambda$ and $^{36}\lambda$, where α is defined as:

$$^{3X}\alpha_{A-B} = \frac{\delta^{3X}S_A + 1}{\delta^{3X}S_B + 1}. \quad (15)$$

This exponent can also be calculated from experimental data or environmental samples (e.g., between sulfide and sulfate pairs) using the equation:

$$^{3X}\lambda_{A-B} = \frac{\ln\left(\delta^{3X}S_A + 1\right) - \ln\left(\delta^{3X}S_B + 1\right)}{\ln\left(\delta^{34}S_A + 1\right) - \ln\left(\delta^{34}S_B + 1\right)}. \quad (16)$$

2.7. Model

We constructed a one-dimensional depth-derived model of sulfide in the deep waters of Rogoznica Lake, modified from Zerkle et al. (2010). The model includes diffusion, advection, phototrophic sulfide oxidation (FotoSox) and sulfate reduction (SR) (Table 1), and considers sulfide concentrations as well as the $\delta^{34}S$ and $\Delta^{33}S$ of sulfide. Sulfide concentrations were calculated by the following equation:

$$\frac{\partial C}{\partial t} + D\frac{\partial^2 C}{\partial z^2} - U\frac{\partial C}{\partial z} + q_{SR} - q_{FotoSox} = 0 \quad (17)$$

where C is the concentration, D is the vertical diffusivity, U is the upwelling velocity, and q terms are the various metabolic rates. We also calculated sulfide $\delta^{34}S$ and $\delta^{33}S$ using the equation:

$$\frac{\partial \delta^{3X}S}{\partial t} = \left(\sum_{i=1}^{n} F_i \cdot \delta^{3X}S_i - \delta^{3X}S\frac{\partial C}{\partial t}\right) \Big/ C \quad (18)$$

where F_i refers to the different sulfur mass fluxes (e.g., via diffusion, upwelling, phototrophic sulfide oxidation and sulfate reduction; Table 1). We solved the system of equations using a FTCS (forward in time centered in space) finite difference approximation, with a time step of 12 h and a spatial step of 0.5 m. The bottom boundary condition for sulfide

Table 1
Parameters for the 1D sulfide models (models B and C shown in Fig. 7). Diffusion rates are given in $m^2\ day^{-1}$, upwelling rates in $m\ day^{-1}$, and metabolic rates in $mmol\ m^{-3}\ day^{-1}$.

Process	Depth (m)	Rate	$^{34}\alpha$	$^{33}\lambda$	Result
A. Transport only					
Diffusion	9.5–13	0.0864	1.000	0.515	Model can fit concentration but not isotope profiles.
Upwelling	9.5–13	0.01	1.000	0.515	
B. Transport + phototrophic H_2S oxidation + sulfate reduction in sediments					
Diffusion	9.5–13	0.0864	1.000	0.515	Model can fit both concentration and isotope profiles with reasonable sulfate reduction rates.
Upwelling	9.5–13	0.01	1.000	0.515	
FotoSox	9.5–11.5	17	1.006	0.518	
SR	12.5–13	43	0.956	0.512	
C. Transport + phototrophic H_2S oxidation + sulfate reduction in sediments and water column					
Diffusion	9.5–13	0.0864	1.000	0.515	Model can fit both concentration and isotope profiles with reasonable sulfate reduction rates.
Upwelling	9.5–13	0.01	1.000	0.515	
FotoSox	9.5–11.5	13	1.006	0.518	
SR	9.5–13	8	0.956	0.512	

concentration was set at 3 mM, assuming a constant trend in sulfide concentrations from 11 to 13 m, with isotope values of $\delta^{34}S = -19.96‰$ and $\Delta^{33}S = 0.16‰$ (as in the deepest sample measured), and 0 mM sulfide at the top boundary. Initial conditions were set at 0 mM sulfide. Sulfate concentration was held constant (i.e., non-limiting) with depth, at 28 mM. We used vertical diffusivity and upwelling velocities similar to those calculated by Torgersen et al. (1981) for meromictic Fayetteville Green Lake (Table 1). We assumed that the diffusivity and upwelling rates are constant and independent of depth, and that no fractionation is associated with either of these transport processes. Changing the diffusivity velocities over orders of magnitude simply changed the amount of time required for the system to reach steady state, and the upwelling velocity had to be increased by 2 orders of magnitude to affect the model results. The model reached steady state from zero in less than 6 months.

The best fit of the model was determined visually. Parameters utilized in three separate models are shown in Table 1. Phototrophic sulfide oxidation was confined to the top 1.5 m of the lake. We first varied sulfide oxidation and sulfate reduction rates with depth to fit the sulfide concentration profile, then varied the $^{34}\alpha$ and $^{33}\lambda$ values to fit the isotope profiles. We tested (A) a model with transport processes only; (B) a model with transport + sulfide oxidation + sulfate reduction in the bottom 1 m of the lake (i.e., assuming most of the sulfate reduction is occurring in the sediments); and (C), a model with transport + sulfide oxidation + sulfate reduction throughout the water column (Table 1).

3. Results

3.1. Physico-chemical water column characteristics

Profiles of salinity and temperature are similar to the ones reported previously in the lake for the same season (Ciglenečki et al., 2005; Bura-Nakić et al., 2009) and point to the thermo-haline nature of lake stratification (Fig. 2a, b). However the chemocline was situated at a more shallow depth than usual for this time of year. This shallowing may be explained by unusually strong stratification of water layers during 2009 (Helz et al., 2011; Plavšić et al., 2011). The salinity profile from the first sampling shows an increase from 35 to 36 in the epilimnion to 38 in the bottom water layer (Fig. 2a). The temperature profiles were very similar during two samplings. In the epilimnion temperatures of 23.9–24.4 °C were recorded. In the chemocline, the temperatures reached maximum of 25.7 °C. A sharp decrease of temperature with depth was recorded in the hypolimnion. The lowest temperatures (19.5 °C and 17.3 °C during the first and second samplings, respectively) were detected at 13 m depth (Fig. 2b).

