Atmospheric Methanethiol Emitted from a Pulp and Paper Plant on the Shore of Lake Baikal

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Abstract

On-site measurement of methanethiol (CH_3SH) was performed for three years on ships and cars near a pulp and paper plant standing on the shore of Lake Baikal in Siberia, Russia, to investigate the behavior and impact of atmospheric CH_3SH emitted from a point source. Despite its strong odor, there are few reports on atmospheric CH_3SH, while many investigations have been carried out on dimethyl sulfide (DMS). In this work, CH_3SH and DMS were measured every 15 min by a recently developed automated instrument based on single–column–trapping/separation and chemiluminescence measurement. Hydrogen sulfide, sulfur dioxide and ozone were also measured simultaneously by individual instruments. Of these sulfur compounds, CH_3SH was dominant and its concentration sometimes reached several tens of ppbv. The concentration of CH_3SH was high at night, because of the lack of photodecomposition and local winds from the mountain to the lake. Such time variation was marked in the summer. The CH_3SH level decreased significantly downwind, while decreases in concentrations of other compounds such as DMS and SO_2 were relatively small. From these temporal and spatial variations, the behavior of CH_3SH is described in this paper. The impact of CH_3SH near the Siberian big sources is discussed with the presented data.

Keywords: Methanethiol (methyl mercaptan); pulp and paper plant; Lake Baikal; spatial and daily variations.

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1. Introduction

In Siberia, pulp and paper plants are an important part of the economy, based on the huge forest resources. They are located by rivers or lakes and the mega pulp plant in Baikalsk is on the shore of Lake Baikal. Seventeen thousand people live in the town and the major economic activities are the pulp industry and the ski area. Lake Baikal is the world's deepest lake (1,637 m) and has the most transparent water. However, several kinds of environmental pollution have entered the lake over the past two decades. The pulp plant is a source of pollution such as organochlorine compounds (Maatela et al., 1990; Koistinen et al., 1995; Mitroshkov et al., 1997) and nutrients (Kozhova and Silow, 1998; Lindström-Seppä et al., 1998). Much effort has been made by industry to reduce its output of pollution, and most issues have been resolved or dramatically reduced. Selenga Pulp & Paper Company has started recycling waste water to prevent water pollution (Kenny et al., 1994, 1995). On the other hand, air pollution is still a problem in Siberia, except for the reduction of harmful emissions into the atmosphere from coal-fired boilers of an industrial cogeneration station (Belikov and Kotler, 2004). The pulp plant in Baikalsk can treat five thousand tons of wood a day and wood chips are treated in a boiling autoclave with sodium sulfide and caustic at 160~175°C. According to State Report on Lake Baikal Environment Condition and Steps on its Protection (2007), the formed vapors are vented after cleaning by condensation removal. Liquids and foams are collected from bottom of the autoclave and wasted with washing of gases. In Europe and North America's pulp mills, new technologies, such as phase transition cooking (Zhu et al., 2002), are investigated to reduce sulfur gas emissions. But still sulfur gases are emitted via the vents of the Russian mills. Sakurai (1986) reported that Russian woods contain sulfur levels of 0.041 to 0.061% in their bark (not detected in the core, <0.01%). The sulfur content in Russian wood is much lower than that in North American wood. Contribution of the original sulfur in wood to sulfur gas emissions is thus negligible. The sulfur gases are generally odorous and impact on the people living in town. In addition, the sulfur species contribute to acid deposition and climate *via* aerosol formation and their influence on Siberian fir trees (Tret'yakova et al., 1996). To evaluate the effect of emission from the giant point source, sulfur gases were monitored in near-real time from a boat on the lake water. Azad et al. (2006) have developed a highly sensitive instrument for field measurement of CH_3SH and dimethyl sulfide (DMS) in our laboratory at Kumamoto University. The device is useful to measure detailed variations of unstable species such as the sulfur compounds. We carried out further improvements and brought the system to Russia on several expeditions. It was found in the first expedition that the major component was CH_3SH rather than hydrogen sulfide (H_2S) or DMS. Here in this paper, three

years worth of data are presented and we focused on atmospheric CH_3SH near the pulp plant: spatial and daily variations are presented in this paper and the impact of CH_3SH on the atmosphere is discussed.

2. Experimental

2.1. Sampling sites

Lake Baikal is located in the middle of Siberia. The lake is crescent-shaped and approximately 40~60 km in width and 700 km in length, surrounded by two to three thousand meter-high mountains. We carried out three expeditions on the lake; August, 2007, August, 2008 and April, 2009. The main site was around the pulp plant in Baikalsk located at the south of Lake Baikal (N 51° 31', E 104° 11') as shown in Fig. 1. The summer measurements were performed on the research ships "Vereshagin" and "Papanin" in 2007 and 2008, respectively. Measurements were also taken in the rural area of Koty (N 51° 54', E 105° 04') where there was no effect from cars and pulp plants. The winter sampling expedition was going to take place on the thick ice formed on the lake water in the same place, but unfortunately for this work, the Baikalsk plant was closed in December 2008. Therefore the winter expedition was performed around another plant in Selenginsk (N 52° 01', E 106° 52'), 180 km ENE of the Baikalsk plant from March 29 to April 9, 2009. The Selenginsk plant is located by the Selenga river, the largest river flowing into Lake Baikal, at a distance of 60 km from the lake shore. In Selenginsk, the measurements were carried out in a car.

2.2. Measurement instruments

The gases CH_3SH and DMS were determined by single column trapping/separation and subsequent ozone induced chemiluminescence measurement (SCTS-CL) (Azad et al., 2006). Both collection and separation were performed by using a single column packed with Davidson silica gel (grade 12, 60/80 mesh, from Supelco, Bellefonte, PA). After 3 min of collection, the column was subjected to stepwise heating to 150°C and then 250°C, to release CH_3SH and DMS, respectively. The released compounds were introduced to the CL cell. After measurement, the column was cooled down by a fan to ambient temperature to be ready for the next collection. The measurement was repeated every 15 min.

