

# Quadruple sulfur isotope constraints on the origin and cycling of volatile organic sulfur compounds in a stratified sulfidic lake

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## Abstract

We have quantified the major forms of volatile organic sulfur compounds (VOSCs) distributed in the water column of stratified freshwater Fayetteville Green Lake (FGL), to evaluate the biogeochemical pathways involved in their production. The lake's anoxic deep waters contain high concentrations of sulfate ( $12\text{--}16\text{ mmol L}^{-1}$ ) and sulfide ( $0.12\text{ }\mu\text{mol L}^{-1}$  to  $1.5\text{ mmol L}^{-1}$ ) with relatively low VOSC concentrations, ranging from  $0.1\text{ nmol L}^{-1}$  to  $2.8\text{ }\mu\text{mol L}^{-1}$ . Sulfur isotope measurements of combined volatile organic sulfur compounds demonstrate that VOSC species are formed primarily from reduced sulfur ( $\text{H}_2\text{S}/\text{HS}^-$ ) and zero-valent sulfur (ZVS), with little input from sulfate. The data support a role of a combination of biological and abiotic processes in formation of carbon–sulfur bonds between reactive sulfur species and methyl groups of lignin components. These processes are responsible for very fast turnover of VOSC species, maintaining their low levels in FGL. No dimethylsulfoniopropionate (DMSP) was detected by Electrospray Ionization Mass Spectrometry (ESI-MS) in the lake water column or in planktonic extracts. These observations indicate a pathway distinct from oceanic and coastal marine environments, where dimethylsulfide (DMS) and other VOSC species are principally produced via the breakdown of DMSP by plankton species.

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## 1. INTRODUCTION

The use of stable isotopes to understand the biogeochemical cycling of sulfur in oceanic (Rees et al., 1978; Jørgensen et al., 2004; Böttcher et al., 2006), freshwater (Fry, 1986; Canfield et al., 2010; Zerkle et al., 2010), and terrestrial systems (Goldhaber and Kaplan, 1980; Habicht and Canfield, 2001) has focused mostly on the dynamics of inorganic sulfate, sulfide and their intermediate species. Few studies (e.g., Amrani et al., 2009; Oduro et al., 2011) have examined organic sulfur compounds, such as dimethylsulfide (DMS;  $\text{CH}_3\text{SCH}_3$ ), methanethiol (MT;  $\text{CH}_3\text{SH}$ ),

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dimethyldisulfide (DMDS;  $\text{CH}_3\text{SSCH}_3$ ), carbon disulfide ( $\text{CS}_2$ ), and carbonylsulfide (OCS). These compounds are reactive and are found at pico- to micromolar concentrations in oxic and anoxic natural waters (Radford-Knoery and Cutter, 1993; Gun et al., 2000). Most studies of volatile organic sulfur compounds (VOSCs) in the past few decades have been focused on the flux of VOSCs from ocean to atmosphere due to their potential role in climate regulation (Charlson et al., 1987; Calhoun et al., 1991; Andreae and Crutzen, 1997).

Three major biotic and abiotic processes have been suggested to be responsible for the production of VOSCs in aquatic natural environments: methylation of free sulfide ( $\text{H}_2\text{S}_{(\text{aq})}$ ,  $\text{HS}^-$ , and  $\text{S}^{2-}$ ) (Kreft and Schink, 1993; Lomans et al., 2002), zero-valent sulfur (ZVS) and polysulfide (Gun et al., 2000); degradation of sulfur-containing amino acids (Kadota and Ishida, 1972; Kiene and Capone, 1988; Higgins et al., 2006); and enzymatic cleavage of  $\beta$ -dimethylsulfoniopropionate (DMSP;  $(\text{CH}_3)_2\text{S}^+\text{CH}_2\text{CH}_2\text{COO}^-$ ) by marine algae (Kiene and Taylor, 1989; Ginzburg et al., 1998; Kiene et al., 2002; Yoch, 2002). The latter process is believed to be the dominant route for production of VOSCs (particularly DMS) in freshwater (Ginzburg et al., 1998) and marine environments (Kiene and Taylor, 1989; Stefels, 2000; Simo et al., 2002).

In freshwater systems, a combination of the above processes may produce VOSCs, depending on water chemistry, density stratification, and the type of bacterioplankton community that is present. For instance, Gun et al. (2000) argued that nucleophilic polysulfides are the direct precursors for DMDS and probably other volatiles, such as OCS, in Lake Kinneret (Israel). In the same freshwater system, Ginzburg et al. (1998) found the DMS precursor, DMSP (up to 5.5 pg/cell) was produced by a freshwater dinoflagellate *Peridinium gatunense*. This organism dominates the phytoplankton population in Lake Kinneret.

