

## Dimethyl sulfide emissions to the atmosphere from lakes of the Canadian boreal region

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**Abstract.** Dimethyl sulfide (DMS) concentrations were measured over 2 years in 10 lakes situated in northwestern Ontario. Concentrations varied from  $0.1 \text{ nmol L}^{-1}$  to  $100 \text{ nmol L}^{-1}$  (geometric mean of  $1.2 \text{ nmol L}^{-1}$ ) during the ice-free season (April to November) of 1995 and 1996. Shallow (1–5 m depth and 1–5 ha area) and medium depth (5–10 m depth and 5–15 ha area) lakes exhibited higher surface water DMS concentrations than deeper and larger lakes (32 m depth and 20–56 ha area). During the fall in the medium size lakes (5–12 m depth and <15 ha area), DMS concentrations increased markedly by a factor of as much as 100 because of circulation of deeper, high-DMS water from the hypolimnion (lake turnover). The estimated seasonal mean fluxes of DMS from shallow and medium-depth lakes to the atmosphere ranged between  $0.058$  and  $15 \mu\text{mol S m}^{-2} \text{ d}^{-1}$  respectively. The shallow and medium depth lakes tend to release higher DMS than the large and deeper lakes. Extrapolation of flux estimates indicates that the lakes of the Canadian Boreal Shield emit  $1.5 \text{ Gg yr}^{-1}$  biogenic sulfur (DMS) to the atmosphere, and this is approximately 83% of the total annual biogenic sulfur (DMS) emissions from the Canadian Boreal Shield (lakes plus terrestrial). Compared to the annual anthropogenic emissions by five smelters in the boreal region, these emissions are small (0.08%).

### 1. Introduction

The abundance of dimethyl sulfide (DMS) in the oceans and lake surface water and its reactivity in the troposphere makes it an important component of the global sulfur cycle [Bates *et al.*, 1992]. DMS is the dominant biogenic sulfur compound in stratified lakes [Richards *et al.*, 1991, 1994]. Although lakes are likely a small part of the global sulfur budget (because of small surface area coverage compared to oceans), DMS emissions from lakes could be important on a regional basis, contributing significantly to a region's natural sulfur budget [Richards *et al.*, 1994]. Sulfur isotopic measurements support this hypothesis and reveal that biogenic sources account for 30% of the acidifying burden in the atmosphere in remote regions of Canada [Nriagu *et al.*, 1987].

A limited number of studies, done in the freshwater lakes of the Hudson Bay lowland to hypersaline lakes of southern Saskatchewan [Richards *et al.*, 1994], have indicated that DMS concentrations in lake water and wetlands could be of the same order of magnitude or higher than that measured in the oceans [Richards *et al.*, 1991, 1994; Sharma, 1997], varying from  $0.32$  to  $1290 \text{ nmol L}^{-1}$ . Thus, on a per square meter basis some lakes emit more DMS to the atmosphere than oceanic surfaces. The estimated emissions of DMS from the lakes vary between  $0.4$  to  $590 \mu\text{mol S m}^{-2} \text{ d}^{-1}$ .

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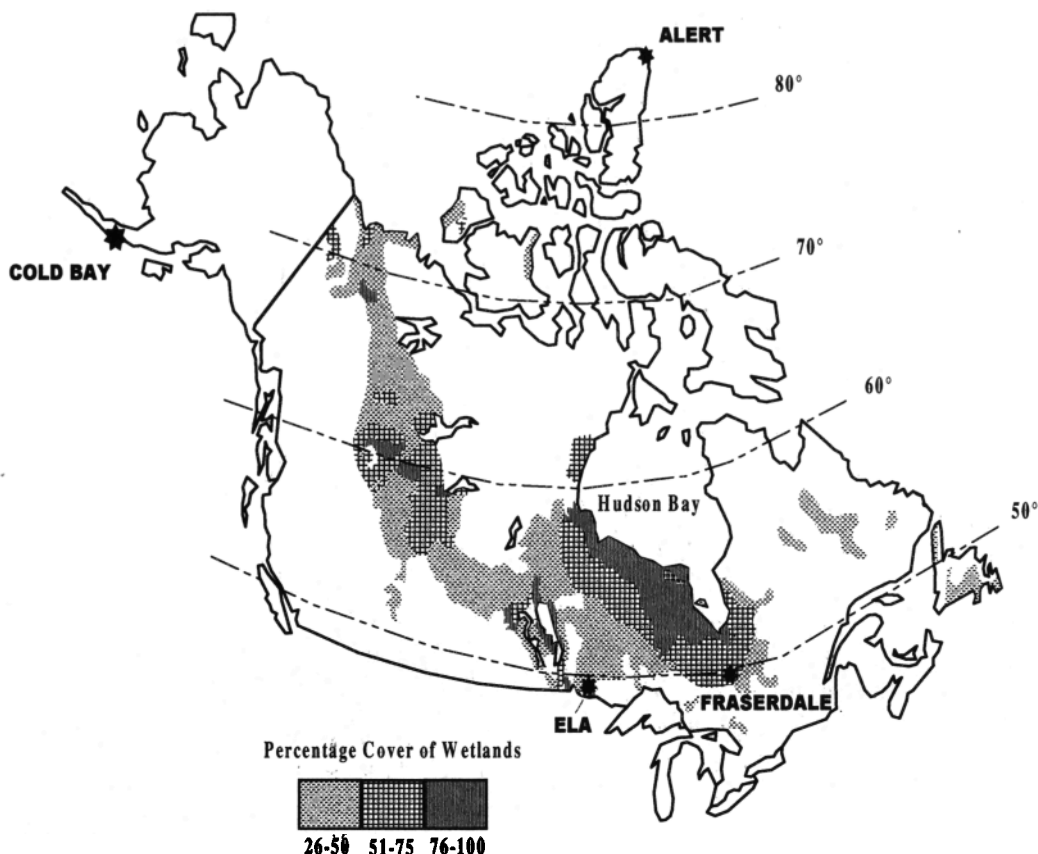
Concentration of DMS in the water column depends on rates of its production and consumption. There are several suggested mechanisms for the production of DMS. The breakdown of algal dimethyl sulfoniopropionate and S-containing organic compounds such as methionine and cysteine in sediments could contribute to its production. In the anoxic hypolimnion of these lakes, dissimilatory sulfate reduction could also produce DMS and  $\text{H}_2\text{S}$ . The methylation of  $\text{H}_2\text{S}$  in this anoxic medium could also produce DMS [Rudd *et al.*, 1986]. However, DMS can be removed by photooxidation to form dimethyl sulfoxide, consumption by bacteria, or complexation by metals.