H_2S was measured by a micro gas analysis system (μGAS) (Ohira and Toda, 2005; Toda et al., 2009). H_2S gas was collected into a gas absorbing/reaction solution in a honeycomb-patterned microchannel scrubber to react with fluorescein mercuric acetate (FMA). Subsequently, quenching of

FMA fluorescence was monitored by a microdetector. The whole system was driven by a 12-V motorcycle battery and was carried out to the land analyses.

Ozone and SO_2 were monitored simultaneously with commercial instruments model 1006-AHJ (Dylec, Ibaraki, Japan) and model 310 (Optec, St. Petersburg, Russia), respectively, which were provided by our Russian counterpart. Aerosols were collected by silica fiber filters, QR-100 (ϕ37 mm) from Advantec (Tokyo), at a flow rate of 6.5 L/min, and sulfate and methane sulfonate (MSA) were measured after bringing back to Kumamoto, Japan by ion chromatography (DX500, Dionex, Sunnyvale, CA) using AS4A-SC and AS18 separation columns (both from Dionex), respectively.

3. Results and discussion

3.1. Performance of the instrument and data obtained in the expeditions

The SCTS-CL instrument for CH_3SH and DMS measurements was developed previously and good accuracy and precision has been obtained (Azad et al., 2006). We further improved this instrument for the expedition to Lake Baikal. The main change was the column size: the original 2 mm i.d. and 150 mm effective length was changed to a 4 mm i.d. and 60 mm effective length. This enabled a high sampling rate (80~200 mL/min → 300~500 mL/min). Higher sensitivity could therefore be obtained with a shorter sampling time. The wider and shorter column also unexpectedly resulted in a much better column lifetime. In the test just before the first expedition, the column was damaged in a short period of time (*e.g.* in one day) in the Japanese rainy season. The main reason was clogging of the column with the expansion of the silica gel material: it greatly decreased the maximum sample air flow rate. The wider current column could be used for a long time, at least a month. In addition, the sampling time and temperature program were changed to shorten the time for one cycle from 23 min to 15 min. As a result, the throughput was four cycles an hour. With this system, 0.08 to 80 ppbv of CH_3SH and 0.2 to 150 ppbv of DMS could be measured in the typical condition Limits of detection (LODs) were 0.03 ppbv for CH_3SH and 0.06 ppbv for DMS. Relative standard deviations in 20 times of measurement were within 3% for 10 ppbv CH_3SH and DMS. The performance was comparable with conventional methods such as solid-phase microextraction – gas chromatography (SPME-GC-MS) (Ras et al., 2008) and thermal desorption – gas chromatography (TD-GC) (Jean et al., 2009) with a flame photometric detector (FPD) (Lestremau et al., 2003; Devai and DeLaune, 1997; Tarver and Dasgupta, 1997), pulsed flame photometric detector (PFPD) (Kim, 2005) or sulfur chemiluminescence detector (SCD) (Benner and Stedman, 1990) even though this instrument could be carried on a flight from Japan to Russia for every expedition. Examples of SCTS-CL raw data

obtained in the expedition are shown in Fig. 2. The μGAS data was recorded concurrently with the same logger. Data for SO_2 and O_3 were recorded by a computer.

Whereas neither CH_3SH nor DMS was detected in the rural area (Koty, from August 4 to 6, 2007), the sulfur gases were observed in Baikalsk and Selenginsk. The main sulfur gas around the pulp plant was CH_3SH. The second peaks of the SCTS-CL signal (Fig. 2), those for DMS, were less than 1/10 the intensity of the first peaks for CH_3SH. That meant that the DMS concentrations were much lower than those of CH_3SH. In addition, it was difficult to distinguish the DMS peak itself from carryover of CH_3SH because of the small size of the second peaks. (The carryover in the second peak was 1~3% of the first peak.) Therefore, it was decided that accurate determination of DMS concentrations around the pulp and paper industries was difficult in these special conditions where the dominant species was CH_3SH. H_2S levels were also low compared to those of CH_3SH. Responses to H_2S were obtained every 5 min as negative peaks (quenching of FMA). The μGAS responded to CH_3SH as well (1/3 of the H_2S response), and determination of the H_2S concentration needed subtraction of the signal corresponding to CH_3SH. The H_2S level thus estimated was much lower than that for CH_3SH, and it was also difficult to determine H_2S accurately by the subtraction though μGAS itself had good accuracy and precision (Ohira and Toda, 2005, 2006) for the normal atmosphere. However, μGAS was useful for monitoring the atmospheric sulfur levels because μGAS presented signals in real time in a continuous measurement mode with a good LOD 0.1 ppbv. In the expeditions, the SO_2 concentration reached 10 ppbv whereas the maximum CH_3SH concentration was ~70 ppbv. In conclusion, the main sulfur component near the pulp and paper industry was CH_3SH. Usually H_2S emission is highest among the sulfur compounds and DMS is also present, *e.g.* in landfill emissions (Shon et al., 2005; Song et al., 2007, 2008, 2009). In the case of the pulp and paper industry, H_2S emission was thought to be difficult as a result of the alkalinity of the reactors. CH_3SH would be formed in the reactor by methylation of sulfide and would be vaporized relatively easily because of its weak acidic property. In fact, the acid dissociation constant (K_a) of CH_3SH is four million times smaller than that of H_2S (pK_a for CH_3SH 13.6, for H_2S 7.0 and 12.9). DMS can be vaporized more easily, but formation of DMS is likely much slower because of the necessity of further methylation in the reactor. These must be the main reasons why CH_3SH was the dominant sulfur gas in the exhaust from the pulp and paper factories. Therefore, of the reducing sulfur gases, the levels of CH_3SH will be focused on in the following sections.