Yoch et al. (2001) also observed the production of DMS in freshwater sediment slurries upon addition of DMSP, and suggested that DMS-producing Gram-positive bacteria were present in non-marine environments.

Here we report the presence of a number of VOSC species (including DMS, MT, DMDS,  $\text{CS}_2$ , and OCS) in the anoxic and sulfidic deep waters of density-stratified Fayetteville Green Lake (FGL). We have coupled a sulfur isotope approach, using variations in the relative abundances of the four stable sulfur isotopes, with concentration analysis to examine the mechanisms and pathways responsible for VOSC formation in this freshwater system. This contribution concentrates on the relative role of abiotic and biogenic pathways between organic and inorganic sulfur species in the lake water column using sulfur isotope measurements.

### 1.1. Geographic settings and geochemical parameters

FGL is a freshwater system located near the town of Fayetteville, New York, USA (Fig. 1). The lake is meromictic (permanently stratified), with oxic waters (the mixolimnion) occupying the uppermost  $\sim 20$  m depth, a redox interface (chemocline) at around 20–21 m depth, and sulfidic anoxic waters (the monimolimnion) extending to the deepest part of the lake, at  $\sim 52$  m depth. The lake's small size ( $\sim 0.26 \text{ km}^2$ ), areal geometry, and density profile stabilize the stratification in the water column. Stratification of FGL is maintained in large part by an inflow of calcium and sulfate-rich saline groundwater at  $\sim 18$  m water depth (Brunskill and Ludlam, 1969; Hilfinger and Mullins, 1997). Sulfate, which occurs at high concentrations throughout the water column, is the ultimate source of reduced inorganic and organic forms of sulfur in FGL (Takahashi et al., 1968; Brunskill and Harris, 1969; Thompson et al., 1997). One striking feature of the

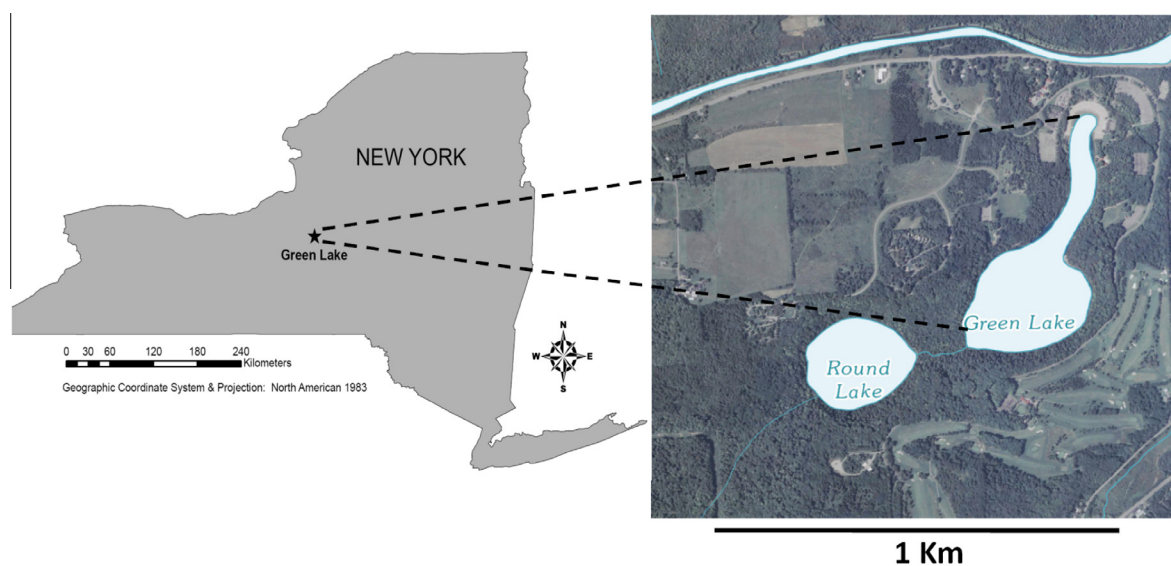


Fig. 1. Geographic and aerial photo map of Green Lake and nearby Round Lake in Fayetteville, New York. Aerial imagery extracted from manilius NY 2010 quadrangle of USGS topographic map.

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