Considering the potential importance of DMS in the freshwater environments, a 2-year study was conducted in the Canadian boreal forest region. In this paper we present observations of the seasonal and year to year variation of surface water DMS concentrations in 10 lakes at the Experimental Lakes Area, northwestern Ontario. The main goal of this study was to estimate biogenic sulfur (DMS) emissions from these lakes to the atmosphere and then to assess the impact of these types of lakes on the sulfur budget of the Canadian boreal region. This paper summarizes results given in more detail by Sharma [1997].

### 2. Experiment

#### 2.1. Sampling Site

The 10 lakes investigated were located in the Experimental Lakes Area (ELA), 52 km east southeast of Kenora in north-



**Figure 1.** The classification of wetland regions of the Precambrian shield. The Experimental Lakes area is situated in the region classified as low boreal and covers 26–50% wetlands region [National Wetlands Working Group, 1988]. Figure 1 is modified from Worthy *et al.* [1998].

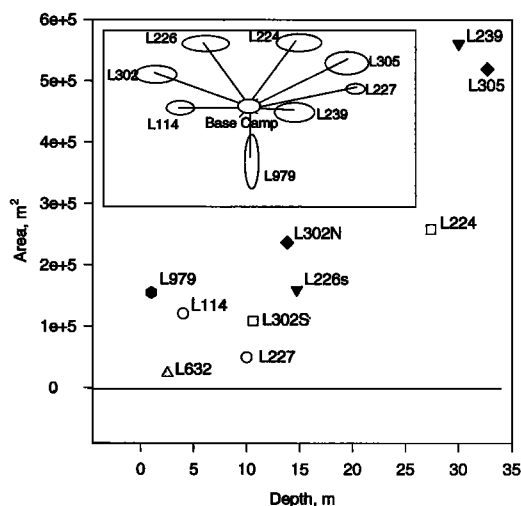
western Ontario (Figure 1). ELA is classified as “low boreal wetland” with a 26–50% wetland coverage [National Wetlands Working Group (NWWG), 1988]. It was chosen because it is representative of the Precambrian Canadian Shield topography and the biota and water chemistry are well characterized. The vegetative cover includes stands of black spruce, trembling aspen, white birch, and jack pine along with peat, moss, and lichens. The 10 lakes selected for study (L632, L979, L239, L114, L302s, L305, L227, L226s, L224, and L302N) were located within a radius of approximately 11 km of the base camp (Figure 2). These lakes were between 2.4–52 ha in area and 1–32 m in depth and had varying amounts of wetlands in their watershed. Lakes deeper than 5 m were thermally stratified during the summer.

Some of the lakes had been modified by addition of acids to investigate the response of these lakes to air pollution [Schindler and Turner, 1982]. Lake L302 had been acidified every year with sulfuric acid in the south basin and with nitric acid in the north basin between 1986–1996. Lake L227 was artificially eutrophied by addition of  $H_3PO_4$  to look at the affect of eutrophication on the primary productivity. Further details of these lakes are given by Sharma [1997].

## 2.2. Method

Lake surface water samples were collected by hand in the middle of the lake by dipping 125-mL black perfluoroalkoxy bottles at a depth of 100 cm below the surface. During 1995 the bottles were capped tightly ensuring no headspace, refriger-

ated, and analyzed on site within a few hours of collection. In 1996 we added a combination of antibiotics 125 mg  $L^{-1}$  of chloramphenicol and 75 mg  $L^{-1}$  of tetracycline [Kiene and Bates, 1990] to samples before shipping them overnight from Experimental Lakes Area to the Toronto laboratory for anal-



**Figure 2.** Relationship between area and depth for the 10 lakes at the Experimental Lakes area. Inset shows approximate location of the lakes from the base camp.

ysis. All of the samples were analyzed within 2 days of collection. Tests showed that DMS in lake water samples was stable up to 2 days, and any bacterial activity contributing to the production was inhibited by antibiotics for up to 5 days.