3.2. Daily variation

The data obtained at fixed points in summer are shown in Fig. 3. The abscissa is the time of day from

noon to noon of the next day. The center of the horizontal axis is midnight, and the vertical dashed lines indicate sunset and sunrise. As can be seen in the data, clear daily variation was observed in the concentration of CH_3SH, especially in the first expedition in 2007. A high level of CH_3SH was observed in nighttime in the summer. The concentration was almost zero in the daytime, especially on fine days. There were two possible reasons for this. The slender lake is sandwiched between high mountains (almost 3,000 m in height) while the lake surface is located 456 m above sea level. The deep lake has a large heat capacity. Therefore, the mountains are warmer in the daytime and colder in the nighttime than the lake surface. According to the updrafts occurring in the mountains, wind blows from the lake to the mountain in the daytime, and vice versa at night. The actual wind direction was from the northwest in the daytime and changed to southwest in the nighttime during the 2007 expedition. The monitoring site was on a ship on the surface of the lake water, hence the plume came down to the ship mainly at night. This is one of the reasons why high concentrations of sulfur gases were obtained at night. In addition, at night, height of boundary layer is usually small and it would make the exhaust gas concentration higher. Another reason could be photodecomposition of the gases or reactions with photo-induced oxidants in the daytime. Ratio of the rate constants of decomposition by OH radical for SO_2 (1.3×10^{-12}), H_2S (4.7×10^{-12}), DMS ($4.8 \times 10^{-12} + 2.2 \times 10^{-12}$) and CH_3SH (3.3×10^{-11} molecules^{-1} cm^3 s^{-1}) are 1 : 3.6 : 5.4 : 25 at 298 K (the kinetic constants are from IUPAC Subcommittee for Gas Kinetic Data Evaluation: http://www.iupac-kinetic.ch.cam.ac.uk/index.html). Namely, decomposition of CH_3SH in the daytime was thought to be very fast compared to the other sulfur compounds. Lifetimes estimated from the rate constants and daytime OH average (1.5×10^6 molecules cm^{-3}, Seinfeld and Pandis, 2006a) were SO_2 205, H_2S 40, DMS 39 and CH_3SH 5.6 h. Such daily variation was observed not only in 2007 but also on all three days in the 2008 summer at the same sampling site. On August 17 in 2008, very high levels of CH_3SH were observed in the early evening; operation of the mill was full on that day. Though good time variation data was expected on that day, the ship unfortunately had to return to the harbor to escape from big waves before midnight.

In contrast to the summer campaigns, such daily variation was not observed in winter around the Selenginsk pulp plant. Data is shown in Fig. 4. High concentrations of CH_3SH were observed even in the daytime. During the winter expedition, there was only a small effect from sunlight due to cloudy weather in low temperature. Therefore, OH concentration was supposed to be lower than in the summer expeditions (Ren et al., 2006), and the decomposition rate was slower. The temperature decreased to –5°C during the night. In the nighttime, the station was unfortunately upstream of the wind, and high concentrations of the sulfur gases were not observed. While the wind was from the west before 21:00, the wind direction suddenly changed and was from the east after 22:00. In

addition, that factory seemed to not emit sulfur gases at night. We drove around the factory several times during the night, but there was no smell, not even just under the plume. Our original monitoring site was east-south-east of the factory. In order to catch the gases, the monitoring place was changed to the opposite side of the factory in the early morning, April 4, and then high concentrations of CH_3SH were detected again.

3.3. Spatial variation

Data obtained by moving around the Baikalsk pulp plant in a ship and a car in summer 2008 are shown in Fig. 5. The air sampled near the mountain contained a relatively high SO_2 level as the major sulfur component. CH_3SH was emitted from the factory directly or via low stacks. On the other hand, SO_2 was emitted from the high stacks of the power plant which supplied electricity to the factory and the town. This is probably the reason why SO_2 was dominant in the mountain area. The CH_3SH levels were very high near the pulp plant and declined quickly with distance from the source. The SO_2 levels also declined with increasing distance from the shore, but the rate of decrease was much smaller compared to that of CH_3SH. Changes in estimated levels of H_2S and DMS were also smaller than that of CH_3SH. Namely, CH_3SH was decomposed rapidly compared to other sulfur compounds, in addition to the dispersion to the atmosphere. The CH_3SH level decreased rapidly over a few to several kilometers.

The ship stopped at a harbor on the night of Aug. 16, 2008. Early the next morning, the water surface near the factory was covered with fog while the harbor was out of the fog. After waiting for some visibility, the ship left the harbor and entered in the fog to start the gas measurements while moving through the fog. The gas data obtained that morning are shown in Fig. 6. The numbers along the bottom are time and distance from shore. The ship moved from near the shore in front of the factory to far from the shore until it was out of the fog. Then, the ship moved back to the original place near the shore as the fog receded. A relatively high CH_3SH concentration was observed in the fog (~10 ppbv), and the concentration decreased with an increasing distance from the shore. On the way back, there was no fog and the CH_3SH level remained low. Slightly higher SO_2 was observed after fog disappeared instead of decrease in CH_3SH concentration; SO_2 is known as product of CH_3SH photo oxidation (Shon and Kim, 2006). In this way, high concentrations of CH_3SH was observed in the fog and it was low out of the fog. As described in the next section, sulfate and methane sulfonate (MSA) were also higher in the fog. The exhaust from the pulp mill contributed to the formation of fog. Another interesting point was the ozone concentration during the fog. When the ship went in the fog, the O_3 level decreased. The O_3 level reached almost zero when high CH_3SH