Decreases in pH and redox potential are also standard features for stratified water bodies due to sulfate reduction coupled to degradation of organic matter (Fig. 2c, d). Redox potential decreases sharply from 138–170 mV at 2–9.6 m depths to −272 to −362 mV at >10 m depths (Fig. 2d). Concentrations of dissolved oxygen decrease slowly with depth in the epilimnion from 234–238 μmol L^{-1} at 1–2 m depth to 185–221 μmol L^{-1} at 8 m depth, followed by sharp decrease to <5 μmol L^{-1} at 8.6–8.8 m depth (Fig. 2e).

3.2. Sulfur speciation

Sulfate concentrations in the lake were relatively constant throughout the water column, and in the range of 26.0–29.3 mmol L^{-1} at all depths (Fig. 3a). Sulfide concentrations reached 1 μmol L^{-1} at 9.5 m depth in both profiles. A very high sulfide concentration gradient, from 0.77 to 0.98 mmol L^{-1} m^{-1}, was recorded in the chemocline and hypolimnion. At 12 m depth the sulfide concentration was 1.74–2.35 mmol L^{-1} (Fig. 3b). Sulfide flux from the sediment was estimated to be c.a. 30 mmol m^{-2} $year^{-1}$ according to the Fick's First Law

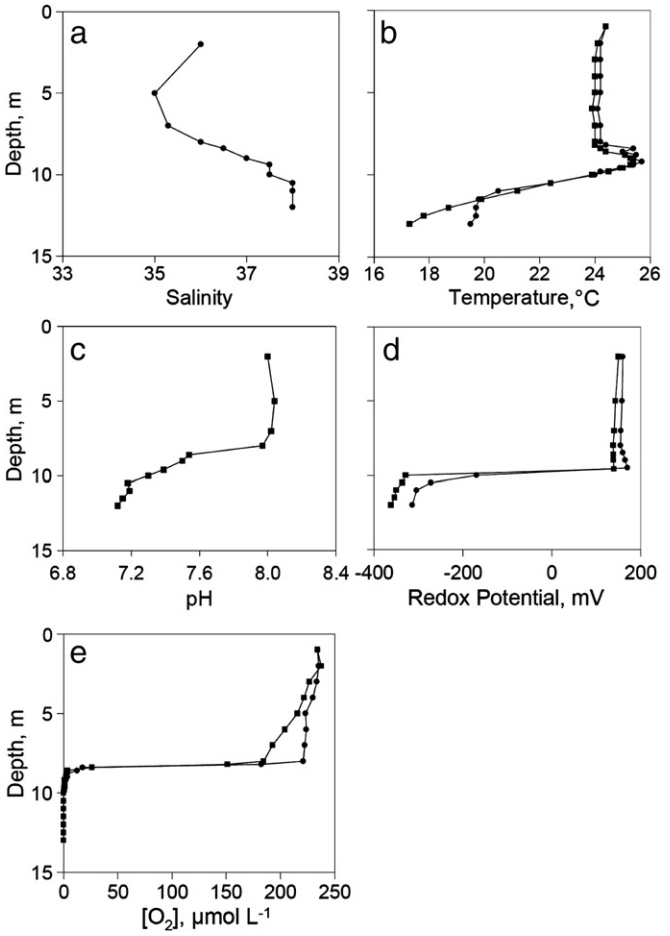

Fig. 2. Profiles of a) salinity, b) temperature, c) pH, d) redox potential, and e) dissolved oxygen in Lake Rogoznica during 16 September 2009 (circles) and 19 September 2009 (squares).

(Eq. (19)) using a vertical diffusion coefficient of 0.1 m^2 day^{-1}, which was of the same order of magnitude as one calculated for Fayetteville Green Lake (Torgersen et al., 1981).

$$J = -D\frac{\partial C}{\partial x} \tag{19}$$

A sharp peak of total ZVS concentration was detected in the chemocline. During the first sampling, 5.42 μmol L^{-1} of total ZVS was detected at 9.5 m depth, where the sulfide concentration was 1.45 μmol L^{-1}. During the second sampling, the highest total ZVS concentration was detected at 9.0 m depth, where the sulfide concentration was 0.78 μmol L^{-1}. In the epilimnion, the concentration of total ZVS was 10–85 nmol L^{-1}. In the hypolimnion 158–673 nmol L^{-1} of total ZVS was detected (Fig. 3c). Peak ZVS concentrations differed nearly four-fold, but we cannot exclude the possibility that we missed a sharp ZVS concentration maximum, as we sampled the water column with the 50 cm depth intervals.

The fraction of ZVS that passed through a 1.2 μm filter during the second sampling is presented in Fig. 4. It is above 70% at 8 m and 11–12 m depths and below 8% at 9–10 m depth. Inorganic polysulfides were below the detection limit, corresponding to <1 μmol L^{-1} of polysulfide ZVS, although the presence of polysulfides was detected electrochemically in previous studies (Bura-Nakić et al., 2009).