Water phase DMS concentration was measured using a purge and trap method which has been used widely [Bates *et al.*, 1987; Leck and Bagander, 1988; Richards *et al.*, 1991]. The technique involved the stripping of DMS from the aqueous phase by a carrier gas and subsequent trapping on Tenax-TA. The Tenax traps were desorbed by heating to 170°C, and the DMS was removed and transferred to a 60-m DB-1 microbore column in series with a 30-m narrow-bore column for separation. The effluents were then measured with a flameless sulfur chemiluminescence detector (SCD). The analysis was done with a 5890 series II Hewlett Packard (HP) gas chromatograph, and the signal was acquired by a HP chemstation software.

Calibration was done as follows: A 8.47- $\mu\text{mol L}^{-1}$  stock solution was prepared by a two-step serial dilution of 99.98% liquid DMS in ethylene glycol. It was refrigerated and used for preparing various DMS concentrations. A linear response ( $r^2 = 0.997$ ) of the SCD was obtained. The limit of detection was found to be 0.1  $\text{nmol L}^{-1}$  for the system (signal/noise = 2:1) with a precision of  $\pm 15\%$  obtained in the analysis of triplicate tubes. The accuracy of these measurements was within  $\pm 20\%$ .

The atmospheric DMS samples were collected in glass tubes packed with 0.5 g of molecular sieve 5A adsorbent because of higher breakthrough of this adsorbent than Tenax [Davison and Allen, 1994]. Ten liters of air at 500  $\text{mL min}^{-1}$  was pumped through these tubes at ambient temperature and analyzed in a similar manner to water samples [Sharma, 1997]. About 96% of DMS was recovered from these tubes at a desorption temperature of 300°C. A permeation device was used to calibrate the atmospheric samples at hundreds of parts per trillion by volume (pptv) level, and oxidants from the air stream were removed by placing a glass fiber filter coated with 5% KI, 5% glycerol, and 0.5% Vitex (visual indicator) in front of the sample line [Kittler *et al.*, 1992]. The precision and accuracy within a triplicate analysis was  $\pm 20\%$ .

### 2.3. Flux Calculations: Gas Exchange Model

A gas exchange model [Wanninkhof *et al.*, 1991] was used to estimate fluxes from these lakes. According to the gas exchange model the flux ( $F$ ) from lake to the atmosphere is related to the concentration of DMS in water ( $C_w$ ) and air ( $C_a$ ) as follows:

$$F = k_T (C_w - C_a/H) \quad (1)$$

where  $k_T$  is the transfer velocity and  $H$  is Henry's law constant for DMS. For DMS the Henry's law constant depends on water temperature ( $T_w$ ) as follows:

$$H \text{ (atm L mol}^{-1}\text{)} = e^{(A/T_w + C)} \quad (2)$$

where  $A = -3463 \pm 75$  (per kelvin) and  $C = 12.2 \pm 0.26$  for DMS in distilled water at various temperatures ranging from 0 to 32°C [Dacey *et al.*, 1984]. Results of several studies have indicated that the  $C_a/H$  term in (1) is very small compared to  $C_w$  [Andreae and Barnard, 1984; Levasseur *et al.*, 1997]. This study also showed that DMS concentrations above the lake surface did not exceed 60 pptv during the time of our measurements (results not shown). Thus the second term in (1) can be neglected, and the equation can be written as

$$F = k_T C_w \quad (3)$$

$k_T$  is the reciprocal of resistance to air surface exchange and has been empirically determined by Wanninkhof *et al.* [1991] for three wind speed regimes. Since wind speeds over the lakes never exceeded 6  $\text{m s}^{-1}$ , the third regime ( $>13 \text{ m s}^{-1}$ ) was not used. The  $k_T$  used in flux estimations were as follows:

For  $u < 3 \text{ m s}^{-1}$ ,

$$k_T = k_{\text{SF}_6} \times (Sc_{\text{SF}_6})^{0.65} / (Sc_{\text{DMS}})^{0.65} \quad (4)$$

where  $k_{\text{SF}_6} = 0.76u$

and for  $u \geq 3 \text{ m s}^{-1}$ ,

$$k_T = k_{\text{SF}_6} \times (Sc_{\text{SF}_6})^{0.5} / (Sc_{\text{DMS}})^{0.5} \quad (5)$$

where  $k_{\text{SF}_6} = 5.6u - 14.4$

where  $u$  is wind speed in the middle of the lake. The Schmidt numbers  $Sc_{\text{SF}_6} = 600$  at 20°C and  $Sc_{\text{DMS}} = \nu/D$ , where  $D$  is diffusion coefficient for DMS and  $\nu$  is the kinematic viscosity of water, were determined as a function of temperature. An experimental determination of  $D$  for freshwater environments was used [Saltzman *et al.*, 1993]:

$$D = 0.020e^{(-18.1/R T_w)} \quad (6)$$

where  $R$  is the gas constant and is equal to  $8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ }^\circ\text{K}^{-1}$ .

### 2.4. Wind Speed Over a Lake

Measurements of wind speed ( $u$ ) were made at a height of 1 m above the lake surface in the middle of two shallow lakes L979 and L632 during 1995 and in L239 (a large and deep lake) and L979 (a smaller, shallow lake) during 1996. R. M. Young type anemometers, accurate to 0.3  $\text{m s}^{-1}$ , were used.