levels were present in the fog. This showed that O_3 was almost completely consumed by pulp mill exhaust gases. Though the mechanism was not identified, the exhaust of the pulp mill in the fog was a strong O_3 scavenger. Dominant compound in the fog, CH_3SH, can react with O_3 (Glinski et al., 1981, 1982; Toda and Dasgupta, 2008). To the best of our knowledge, however, the rate constant of this reaction is unknown, and Tyndall and Ravishankara (1991) said that the rates of reactions of reduced sulfur compounds with O_3, NO_2, O_2 and RO_2 were too slow to compete with OH reactions in the atmosphere. Accordingly it is difficult to say that there was some contribution of CH_3SH to the ozone scavenging. This phenomenon was likely due to the fast aqueous reaction of S(IV) with O_3 (Seinfeld and Pandis, 2006b) occurring in the fog aerosols.

3.4. Compounds found in aerosols

Gaseous CH_3SH was the major sulfur compound in the atmosphere near the pulp plant. To investigate sulfur compounds in aerosol, sulfate and MSA collected with filters were determined. The values of these compounds are shown in Table 1 together with the gaseous species. As a long time (2 ~ 12 h) was required for aerosol collection, the gas concentrations are shown as the average during the aerosol collection time for comparison. Note that concentrations of aerosol species are shown in ppb (in mol per 1-mol air) to make it easy to compare with gaseous species in mole base. Sulfate was found at almost the same level as SO_2. We originally thought that CH_3SH would end up as sulfate in the atmospheric reactions. However, we now think this hypothesis is unlikely, because sulfate levels are low compared to the CH_3SH concentrations. If the final fate of CH_3SH was sulfate, the sulfate level should be higher than that of CH_3SH because the lifetime of CH_3SH seems very short compared to that of SO_2, as shown in Fig. 6 as well as Fig. 5. According to publication by Shon and Kim (2006), stable end products of CH_3SH can be SO_2 and MSA. Formation of sulfate from the formed SO_2 needs further oxidation which is relatively slow. MSA was also found when the CH_3SH concentration was high, especially in the aerosol collected in the fog. The sulfate level was also the highest in the fog. However, the MSA and sulfate concentrations were not as high as those obtained in an anthropogenically polluted area (Biswas et al., 2008). The ratios of MSA to gaseous CH_3SH and aerosol sulfate were very low.

3.5. Behavior and impact of CH_3SH emitted from the big point sources

As described above, significant levels of CH_3SH were measured in the ambient air around the two kraft pulp mills in this study. The CH_3SH concentration increased to several tens of ppbv near the pulp plants. CH_3SH is not stable in the atmosphere, especially in the daytime, and its concentration

decreased greatly over time and downwind of the plants.

It is reported that CH_3SH is decomposed by reaction with OH in daytime and NO_3 in nighttime (Berresheim et al., 1995). The second order reaction rate constants are 3.3 x 10^{-11} and 8.9 x 10^{-13} cm^3 $molecule^{-1}$ s^{-1}, respectively (Sander et al., 2006). Lifetimes of CH_3SH in daytime can be roughly estimated with the constant and assumption of daytime OH average concentration 1.5 x 10^6 molecules cm^{-3} to be 5.6 h. In actual atmosphere in the monitoring area, it seemed that the reactions of CH_3SH were complex and were decomposed more. Bentley (1975) reported experimental results that photolysis of CH_3SH yields dimethyl disulfide (DMDS) (51%) and MSA (17%). DMDS is formed by recombination of methanethiyl radicals ($CH_3S\cdot$) which is primary formed from CH_3SH (Steer and Knight, 1968). Chance of such recombination in atmosphere would be smaller compared to these experiments (~26,000 ppmv) due to its low concentration of CH_3SH (less than 0.001 ppmv); the DMDS formation rate is in proportional to square of the methanethiyl concentration. Also photolysis rate was supposed to be low due to weak radiations in high latitude region.

Since Lovelock proposed the biogenic formation of DMS as a missing source of the sulfur cycle (Lovelock et al., 1972; Liss and Lovelock, 2007) and its effect on climate as cloud condensation nuclei (CCN) (Cainey, 2007), many researchers have investigated the reactions and dynamics of DMS. Arsene et al. (2002) demonstrated that DMS is converted to dimethyl sulfoxide (DMSO) in the presence of light, then becomes methane sulfinite (MSIA) on reaction with an OH radical, and is then transformed to methylsulfonylmethane ($DMSO_2$), SO_2, MSA, and methane sulfonyl peroxynitrate (MSPN). Oxidation of DMS and DMSO has also been investigated (Barnes et al., 2006; Librando et al., 2004) and the sulfur cycle has been reviewed by Berglen et al. (2004). CH_3SH behaves in atmosphere similar to DMS. Data shown here is the first demonstration of changes in CH_3SH levels over time and space around a big point source, indicating high reactivity of CH_3SH. We have previously shown that H_2S decomposed rapidly on a sunny day (Toda et al., 2004). The decline in CH_3SH is thought to be larger than that of H_2S, from the rate constant of reaction with an OH radical (Wine et al., 1981). The volatile sulfur compounds were emitted not only from point sources but also from planar sources such as tidal flats and agricultural sediments (Azad et al., 2005; Kinsela et al., 2007). The results obtained here would be useful to investigate dynamics of CH_3SH emitted from sediments which are difficult due to low concentration.