Thiosulfate and sulfite concentrations were measured in the second profile. No significant trend in thiosulfate concentrations was found, though the highest concentration (4.69 μmol L^{-1}) was detected in the

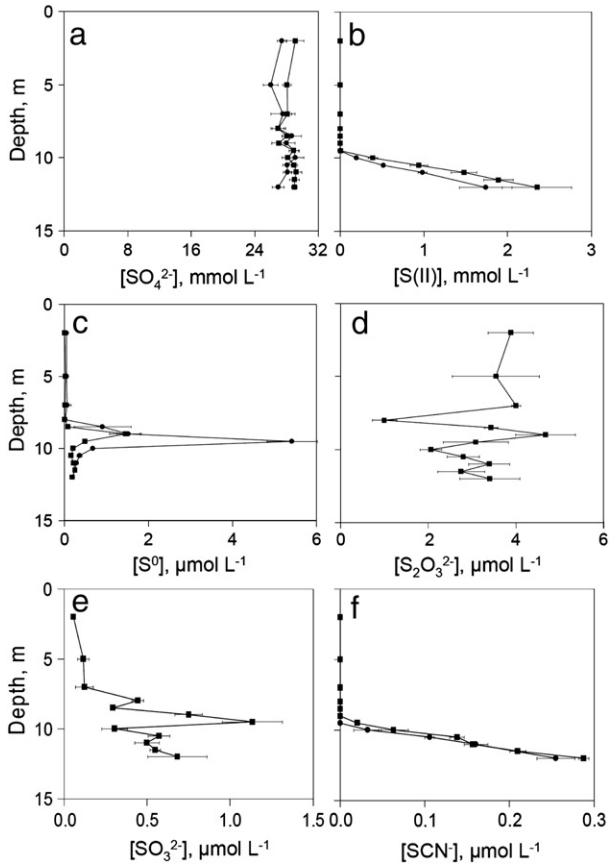

Fig. 3. Concentrations of a) sulfate, b) total S(II), c) total ZVS, d) thiosulfate, e) sulfite, and f) thiocyanate in Lake Rogoznica during 16 September 2009 (circles) and 19 September 2009 (squares).

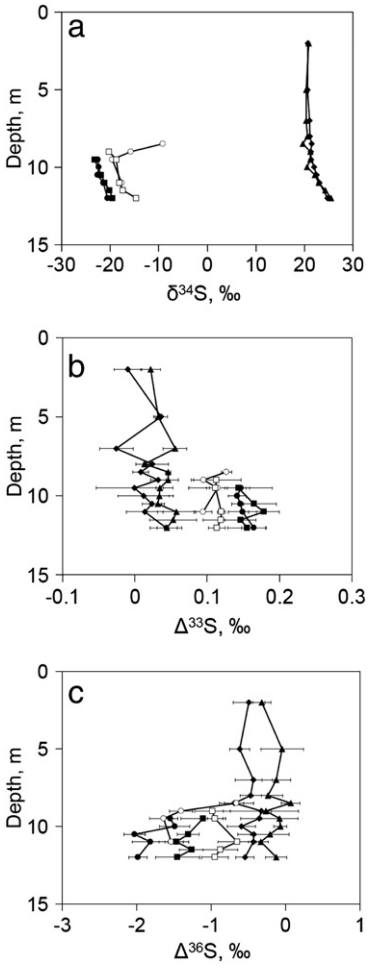

Fig. 5. Isotope composition of sulfur species in Lake Rogoznica: a) $\delta^{34}S$, b) $\Delta^{33}S$, and c) $\Delta^{36}S$. Closed circles — AVS (16 September 2009), closed squares — AVS (19 September 2009), opened circles — ZVS (16 September 2009), opened squares — ZVS (19 September 2009), closed diamonds — sulfate (16 September 2009), closed triangles — sulfate (19 September 2009).

chemocline at 9 m depth (Fig. 3d). Sulfite concentrations in the range of 0.06–1.13 μmol L^{-1} were detected with the highest concentration at 9.5 m, 0.5 m below the onset of sulfide (Fig. 3e).

Thiocyanate was detected only in the sulfidic waters with [S(II)]> 7 μmol L^{-1}. Thiocyanate concentrations linearly increased with depth, and reached 255–288 nmol L^{-1} at 12 m depth (Fig. 3f). Thiocyanate concentrations differed nearly twice at 10 m between two samplings, but the difference between these values is less than the sum of standard deviations calculated from triplicate analyses.

3.3. Quadruple sulfur isotope composition

Sulfate $\delta^{34}S$ values were 20.4–21.5‰ in the epilimnion and chemocline (≤9.5 m depth) with one outliner (19.6‰). In the hypolimnion, sulfate became heavier with depth, reaching $\delta^{34}S$ values of 24.7–25.5‰ at 12 m (Fig. 5a, Table 2). AVS $\delta^{34}S$ values increase with depth from −23.1 to −22.5‰ at 9.5 m to −20.5 to −19.4‰ at 12 m depth. ZVS was 2.8 to 4.8‰ more enriched in ^{34}S than sulfide.

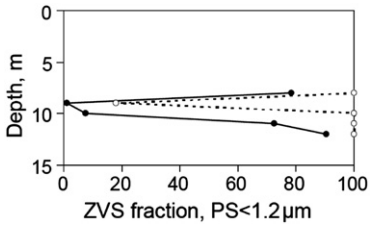

Fig. 4. Fraction of ZVS which passes 1.2 μm pore-size filter (closed circles and solid line) and calculated maximum fraction of soluble ZVS (opened circles and dashed line) (see details in text).