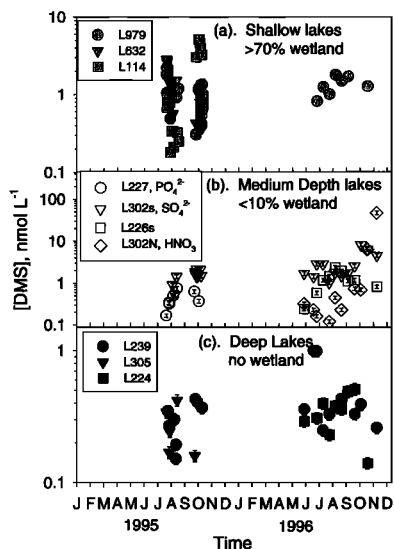
The guidelines program of Walmsley *et al.* [1989] was used to estimate wind speeds over lakes of other sizes using the observed wind speed on selected lakes. Wind speeds measured over one lake were input to the model to determine the ratio of wind over land to that over water. These ratios were then applied to estimate wind speeds over lakes of other sizes as a function of fetch over water.

Considering the importance of the horizontal wind variation as a function of over-water fetch, a model was used to estimate wind speeds for all seven lakes. A comparison between computed and measured results for lake L632 showed that predicted wind speeds were underestimated by at most 30% in 1995 and were underestimated for L239 by about 6% in 1996. Wind speeds were estimated for other lakes in this manner. The transfer velocities were calculated for every hour, and an averaged value per day was used in the flux estimations.

## 3. Results and Discussion

### 3.1. Lake Surface DMS Concentration

DMS lake water concentrations (hereafter called  $\text{DMS}_w$ ) are shown in Figure 3 as a function of time and lake type. They varied from 0.1  $\text{nmol L}^{-1}$  to 100  $\text{nmol L}^{-1}$  during the ice-free season of 1995 and 1996. These observations are categorized on the basis of lake depth with Figure 3a representing shallow lakes with depths between 1 and 5 m, Figure 3b representing medium-depth lakes between 5 and 20 m, and Figure 3c representing deeper lakes with depth  $> 20$  m. The data are also



**Figure 3.** Variation in lake water dimethylsulfide (DMS) concentration (plotted on the log scale) measured in 10 lakes during summer and fall of 1995 and the ice-free season of 1996 at the Experimental Lakes Area (ELA). (a) Shallow lakes with depths of 1–5 m. (b) Medium-depth lakes of 5–20 m. (c) Deeper lakes with depths > 20 m. Lakes are identified by their ELA code number and previous anthropogenic manipulation compound. Symbols represents different lake types.

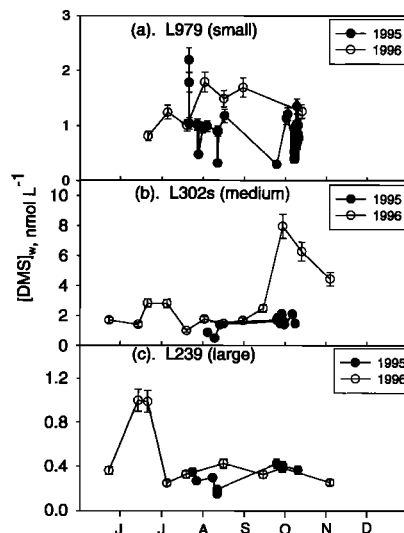
segregated on the basis of the fraction of the lake watershed containing wetlands. L979 and L632 were 100% surrounded by wetland; L114 was 70% surrounded; L239, L227, L226s, L302s, and L302N were < 10% surrounded by wetlands. L305 and L224 had no wetlands surrounding them.

The shallow and medium-depth lakes tend to have higher DMS<sub>w</sub> than the larger lakes. Since these lakes also had drainage from wetland surrounding them, it is crucial to look at this effect. The results indicate that the lakes surrounded by more than 70% by wetlands had 4 times higher DMS concentration than those with less than 10% wetlands. However, from this data set the influence of wetland coverage could not be separated from other variables because the lakes surrounded by higher wetlands were also shallower. It is unclear which variable was more controlling.

### 3.2. Seasonal and Interannual Variation in DMS Concentrations

To check the spatial representativeness of single-point DMS<sub>w</sub> measurement data, horizontal transects were made across lakes L302s, L114, L632, and L979 once each per summer and fall season. The results (not shown here) indicated at most  $\pm 30\%$  variability along the north to south transect.

There is a small seasonal variation in DMS<sub>w</sub> (Figure 3). The exception to this is the fall time circulation period in some lakes, especially L302N and L302s where higher DMS concentrations were obtained during 1996. However, in a shallow lake such as L979 some seasonality was found during 1996 where concentrations peaked during the summer. During 1995 it is difficult to see the seasonality because the measurements did not start until mid-July. This seasonal variation may be more evident in smaller and shallower lakes because they warm faster than larger lakes and thus could have higher rates of degradation of leaves and algae contributing to higher DMS<sub>w</sub>.