4. Conclusions

Sulfur gases emitted from the two Siberian pulp and paper industries have a serious effect on local

areas as odorous compounds. It was confirmed that the main volatile sulfur compound from the industries was CH_3SH. The CH_3SH concentration sometimes increased to several tens of ppbv in the vicinity of the studied pulp and paper plants. Interestingly, diurnal variation was observed: the CH_3SH level was high at nighttime and low in the daytime over the lake water, as a result of local winds formed by the topographical features and photochemical decomposition. The CH_3SH concentration was high near the point source but declined significantly with distance from the source. CH_3SH is an unstable compound in the atmosphere. When fog was formed, a relatively high CH_3SH concentration was observed and the ozone level was near zero ppbv. Compounds emitted from the pulp and paper mills acted as a strong ozone scavenger in the fog. This was the first detailed investigation on CH_3SH from a large point source and variations in the real atmosphere were presented. The impact of CH_3SH from the large source was demonstrated. Further investigations including laboratory experiments with atmospheric level of CH_3SH to clarify the behavior of CH_3SH in the atmosphere would be useful.

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Figure captions

Fig. 1. Locations of sampling areas. Measurements were performed in the rural area Koty and around the two pulp and paper mills located in Baikalsk and Selenginsk. The three sites are indicated as the open circles. Before the expeditions, the instrument tests and reagent preparation were carried out at Limnological Institute located in Irkutsk (solid circle).

Fig. 2. Raw data obtained during the expedition. SCTS-CL signals were obtained every 15 min and the first and second peaks correspond to CH_3SH and DMS, respectively. Negative peaks of the μGAS signal indicate H_2S levels. SO_2 and O_3 data were recorded by a computer. The data was obtained by moving around on the lake on the survey boat.

Fig. 3. Summer daily variation of sulfur gases and ozone obtained Aug. 7 – 8, 2007 and Aug. 14 – 18, 2008 at a fixed point on the lake near the Baikalsk plant. The maximum concentration of CH_3SH (out of scale) at 18:55 and 19:40, Aug. 17 were 30.8 and 60.4 ppbv, respectively.

Fig. 4. Daily variation of sulfur gases and ozone obtained in the end of winter, April 3 – 4, 2009 around the Selenginsk pulp plant.

Fig. 5. Spatial variation of CH_3SH (left) and SO_2 (right) obtained in Aug., 2008. Measured concentrations are indicated as the size of circle and measured locations are centers of the circles. Concentration of SO_2 shown in a certain size circle is half of CH_3SH shown in the same size. PPI: pulp and paper industry; H: harbor; FF: factory front. Arrows are trace of measurement in fog early morning Aug. 17.

Fig. 6. Changes in concentrations of sulfur gases in fog. Numbers in km are distance from the shore.