During the first sampling, ZVS above the sulfidic zone was more ^{34}S-enriched (6.8–13.4‰) than AVS in the chemocline.

The only sample which contained enough organic sulfur for isotope analysis after Raney-nickel reduction was collected, was a combined sample from 8.5 to 10 m depths from the second profile. The sample size was too small for precise determination of minor sulfur isotope values (117 μg Ag_2S). The $\delta^{34}S$ value for this sample was −3.45 ± 0.13‰.

Sulfate, AVS and ZVS showed no clear $\Delta^{33}S$ trends with depth. Sulfate had the lowest $\Delta^{33}S$ values, from −0.026 to 0.056‰. ZVS $\Delta^{33}S$ values were higher, from 0.094 to 0.127‰. The highest $\Delta^{33}S$ values were those of AVS, from 0.141 to 0.178‰ (Fig. 5b, Table 2). $\Delta^{36}S$ values were more scattered, showing similar trends to $\Delta^{33}S$ values. Sulfate had the highest range (−0.69 to 0.07‰), followed by ZVS (−0.65 to −1.64‰), and AVS had the lowest range of $\Delta^{36}S$ values (−1.11 to −2.03‰) (Fig. 5c, Table 2).

Variability of the isotope compositions between the sampling times was minimal. Average values for $\delta^{34}S$ for sulfate–AVS fractionation were 44.54‰ during the first and 44.31‰ during the second sampling. The difference of 0.23‰ is larger than the standard deviation of analysis, but smaller than the fractionation variability with depth at the same sampling (c.a. 0.5‰). Average values for $\Delta^{33}S$ for sulfate–AVS fractionation were 0.131‰ during first and 0.113‰ during second sampling. The difference of 0.018‰ lies in the range of standard deviation for $\Delta^{33}S$ determination (0.01–0.02‰). Differences

Table 2
Sulfur isotope values of sulfate, AVS, and ZVS in the water column of Rogoznica Lake, normalized to VCDT (in ‰). Standard deviations (σ) of individual analyses are based on three runs per sample. Data points are plotted in Fig. 5.

S species	Depth, m	$\delta^{34}S$	$\Delta^{33}S$	$\Delta^{36}S$	$\sigma(\delta^{34}S)$	$\sigma(\Delta^{33}S)$	$\sigma(\Delta^{36}S)$
16 September 2009							
Sulfate	2	20.712	−0.010	−0.491	0.024	0.019	0.213
	5	20.628	0.036	−0.614	0.095	0.009	0.132
	7	21.062	−0.026	−0.429	0.049	0.023	0.249
	8	21.098	0.024	−0.468	0.053	0.023	0.143
	8.5	21.471	0.008	−0.688	0.057	0.011	0.128
	9	21.256	0.032	−0.326	0.048	0.011	0.507
	9.5	21.327	−0.001	−0.352	0.048	0.053	0.252
	10	21.927	0.012	−0.592	0.025	0.035	0.190
	10.5	22.512	0.023	−0.425	0.050	0.013	0.219
	11	23.034	0.014	−0.428	0.004	0.026	0.071
	12	24.732	0.043	−0.543	0.061	0.022	0.125
AVS	9.5	−22.485	0.147	−1.547	0.044	0.044	0.099
	10	−22.311	0.141	−1.487	0.021	0.012	0.204
	10.5	−22.565	0.146	−2.028	0.037	0.004	0.145
	11	−21.341	0.149	−1.816	0.028	0.020	0.243
	12	−20.476	0.164	−1.984	0.013	0.017	0.122
ZVS	8.5	−9.118	0.127	−0.658	0.019	0.007	0.229
	9	−15.695	0.095	−1.402	0.039	0.014	0.155
	9.5	−19.593	0.114	−1.637	0.021	0.039	0.189
	11	−17.622	0.094	−1.534	0.030	0.012	0.162
19 September 2009							
Sulfate	2	20.825	0.022	−0.317	0.003	0.014	0.120
	5	20.374	0.032	−0.044	0.012	0.006	0.284
	7	20.384	0.056	−0.122	0.013	0.016	0.192
	8	20.631	0.013	−0.235	0.009	0.002	0.199
	8.5	19.625	0.046	0.070	0.003	0.004	0.128
	9	21.221	0.046	−0.261	0.007	0.014	0.073
	9.5	21.222	0.034	−0.077	0.003	0.005	0.243
	10	20.509	0.034	−0.070	0.002	0.019	0.087
	10.5	22.102	0.032	−0.208	0.006	0.009	0.259
	11	22.884	0.058	−0.327	0.002	0.026	0.096
	11.5	24.310	0.053	2.840	0.005	0.032	0.016
	12	25.505	0.045	−0.125	0.010	0.014	0.141
AVS	9.5	−23.127	0.143	−1.108	0.006	0.015	0.302
	10.5	−21.778	0.164	−1.308	0.008	0.031	0.143
	11	−21.073	0.178	−1.463	0.015	0.021	0.160
	11.5	−20.107	0.146	−1.264	0.003	0.021	0.161
	12	−19.447	0.155	−1.451	0.012	0.026	0.293
ZVS	9	−20.164	0.113	−0.981	0.003	0.035	0.239
	9.5	−18.726	0.111	−0.947	0.003	0.012	0.102
	11	−18.044	0.119	−0.651	0.004	0.005	0.260
	11.5	−17.335	0.119	−0.875	0.011	0.025	0.230
	12	−14.655	0.113	−0.947	0.006	0.012	0.181

for $\delta^{34}S$ and $\Delta^{33}S$ of ZVS–AVS fractionation are 0.44‰ and 0.004‰ respectively. The difference for $\delta^{34}S$ is quite large taking into account small fractionations (3.31‰ and 3.75‰ during first and second samplings, respectively), but it is still smaller than variation of this parameter with depth.