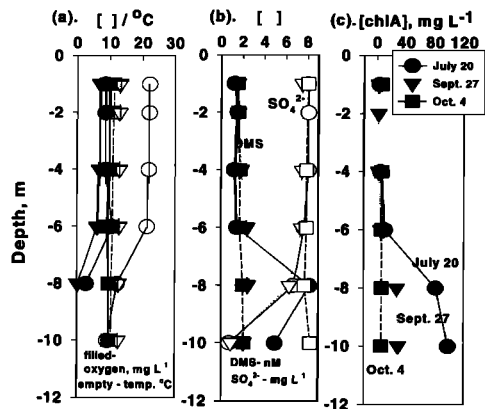


**Figure 4.** A comparison of the seasonal variation of lake DMS<sub>w</sub> concentration for three lakes (a) L979, (b) L302s, (c) L239 during 1995 and 1996.

Also, water residence time tends to decrease in the summer because of lower water input, and concentrations of gases from decomposition activities increase.

The interannual variation in the DMS<sub>w</sub> concentration was also measured in three of the 10 lakes during 1995 and 1996. DMS<sub>w</sub> concentration is 2 times higher in lake L979 during the summer (August to September) of 1996 than 1995 (Figure 4). However, there was not much difference in the DMS<sub>w</sub> concentration in the medium-depth (L302s) and large lakes (L239) during the two summers.

In the fall, L302s showed a high increase (4 times) in 1996 which was not seen in 1995. This is due to the fall circulation. This phenomenon is primarily a destratification of a lake during the fall because of cooling of the lake surface followed by a mechanical mixing caused by winds. During the spring the lakes deeper than 5 m thermally stratify with the bottommost layer cooling off to 4°C. These lakes also tend to be anoxic in the hypolimnion and as a result accumulate high DMS concentrations [Richards *et al.*, 1991]. Upon lake turnover during the fall the accumulated DMS is usually released to the atmosphere as it reaches the lake surface. This phenomenon was observed in several lakes (L302s, L302N, L110, and L226), which were 10 to 15 m deep. Figure 5 shows three depth profiles for lake L302s taken on July 20, September 27, and October 4, 1995. The profile taken on July 20 clearly shows temperature stratification. Corresponding to a decrease in dissolved oxygen in the hypolimnion (6–10 m), there is an increase in DMS concentration and chlA (which is a measure of phytoplankton). However, SO<sub>4</sub><sup>2-</sup>, which upon reduction could form DMS, decreased in concentration in the hypolimnion. Lake turnover is evident from profiles taken between September 27 and October 4. The lake lost stratification, and the concentrations of all species became consistent in the water column. In 1995 the drastic increase in the DMS<sub>w</sub> concentration was not observed because our sampling for the second half of the sampling period did not start until after the onset of the lake turnover, whereas for 1996 an increase can be seen in the DMS<sub>w</sub>. In 1996 the vertical profiles showed a concentration of DMS as high as 120 nmol L<sup>-1</sup> in the hypolimnion and in-



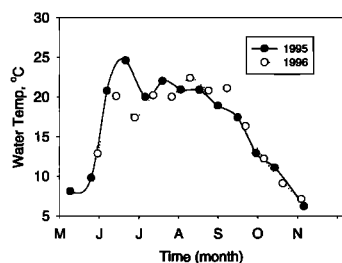
**Figure 5.** Vertical profiles of (a) oxygen (solid symbols) and temperature (open symbols), (b) concentrations of DMS (solid) and  $SO_4^{2-}$  (open) and (c) chlA in lake L302s taken on July 20, September 27, and October 4, 1995. Lake turnover is evident between September 27 and October 4.

creased  $DMS_w$  by as much as 43 times in lake L302N ( $DMS_w$  can be seen in Figure 3).

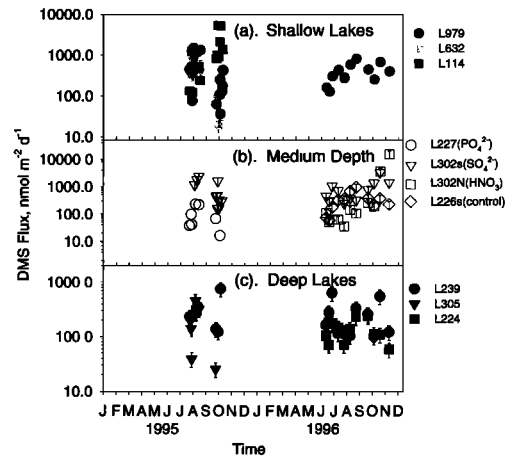
For larger lakes such as L239 (depth 32 m), the accumulation of DMS was not seen because these lakes were too deep (low productivity) and turbulent for any algal accumulation to take place.

The impact of temperature was examined by comparing data from the 2 years. On average, the summer of 1995 was warmer than the summer of 1996 (Figure 6). Also, during 1996 the lakes were not ice free until the middle of May, approximately 3 weeks later than in 1995. The surface water temperatures were 5°C higher in June and 3°C lower in September of 1995 than in 1996. The lower temperatures are apparent in lakes L239 and L979 where the high concentration during the summer has been shifted by approximately 3 weeks in 1996. As a result of a longer ice-free season during 1996, the lake turnover was also delayed by as long as 3 weeks. Thus lake temperature regime plays a role in controlling DMS concentrations.