Figure 1

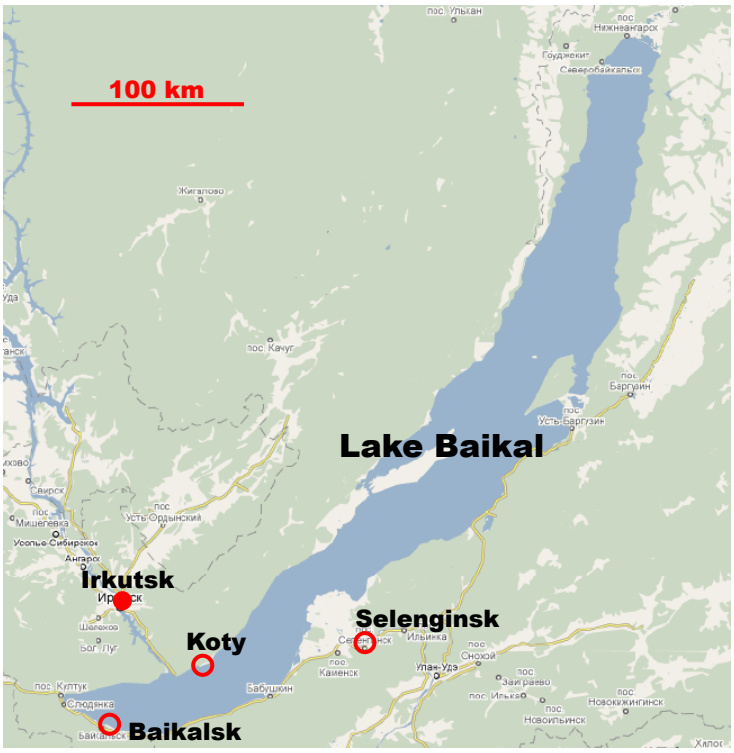


Figure 2

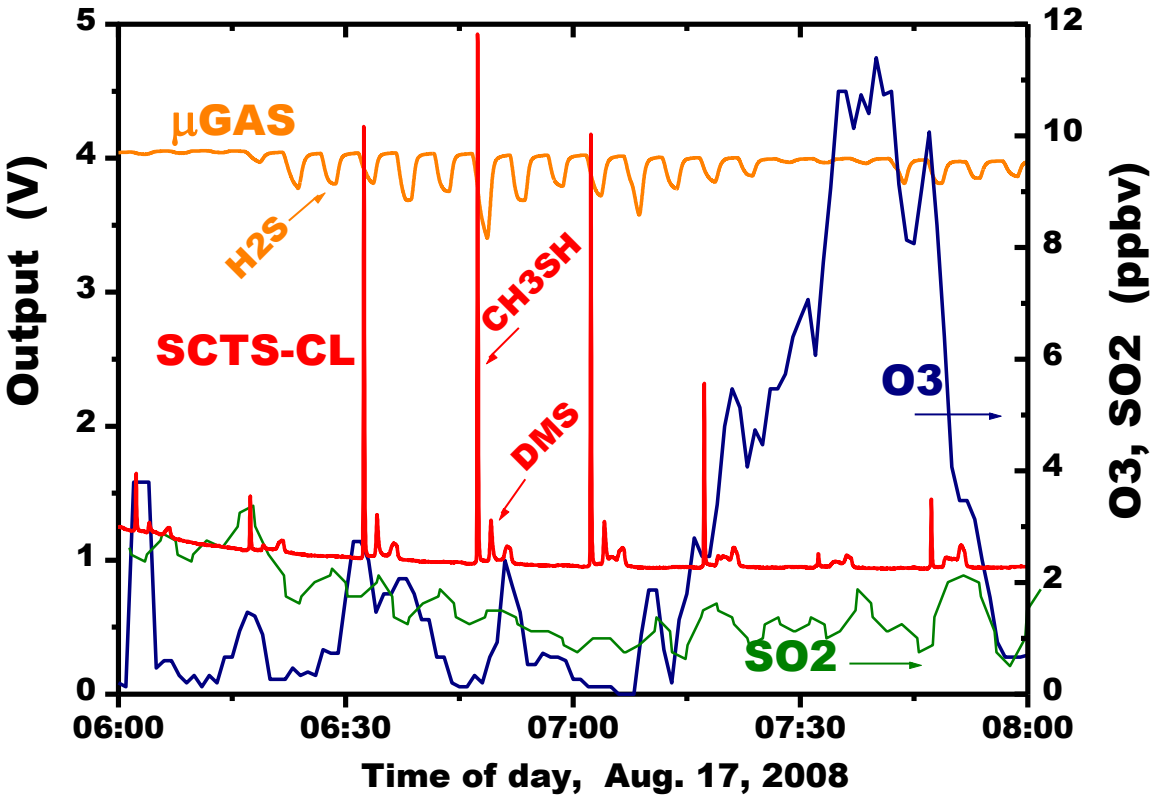

μGAS
H2S
SCTS-CL
CH3SH
DMS
O3
SO2
Output (V)
O3, SO2 (ppbv)
Time of day, Aug. 17, 2008
06:00
06:30
07:00
07:30
08:00
0
1
2
3
4
5
0
2
4
6
8
10
12

Figure 3

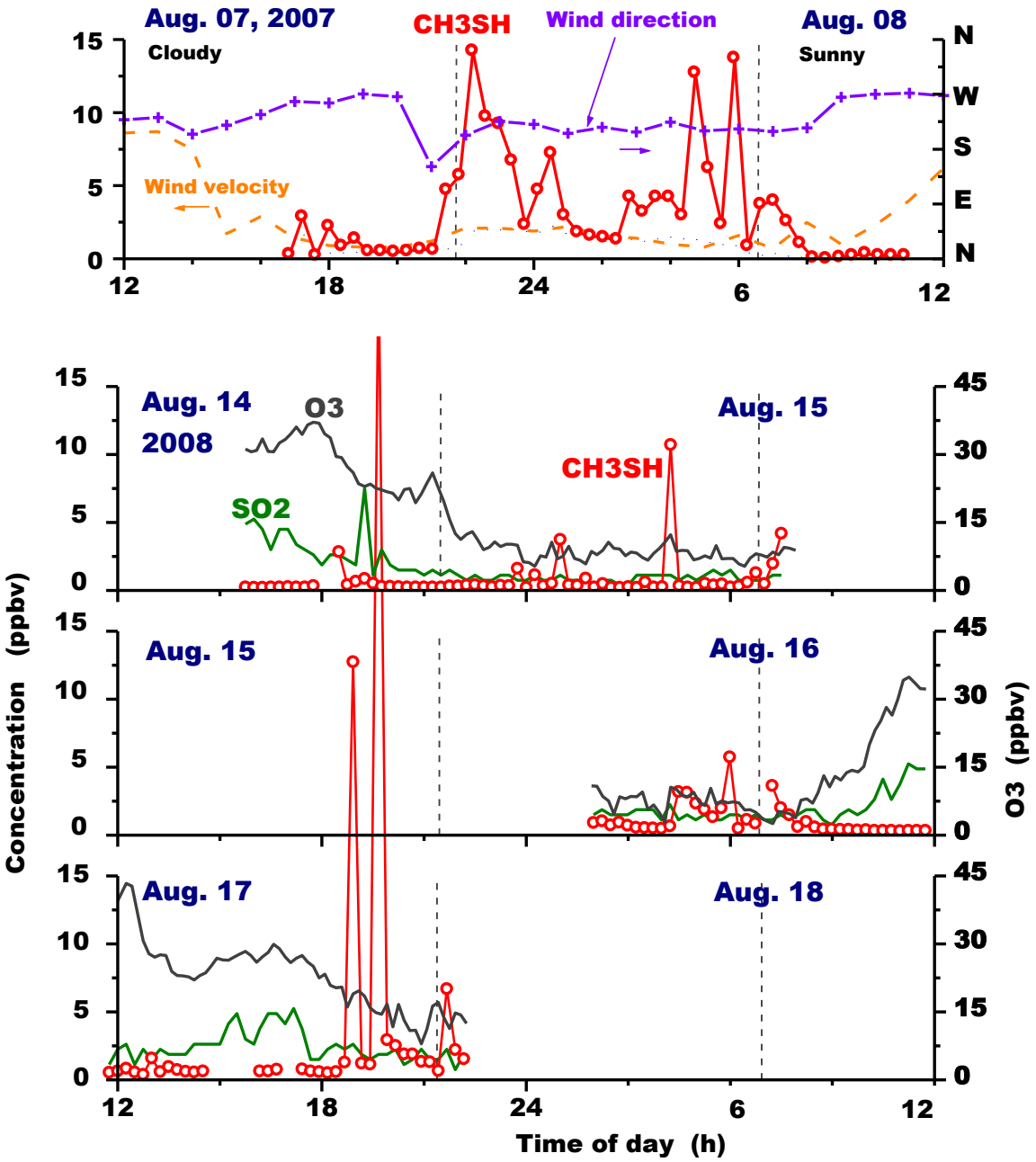

Aug. 07, 2007
Cloudy
CH3SH
Wind direction
Aug. 08
Sunny
Wind velocity
N
W
S
E
N
Aug. 14
2008
O3
SO2
CH3SH
Aug. 15
Aug. 15
Aug. 16
Aug. 17
Aug. 18
Concentration (ppbv)
O3 (ppbv)
Time of day (h)