Shape of the $\Delta^{36}S$ profiles was in most cases a mirror image of the $\Delta^{33}S$ profiles and in our case did not provide additional information regarding biogeochemical processes in the Lake Rogoznica.

4. Discussion

4.1. Sulfur species distributions in Lake Rogoznica

Sulfide oxidation intermediates are principally formed in a redox transition zone where hydrogen sulfide, which diffuses from sediments, meets oxygen, which diffuses from the mixed epilimnion (Zopfi et al., 2001). The chemocline of Lake Rogoznica was relatively stable during the sampling period and was characterized by a small interval of 50 cm where sulfide and dissolved oxygen coexist at very low concentrations, as previously reported by Bura-Nakić et al. (2009). The chemocline was densely populated with purple sulfur bacteria from genus *Chromatium* (Ciglenečki et al., 1998).

ZVS is the most abundant product of sulfide oxidation that we observed in Lake Rogoznica, and we attribute its presence to the activity of the purple phototrophic sulfur oxidizing bacteria present in the chemocline. Although the values of the highest concentration of ZVS varied in two samplings by more than a factor of 3, the shapes of the profiles were very similar. Above the chemocline, ZVS concentrations were 10–85 nmol L^{-1}. These values are lower than the solubility of α-S_8 in sea water at 15 °C (114 nmol L^{-1} S^0, calculated from thermodynamic constants from Kamyshny (2009b)). ZVS concentrations increase starting from ~0.5 m below the depth where hydrogen sulfide concentrations began to rise (to >0.5 μmol L^{-1}). At the shallowest depth where sulfide was detected (1.45 μmol L^{-1} and 0.78 μmol L^{-1} during first and second samplings, respectively), the highest ZVS concentrations were also detected. In the hypolimnion, ZVS concentrations decreased with depth, but were still higher than in the epilimnion.

ZVS may be produced in the redox transition zone by both chemical oxidation and oxidation by phototrophic sulfur oxidizing bacteria (Zerkle et al., 2010). At near neutral and basic pH values, hydrogen sulfide reacts with rhombic elemental S (Kamyshny et al., 2007 and references therein), colloidal elemental S (Boulegue, 1976) and dissolved elemental S (Kamyshny et al., 2008), to form water soluble inorganic polysulfides, according to Eq. (20):

$$HS^- + (n-1)/8S_8 = H^+ + S_n^{2-} \quad (20)$$

The fraction of sulfur passing through 1.2 μm pore-size filter and the maximum fraction of sulfur which can be dissolved in sea-water as soluble and polysulfidic S^0 at 15 °C and pH = 7.5 in equilibrium with α-S_8 (calculation based on thermodynamic constants from Kamyshny et al. (2007) and Kamyshny (2009b)), are shown in Fig. 4. At 8 m depth, the ZVS concentration is below the solubility of S_8 in seawater. In agreement with this calculation, 78% of the detected ZVS passes through a 1.2 μm pore-size filter. At 9 m depth, sulfide is already detectable, but its concentration is too low to support all detected ZVS as the sum of polysulfidic and dissolved sulfur. A calculation shows that only 18% of detected ZVS can exist in various dissolved forms. Experimental results show much lower values: less than 1% of all detected ZVS passes through a 1.2 μm pore-size filter. Most of the ZVS at this depth, representing the chemocline, is stored inside the cells of sulfide oxidizing phototrophic bacteria. At 10 m and greater depths, the concentration of hydrogen sulfide is high enough to solubilize all ZVS in the form of polysulfides. At 10 m, where sulfide oxidizing phototrophs are still abundant, only 7.5% of ZVS passes through a 1.2 μm pore-size filter. At 11–12 m depth, where sinking decomposing microbial cells can release sulfur globules, sinking ZVS particles react with hydrogen sulfide, resulting in the formation of polysulfides. At 11 and 12 m depths, 72% and 90% of ZVS, respectively, passed through a 1.2 μm pore-size filter. Total concentration of ZVS that passed through the filter was always lower than 170 nmol L^{-1}. This agrees with an observation that concentrations of individual polysulfides are below the detection limit, which corresponds to 1 μmol L^{-1} of ZVS. A very similar ZVS particle size distribution was detected in meromictic Fayetteville Green Lake, New York, by Zerkle et al. (2010).

Thiosulfate and sulfite are known products of oxidation of hydrogen sulfide by oxygen, both abiotically (Zhang and Millero, 1993) and by microbial processes (see Zopfi et al. (2004) for review). The sulfite profile here is consistent with production at the chemocline, though its concentration peak at 9.5 m is not much higher than the concentrations above and below the chemocline (1.13 μmol L^{-1} and 0.06–0.68 μmol L^{-1} respectively). Thiosulfate concentrations in agreement with previously published data (Ciglenečki and Ćosović, 1997) do not show a maximum at the chemocline. As nitrate concentrations in the lake are high, up to 19 μmol L^{-1} in the surface waters (Ciglenečki et al., 2005), the reason for low concentrations of sulfite and thiosulfate

in the chemocline may be bacterial nitrate reduction coupled to sulfite and thiosulfate oxidation (e.g., Kamyshny et al., 2011b).