Nutrients, however, did not seem to have a clear impact on the surface DMS concentration. There was no correlation found between  $DMS_w$  and  $SO_4^{2-}$ ,  $NO_3^-$ , total suspended phosphate, dissolved organic carbon, and chlA (results not shown). Results obtained in other studies [Richards *et al.*, 1994] have suggested that a linear correspondence is observed between  $DMS_w$  concentrations and  $SO_4^{2-}$  for the lakes which vary in  $SO_4^{2-}$  by as much as 5 orders of magnitude. However, for dilute lakes, there is no correlation found between  $DMS_w$  and  $SO_4^{2-}$ .



**Figure 6.** Lake surface water temperature (large lake) for the ice-free season during 1995 and 1996 at the Experimental Lakes Area.

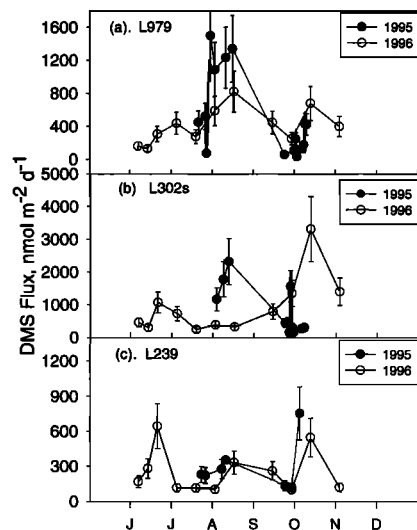


**Figure 7.** Variation in estimated DMS flux (plotted on a log scale) to the atmosphere from 10 lakes of different sizes and depths at the Experimental Lakes Area during 1995 and 1996: (a) shallow lakes between 1 and 5 m in depth, (b) medium depth lakes between 5 and 20 m in depth, and (c) deeper lakes > 20 m in depth.

### 3.3. Variation in DMS Fluxes From Lake to Lake

Figure 7 shows calculated fluxes of DMS as a function of time and lake type. These fluxes varied between 0.058 and 15  $\mu\text{mol m}^{-2} \text{d}^{-1}$  during the ice-free seasons of 1995 and 1996 with the shallow and medium-depth lakes exhibiting higher fluxes of DMS than larger lakes. Although the wind speeds were more than 50% higher over the large lakes than smaller and medium sized lakes, the low  $DMS_w$  concentrations resulted in lower fluxes in larger lakes.

Figure 8 shows the seasonal variability in the DMS flux from three lakes L979, L302s, and L239 to the atmosphere for 1995 and 1996. These lakes are representative of shallow, medium, and large lakes. There is not a consistent trend or pattern. For the shallow lake L979 DMS fluxes were at a maximum during midsummer for 1995 and 1996. The midsize lake L302s had a



**Figure 8.** A comparison of the seasonal variation of DMS fluxes from three lakes (a) L979, (b) L302s, and (c) L239 during 1995 and 1996.

**Table 1.** Geometric Mean and Confidence Interval for DMS Concentrations and Fluxes From 10 Lakes

Lake Size, ha	Depth, m	[DMSW]* Average, nmol L <sup>-1</sup>	95% Confidence Interval,* nmol L <sup>-1</sup>	DMS Flux* $f_g$ , $\mu\text{mol m}^{-2} \text{d}^{-1}$	95% Confidence Interval,* $\mu\text{mol m}^{-2} \text{d}^{-1}$	<i>n</i>	Wind Speed, m s <sup>-1</sup>		
							Average	Standard Deviation	
<i>Wetland-Surrounded Lakes</i>									
L979	15.5	1							
L632†	2.4	2.5	1.2	0.37–3.91	0.35	0.063–1.25	115	1.6	0.9
L114	12.1	5							
L227	5	10							
(H <sub>3</sub> PO <sub>4</sub> ),									
L302S†	10.9	10.6							
(H <sub>2</sub> SO <sub>4</sub> ),			1.2	1.42–3.91	0.26	0.25–1.21	67	1.8	1.0
L302N†	23.7	13.8							
(HNO <sub>3</sub> ),									
L226	16	14.7							
(control)									
<i>No Wetland (Deep Lakes)</i>									
L239	56.1	30.4							
L305	52	32.7	0.33	0.11–0.95	0.17	0.035–1.1	36	2.0	1.2
L224	25.9	27.4							

The data were grouped on the basis of percentage of wetland surrounding these lakes.

\*Values are based on geometric mean and standard deviation.

†Time weighted means are used.

peak in 1995, but in 1996 the profile resembled the large lake L239 which had higher fluxes during spring and fall.

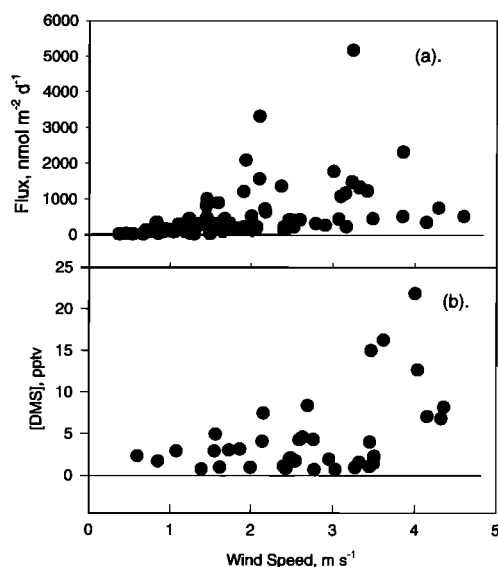
Table 1 shows the relationships of wetland coverage and DMS<sub>w</sub> concentrations and fluxes of DMS from the lakes. Geometric means were used because there was so much variability between summer and fall fluxes that an arithmetic mean would show a bias toward the fall measurements and flux calculations. As with DMS<sub>w</sub> concentrations, the results indicated that the surface DMS fluxes were higher (by 2 times) in lakes surrounded by wetlands than in lakes surrounded by no wetlands. However, this conclusion is ambiguous because the lakes surrounded by wetlands are also shallow and medium-depth lakes, and DMS produced in sediments of shallower lakes might be expected to lead to greater concentration and flux than in deeper lakes.