Figure 4

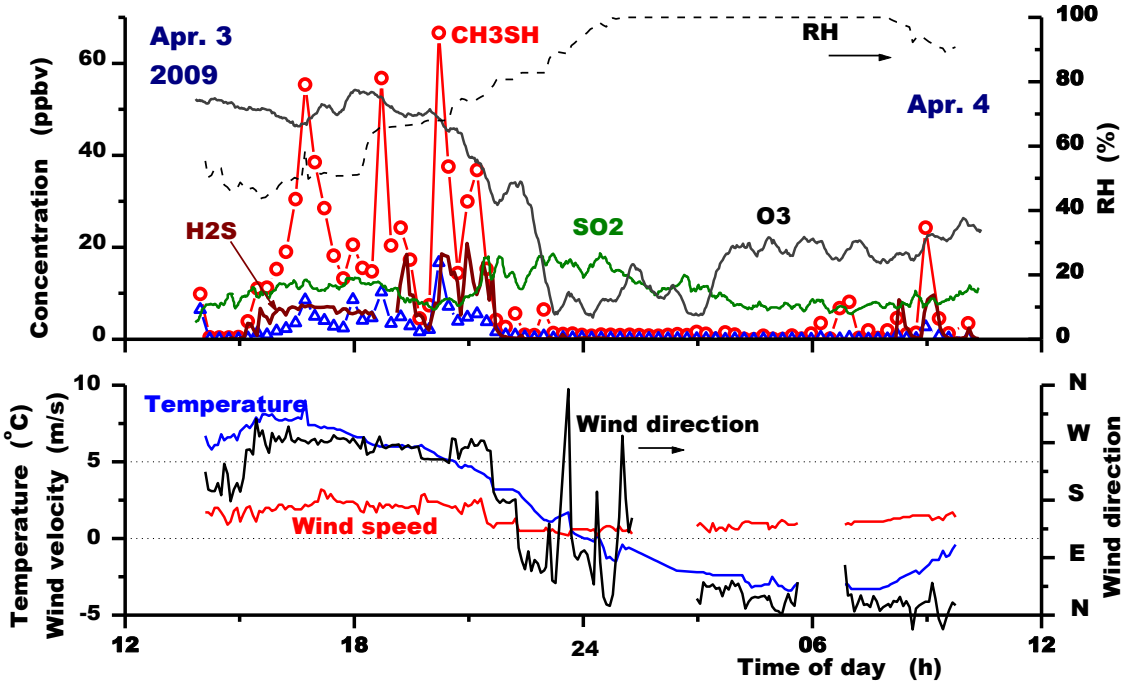

Apr. 3
2009
CH3SH
RH
Apr. 4
H2S
SO2
O3
Concentration (ppbv)
RH (%)
Temperature
Wind direction
Wind speed
Temperature (°C)
Wind velocity (m/s)
Wind direction
Time of day (h)