Another sulfur compound, whose distribution in stratified aquatic systems has thus far not been studied, is thiocyanate. The development of a sensitive and robust technique for thiocyanate analysis by Rong et al. (2005) opened a way for detailed study of thiocyanate distribution in natural aquatic systems. Previous reports showed that concentrations of thiocyanate up to 140 nmol L^{-1} were detected in marine systems strongly affected by pollution, such as Nagoya Port (Rong et al., 2005). Only 13 nmol L^{-1} of SCN^- was detected in non-polluted North Sea water (Kamyshny, 2009a).

We report here for the first time the presence of up to 288 nmol L^{-1} of thiocyanate in a non-polluted natural highly eutrophicated marine system. Like hydrogen sulfide, thiocyanate appears to be produced in the sediment and diffuse towards the chemocline, where it is consumed by abiotic or biologically enhanced oxidation. (The thiocyanate flux from the sediment was estimated similarly to sulfide flux and was found to be c.a. 4 μmol m^{-2} $year^{-1}$.) A very similar profile of thiocyanate characterized by SCN^- concentrations up to 274 nmol L^{-1} near the bottom and an absence of SCN^- in the epilimnion was detected in the meromictic Fayetteville Green Lake, New York, in July 2009 (A. Kamyshny, unpubl.) though flux from the Green Lake sediment was lower (c.a. 0.2 μmol m^{-2} $year^{-1}$).

The most realistic pathway for thiocyanate formation in Lake Rogoznica sediments is the reaction of cyanide, which can be produced by various biotic processes (Wong-Chong et al., 2006), with sulfide oxidation intermediates such as colloidal sulfur, polysulfides, thiosulfate and tetrathionate (6–9). Thiosulfate is available in Lake Rogoznica deep waters (up to 4.7 μmol L^{-1}). Polysulfides, which are especially reactive toward cyanide, were not detected, although the presence of polysulfides was documented during earlier research on Rogoznica Lake by Bura-Nakić et al. (2009). Attempts to measure cyanide concentration in sediments of Lake Rogoznica were not made so far, but high concentrations of iodide (up to 2.27 μmol L^{-1}) are found near the bottom of the lake (Žic and Branica, 2006). Iodide is usually released during remineralization of organic matter (Ullman and Aller, 1983; Ullman et al., 1988), by the same process that is possibly responsible for cyanide release.

As thiocyanate is a relatively stable compound and its solutions can be stored for weeks at room temperature (Kamyshny, 2009a), we suggest that thiocyanate consumption in the chemocline proceeds due to bacterial processes. Biological oxidation of thiocyanate is known to produce ammonia, carbonate and sulfate (Ghosh et al., 2006). We can also not rule out assimilatory uptake of thiocyanate. Thiocyanate may represent an important link between the carbon, nitrogen and sulfur cycles in stratified euxinic lake systems. Further mechanistic and quantitative studies of thiocyanate cycling in anoxic sediments are required for understanding the importance of this compound for sulfur, nitrogen and carbon cycles in anoxic sediments.

4.2. Sulfur isotope composition

In Lake Rogoznica at 2 m depth, the $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$ values of sulfate are 20.71 to 20.83‰, 0.019 to 0.022‰ and −0.49 to −0.32‰, respectively. In the Adriatic Sea over the cliff from the lake, sulfate $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$ values were found to be 21.93, 0.009‰ and 0.03‰, respectively (sampled at the Rogoznica Marina on October 28, 2010). At 100 m depth in the Cariaco basin these values are 21.36‰, 0.034‰ and −0.21‰, respectively (Li et al., 2010).

Fractionation between AVS and sulfate in Lake Rogoznica ranges from 43.8 to 45.2‰ (Fig. 6), within the range of fractionations measured in the laboratory by pure cultures and natural populations of sulfate reducers (e.g., Kaplan and Rittenberg, 1964; Canfield et al., 2010; Zerkle et al., 2010 and references therein).

Canfield and Thamdrup (1994) argued that sulfur disproportionation can lead to high fractionations between sulfate and sulfide in stratified water bodies and sediments. Recent works, utilizing a multiple sulfur isotope analysis approach, showed that presence of disproportionation is not necessary for fractionations as high as 54‰ in the Cariaco Basin (Li et al., 2010) and up to 45‰ in Lago di Cadagno (Canfield et al., 2010). It is highly unlikely that bacterial sulfur disproportionation occurs in sulfidic waters of Lake Rogoznica as sulfide concentration reaches 1 mmol L^{-1} 1 m below the redox-transition zone.

Large sulfur isotope fractionation between sulfate and AVS in the lake may be explained by complete oxidation of highly refractory organic matter, which is known to be present in the Lake Rogoznica water column (Ćosović et al., 2000), to CO_2 (Brüchert, 2004 and references therein). Dissolved organic carbon (DOC) concentrations in the water column of the lake are usually in the range of 1–3 mg L^{-1} (but values as high as 6 mg L^{-1} were documented) with higher concentrations at and below the chemocline (Ćosović et al., 2000; Penezić et al., 2010). Particulate organic carbon (POC) is 0.28–1.5 mg L^{-1} (Penezić et al., 2010).

In Lake Rogoznica, the AVS and ZVS multiple sulfur isotope composition is consistent with phototrophic sulfide oxidation at the chemocline (e.g., with sulfide becoming enriched in ^{34}S with depth across the chemocline). In the chemocline of Fayetteville Green Lake, a sulfide S isotope signal related to abiotic sulfide oxidation was recorded instead (e.g., with sulfide becoming depleted in ^{34}S with depth across the chemocline). This difference can be explained by the stronger overlap between hydrogen sulfide and dissolved oxygen concentrations in Fayetteville Green Lake (Zerkle et al., 2010).