Variation in estimated DMS fluxes not only depends on variations in DMS<sub>w</sub> concentrations but also on the wind speeds. Fluxes of DMS follow DMS<sub>w</sub> concentrations for all three lakes, but concentration is not an absolute predictor because wind speeds tend to be higher in the fall. In other words, when wind speed goes up, DMS<sub>w</sub> in the water mixed layer goes down because it is being ventilated and also diluted as the size of the mixed water layer increases. Hence flux is a product of these two parameters which are not mutually exclusive. Thus the magnitude of the flux depends on which one of the two parameters is predominant.

In the lake L979 these flux estimations are higher during the spring and summer because of high DMS<sub>w</sub> concentrations, whereas a predominant wind effect can be seen in the fluxes during the fall (Figure 8). Similar effects can be seen in the results of L239. For a medium-depth lake L302s, increased DMS fluxes have been due to an increase in DMS<sub>w</sub> for 1996, whereas wind speeds contribute to higher fluxes during the summer of 1995. According to the gas exchange expression, the wind speed measurements have a large influence on the fluxes. The maximum daily average of wind speeds never exceeded 5 m s<sup>-1</sup> for both years, and the average for the ice-free season was  $1.25 \pm 0.77 \text{ m s}^{-1}$  for 1995 and  $1.91 \pm 1.75 \text{ m s}^{-1}$  for 1996.

The mean and variance of wind speed was higher in 1996 than 1995.

An indirect evidence of wind speed control on DMS emissions is found in [DMS]<sub>air</sub>. Figure 9 shows DMS<sub>air</sub> concentrations, measured on top of a hill approximately 43 m above the lake level. This site was chosen to look at the DMS contribution from these lakes at this elevation. One of the reasons for low atmospheric DMS concentrations at this elevation is dilution (chemical removal and vertical mixing). The results compare the dependence of F<sub>DMS</sub> and [DMS]<sub>air</sub> on wind speed. [DMS]<sub>air</sub> also increased for wind speeds (measured over the lake) greater than 3 m s<sup>-1</sup> corresponding to an increase in the



**Figure 9.** Dependence of (a) DMS flux from the lakes to the atmosphere and (b) atmospheric DMS mixing ratio (measured on a top of a hill, 43 m above the lake surface) on wind speed measured at 1 m over the lake.

**Table 2.** Areal Surface Coverage by Lakes in the Canadian Boreal Shield Using Landsat Thematic Mapper Technique

Province	Number of lakes	Lakes of 1–5 ha		Lakes of 5–20 ha		Lakes >20 ha		Total Lake Area, ha
		Area	Number	Area	Number	Area	Number	
Ontario	228,166	242,792	221,522	442,527	43,822	3,771,784	22,822	4,457,103
Quebec	434,661	390,468	343,314	609,477	62,274	5,060,388	29,073	6,060,288
Newfoundland	143,052	142,991	124,549	127,122	14,431	907,835	4,072	1,177,956

Source is Helie et al. [1993]; 1 ha =  $1 \times 10^4$  m<sup>2</sup>.

exchange coefficients and therefore flux as the lake surface became more turbulent. This is consistent with wind speed control of flux indicated by gas exchange model.

### 3.4. Extrapolation of DMS Fluxes to the Canadian Boreal Region

Emissions of DMS from the lakes of ELA region to the atmosphere were extrapolated to the Canadian boreal region. First, the extrapolation was done on the basis of lake size for southeastern Canada, south of 52°N, and, second, by using the total freshwater surface area for the Canadian boreal region. There were several assumptions made for this extrapolation such as the following: (1) DMS<sub>w</sub> concentrations were assumed representative although there is a large uncertainty involved in deducing lake water DMS concentration even within a region, (2) emissions were only significant during the ice-free (April to November) season and were negligible from December to March, and (3) wind speed was assumed to vary little across the Canadian boreal region. The average wind speed of 3–4 m s<sup>-1</sup> for the region was close to the mean wind speed of 2.5 m s<sup>-1</sup> measured at ELA [Canadian Climate Program, 1988]. However, wind speeds for a particular lake would vary depending on the lake size (over-water fetch effect) and topography (channeling effect). Since 6.4% of the lakes were greater than 20 ha in size, which covered 83% of lake surface area, only this fraction will show higher wind speed than observed over land. However, since large lakes exhibited lower DMS<sub>w</sub>, the fetch over-water effect in the wind speeds may be compensated when calculating fluxes.