The relative differences between the isotopic compositions of sulfide and ZVS may be affected by variety of biogeochemical processes. Extracellular and intracellular sulfur is known to exchange isotopes with inorganic polysulfides (Amrani et al., 2006; Zerkle et al., 2009). In equilibrium between sulfide, polysulfide and cyclooctasulfur, polysulfidic ZVS is enriched in ^{34}S by up to 3.4 to 4‰. The exact enrichment is dependent on the average polysulfide chain length (Amrani and Aizenshtat, 2004; Amrani et al., 2006). These results agree with calculations based on chemical equilibrium between sulfide and elemental sulfur, which predict enrichment in ^{34}S of elemental sulfur relative to H_2S by 3‰ at 25 °C (Tudge and Thode, 1950). Fry et al. (1988a), on the other hand, reported that sulfide became 4 to 8‰ depleted in ^{34}S during oxidation by oxygen at conditions which allow polysulfide formation (pH = 8.2). One important difference is that significant amounts of other intermediate sulfur species (namely sulfite and thiosulfate) were also produced in the experiments reported by Fry et al. (1988a). Overall, isotope fractionation produced during sulfide–polysulfide–cyclooctasulfur equilibrium tend to be larger than some fractionations that have been measured in pure cultures of phototrophic bacterial sulfide oxidation (1 to 4‰) (Kaplan and Rittenberg, 1964; Fry et al., 1988b;

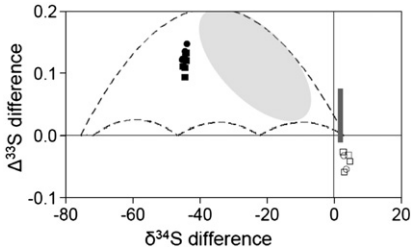

Fig. 6. $\Delta^{33}S$ vs. $\delta^{34}S$ of AVS–sulfate fractionation (closed symbols) and $\Delta^{33}S$ vs. $\delta^{34}S$ of ZVS–AVS fractionation (opened symbols). Circles — 16 September 2009 sampling, squares — 19 September 2009 sampling. Dotted area depicts values for sulfate reduction calculated by Farquhar et al. (2007) for the Brunner and Bernasconi (2005) model. Light gray area shows values for AVS–sulfate fractionation during sulfate reduction measured in bacterial cultures (Johnston et al., 2005a, 2007; Zerkle et al., 2010) (but see recent work by Sim et al. (2011), which expands the field for microbial sulfate reduction). Dark gray area represents values for ZVS–AVS fractionation during sulfide oxidation by phototrophic bacteria (Zerkle et al., 2009 and references therein). See text for detailed explanation.

Zerkle et al., 2009), although measurements of bacterially-associated ZVS in natural systems suggest that phototrophs can produce larger isotope effects, likely due to internal sulfide–polysulfide–cyclooctasulfur equilibration (Zerkle et al., 2009, 2010).

Negative $\Delta^{33}S$ values for fractionation between elemental sulfur and sulfide (Fig. 6) contradict positive or slightly negative values for fractionation between ZVS and sulfide by the culture of phototrophic sulfide-oxidizing bacteria *Chlorobium tepidum* during oxidation of sulfide to ZVS, although negative $\Delta^{33}S$ values for ZVS were produced by these organisms during reoxidation of ZVS to sulfate (Zerkle et al., 2009). Since quadruple sulfur isotope fractionation was studied only for one cultured organism and quadruple sulfur isotope fractionation for sulfide–polysulfide–cyclooctasulfur equilibrium is unknown we cannot rule out phototrophic sulfide oxidation (likely with reoxidation of ZVS to sulfate) as the primary oxidation reaction in the chemocline. This sulfide oxidation pathway is further supported by modeling of the sulfide concentrations and S isotopes (Fig. 7; Table 1).

We detected ZVS strongly enriched in ^{34}S during the first sampling at 8.5 m and 9.0 m depths. Sulfide concentration at these depths was below the detection limit (<0.5 μmol L^{-1}). Since sulfide concentrations of <1 μmol L^{-1} do not allow collection of sample large enough for isotope composition analysis, we have no data for AVS $\delta^{34}S$ for comparison. $\delta^{34}S$ values for ZVS were −15.7‰ and −9.1‰ at 9.0 and 8.5 m, respectively, compared to $\delta^{34}S = -22.5$‰ for AVS at 9.5 m depth. We have two feasible explanations for the ^{34}S-enriched values. First, we cannot rule out the possibility that ZVS may have been produced by oxidation of heavier sulfide at 8.5–9 m depth during recent chemocline depth fluctuations. A second, and we believe more feasible, explanation is that due to the small sample size contamination by heavier organic sulfur during Cr(II) reduction is possible. Although many organic sulfur compounds are thought not to release H_2S during Cr(II) reduction (Canfield et al., 1987; Gröger et al., 2009) sulfur–sulfur and sulfur–oxygen bonds are known to be reactive toward Cr(II) (Kamyshny et al., 2009). Organic compounds cross-linked by $-S_n-$ bridges will be assayed by Cr(II) reduction (Ferdelman, 1994). Reduction of certain fraction of sedimentary organic sulfur by Cr(II) was reported by Canfield et al. (1998). Thus after Cr(II) reduction, we performed sequential Raney-nickel reduction of chloroform extracts, to check the presence and isotopic composition of organic sulfur. A combined sample (8.5–10 m depth, second sampling) yielded enough silver sulfide for isotope composition analysis. Although the sample was collected at the same depth, but three days later than the high $\delta^{34}S$ ZVS sample, a high value of organic sulfur $\delta^{34}S$ (-3.45 ± 0.13‰) was observed, supporting an organic sulfur contamination explanation. This value for organic sulfur isotopic composition is interesting in itself, as it falls between $\delta^{34}S$ values for lake water sulfate and AVS. Further research in this direction may shed a light on mechanisms of microbial sulfur assimilation in the lake. The approach for such research was recently proposed by Oduro et al. (2011), who developed a protocol for analysis of the multiple sulfur isotope composition of volatile organic and humic sulfur.