The lake size classification of Helie et al. [1993] was limited to the lakes in southeastern Canada (Figure 1), south of 52°N, henceforth called southern Canadian boreal region (most of Ontario, part of Quebec, and New Foundland located in the Boreal Shield south of 52°N). Two frequency distributions were obtained: (1) the lake number size distribution (number of lakes on the basis of lake size) and (2) the lake surface area coverage distribution (total surface area covered by different

size lakes) (Table 2). While most of the lakes are in the small size range (1–5 ha), most of the total area is in the largest size range (>20 ha).

Applying estimated lake fluxes to each of these categories (Table 3) yields a total annual S (DMS) emission of  $6 \times 10^5$  kg. In comparison to this, if we consider the total freshwater surface area of  $2.71 \times 10^{11}$  m<sup>2</sup> (I. Marshall, personal communication, 1996) for the Canadian Boreal Shield, which is 2.5 times higher than that of the southern Boreal Shield, the total annual sulfur (DMS) emissions from lakes is estimated to be 1.5 Gg S. This estimate could be an overestimation because the ice-free season is shorter for the lakes in the northern part of the Canadian shield.

These estimates of biogenic emissions of sulfur from the freshwater lakes in the Canadian Boreal Shield can be compared to the emission of sulfur (DMS) from the terrestrial regions. The terrestrial emissions of sulfur were computed by using the flux rate of 0.1 μmol m<sup>-2</sup> d<sup>-1</sup> obtained from the terrestrial regions 50°–65°N [Bates et al., 1992]. Taking the surface area of  $1.5 \times 10^{12}$  m<sup>2</sup> for the Canadian Boreal Shield (excluding lake water), the terrestrial areas emit 1.8 Gg S per year. Thus sulfur emissions from the lakes represent 83% of the total terrestrial sulfur (DMS) emissions from the Canadian Boreal Shield and thus are significant on the regional scale.

These biogenic sulfur emissions were also compared to the total anthropogenic sulfur emissions from five smelters in the Canadian Boreal Shield [Environment Canada, 1995]. In 1995 they contributed approximately 1910 Gg S yr<sup>-1</sup> to the atmosphere. Thus biogenic emissions of sulfur (DMS) from the lakes were only 0.08% of the anthropogenic sulfur emissions. Compared to the large point sources of anthropogenic sulfur, biogenic sulfur (DMS) emissions are small. However, because of the highly dispersed nature of natural sources compared to anthropogenic point source pollution, natural emissions may affect the sulfur budget and thus, in turn, could be a dominant

**Table 3.** Extrapolation of DMS Fluxes to the Lakes of Canadian Boreal Shield South of 52°N Using Helie's Lake Classification for the Ice-Free Season (April to November 1995)

Lake Size, ha	Lake Surface Area, $1 \times 10^4$ m <sup>2</sup>	Mean Annual S Emissions			95% Confidence Interval,* kg S ( $1 \times 10^4$ )	Percentage of Total S Emissions
		Average, mg m <sup>-2</sup>	Standard Deviation	Average, kg S ( $1 \times 10^4$ )		
1–5†	776,251	1.78	1.97	1.5	0.092–6.67	2.45
5–20‡	1,179,126	6.76	8.51	8.0	0.52–26.7	13.08
>20§	9,739,957	5.29	20.02	51.5	1.78–102.8	84.47
1–>20	11,695,334			61.0		100

\*Values are based on geometric mean and standard deviation.

†Average emissions from lakes L632 and L227.

‡Average emissions from lakes L302s, L979, L114, and L226s.

§Average emissions from lakes L302n, L224, L239, and L305.

source of sulfur in large areas where smelter effluent is not present.

#### 4. Summary and Conclusions

Emissions of dimethyl sulfide were determined from 10 lakes of different sizes and depths at the Experimental Lakes Area, northwestern Ontario, during the ice-free season of 1995 and 1996. These emissions were then extrapolated to the Canadian boreal region and were found to be an important component of the terrestrial emissions (soil, forest, and lakes). Regionally, these emissions are important and could affect the regional sulfur budget when anthropogenic point source effluent is not present. Following are the summary and conclusions obtained from this study: (1) During the ice-free seasons of 1995 and 1996, lake surface DMS concentrations varied from 0.1 nmol L<sup>-1</sup> to 100 nmol L<sup>-1</sup> in the ELA area of central Canada. (2) Shallow (1–5 m depth and 1–5 ha area) and medium-sized (1–12 m depth and 5–20 ha area) lakes exhibited on an average 4 times higher surface water DMS concentrations than larger and deeper lakes (15–32 m depth and 20–56 ha area). However, we still need to know the production and consumption mechanisms for DMS in the lake water. (3) During the ice-free seasons of 1995 and 1996, estimated DMS emissions from lakes at ELA to the atmosphere varied from 0.058 to 15 μmol m<sup>-2</sup> d<sup>-1</sup>. Small and medium-sized lakes exhibited on an average 2 times higher fluxes than larger and deeper lakes. (4) The annual biogenic lake emissions of 1.5 Gg S in the Canadian Boreal Shield are significant on the regional scale since these emissions are 83% of the total natural S emissions (terrestrial plus lakes excluding oceans) from the Canadian Boreal Shield [Bates *et al.*, 1992]. (5) Although biogenic S emissions in the Canadian boreal regional are small (0.08%) compared to anthropogenic sulfur emissions from five sulfur smelters, they are more widely dispersed and could impact the regional sulfur budget for much of the summer period.

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