Modeling of the concentration profiles and sulfur isotope composition of AVS suggest that sulfide is produced in the sediments and potentially in the water column, and is oxidized predominantly by biologic processes in the redox transition zone (Table 1; Fig. 7). These models suggest that the fractionations can be produced via diffusion of sulfide from the sediments with or without reasonable rates of sulfate reduction in the water column, combined with phototrophic sulfide oxidation in the chemocline and ZVS–sulfide fractionations of 6‰ (Table 1; Fig. 7). Further oxidative recycling of intermediate sulfur compounds (e.g., via sulfur compound disproportionation) is not necessary in this model to produce the fractionations we measure here between sulfate and AVS, although the model cannot rule these processes out. Sulfide concentrations from ~1 m below the chemocline and deeper are high enough to inhibit ZVS disproportionation without an external sulfide sink (Thamdrup et al., 1993; Canfield and Thamdrup, 1994), further suggesting that disproportionation is not a dominant part of the Lake Rogoznica sulfur cycle.

5. Conclusions

In Lake Rogoznica, a marine, euxinic, thermally-stratified anoxic basin, sulfur cycling broadly stratified into three zones. Reduced sulfur, principally as dissolved hydrogen sulfide, diffuses upward from the sediment toward the chemocline. In the chemocline hydrogen sulfide is oxidized by the purple phototrophic sulfide oxidizing bacteria from the genus *Chromatium*. Although in the chemocline sulfide and oxygen co-exist at low concentrations, no evidence for abiotic sulfide oxidation was found. The main product of bacterial hydrogen sulfide oxidation is zero-valent sulfur. Isotopic fractionation between hydrogen sulfide and zero-valent sulfur differs from fractionation detected in cultures of green sulfide oxidizing bacteria, but agrees with chemical equilibrium of sulfide–polysulfide–rhombic sulfur system. High observed sulfur isotope fractionation between sulfate and sulfide is likely to result from bacterial sulfate reduction, not accompanied by bacterial sulfur disproportionation. Thiocyanate is also detected in Lake Rogoznica. The thiocyanate profile shape suggests

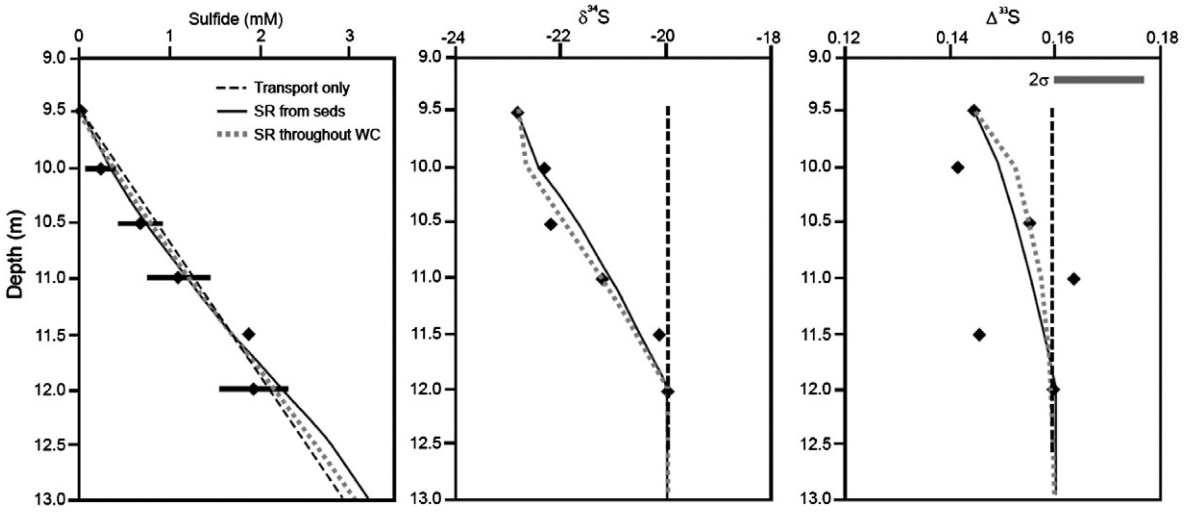

Fig. 7. Concentration (a), $\delta^{34}S$ values (b) and $\Delta^{33}S$ values (c) of the AVS. Diamonds represent averages of values measured during two sampling days. Error bars correspond to standard deviation of values measured during two sampling days. The dashed line corresponds to modeled conditions for transport (diffusion and advection) alone, the solid line corresponds to modeled conditions for microbial sulfate reduction in only the sediment, and the dotted line corresponds to modeled conditions for microbial sulfate reduction in both the sediments and water column. For detailed explanation of model see text and Table 1.

that it diffuses from the sediment and is consumed or oxidized at the chemocline. Reactions of sulfide oxidation intermediates with hydrogen cyanide are a possible source of thiocyanate in the sediment. Thus, thiocyanate provides a link between the sulfur, carbon and nitrogen cycles both in reducing sediments and at the oxidative chemocline.

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