Figure 5

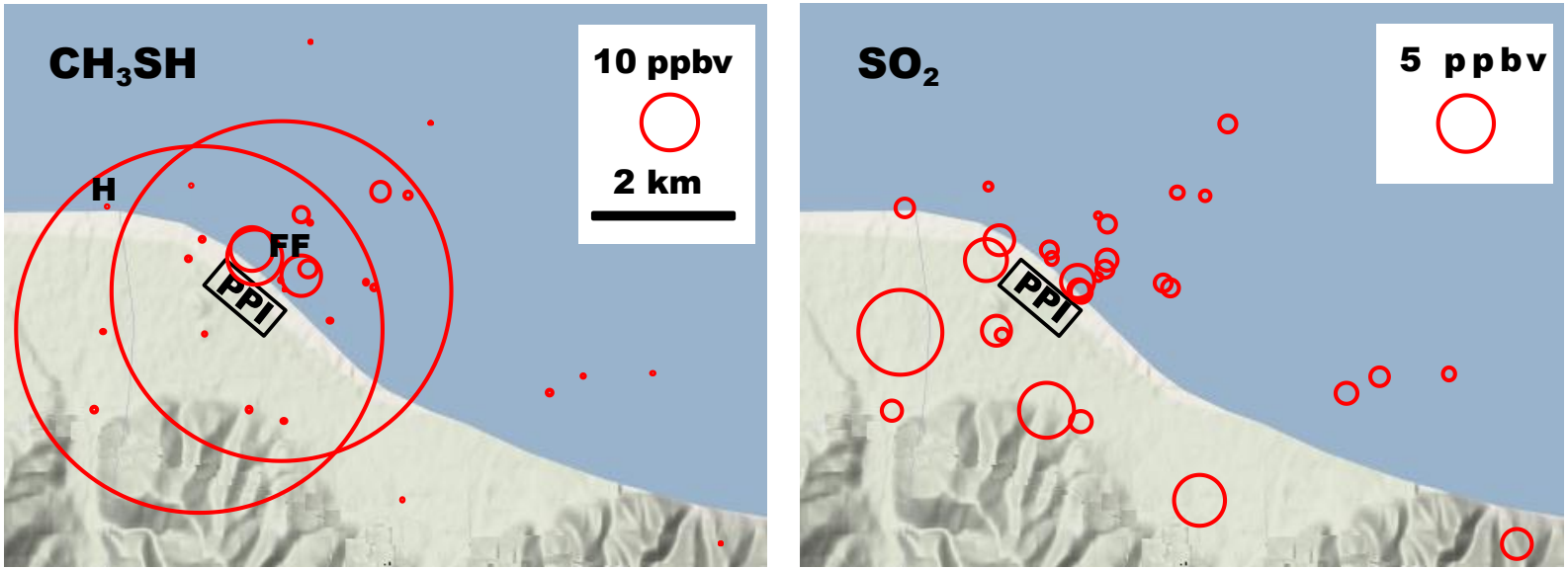
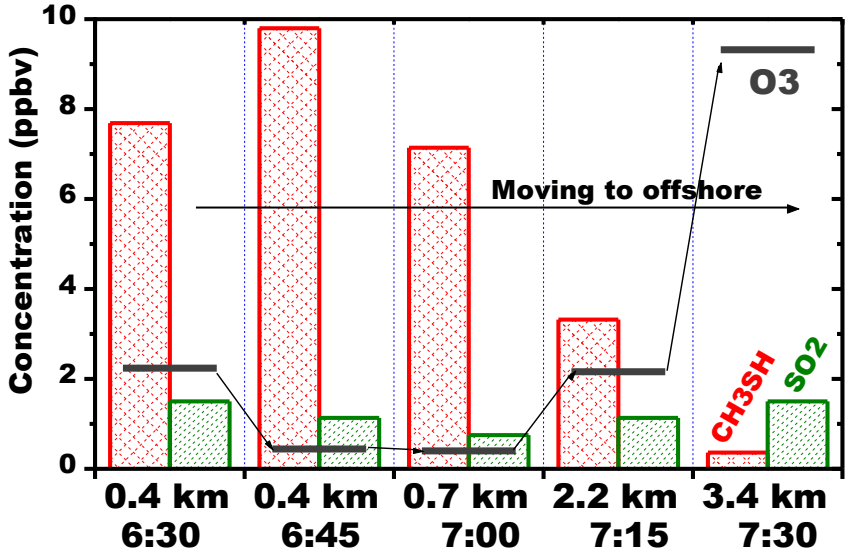


Figure 6


Concentration (ppbv)
10
8
6
4
2
0
O3
Moving to offshore
CH3SH
SO2
0.4 km 6:30
0.4 km 6:45
0.7 km 7:00
2.2 km 7:15
3.4 km 7:30

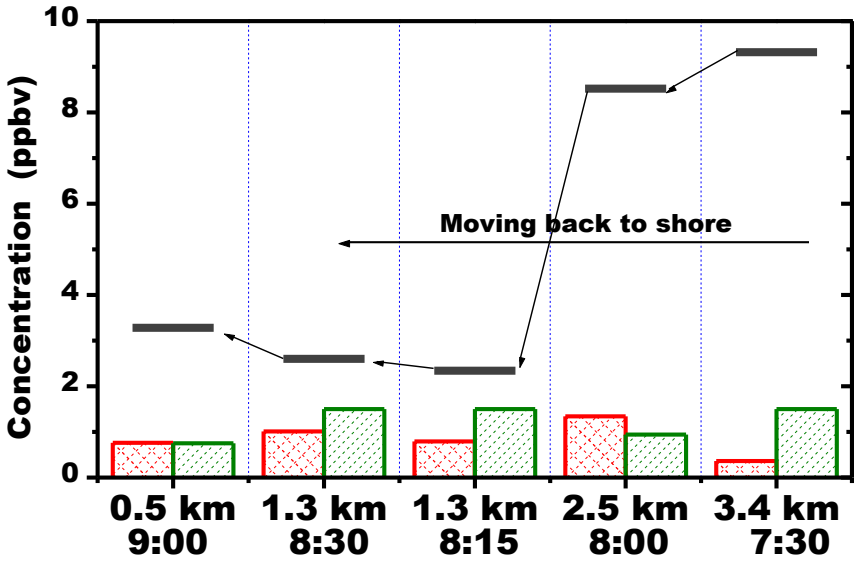

Concentration (ppbv)
10
8
6
4
2
0
Moving back to shore
0.5 km 9:00
1.3 km 8:30
1.3 km 8:15
2.5 km 8:00
3.4 km 7:30

Table
Click here to download Table: Table 1.doc

Table 1.

Sulfur species found in aerosols and gases

					Aerosol (ppb)*		Gases (ppbv)		
No.	Date	Time	(h)	Place**	Sulfate	MSA	CH_3SH	SO_2	O_3
1	Aug. 14	17:00-20:00	3.00	Harbor	0.38	ND	0.68	2.59	29.2
2	Aug. 14	20:00-23:00	3.00	Factory front	0.67	ND	0.30	1.13	17.4
3	Aug. 15	07:30-19:30	12.00	Harbor	0.65	ND	–	1.90	23.4
4	Aug. 15	10:10-13:50	3.67	Land drive	1.64	ND	0.55	3.05	–
5	Aug. 15	21:00-01:30	4.50	Factory front	1.13	0.0134	0.84	1.46	9.5
6	Aug. 17	06:20-09:00	2.67	Fogs	9.12	0.0356	3.29	1.25	3.3
7	Aug. 17	18:30-20:10	1.67	Factory front	4.28	0.0067	5.80	1.64	14.7
	Average				2.56	0.0186	1.91	1.86	16.6

* Note that aerosol concentrations are shown in ppb (in mole per 1-mol air), compared with gaseous data in mole bases. ND: not detectable.

** Locations of the harbor and factory front are shown in Fig. 5. The harbor was 3 km west from the factory. The factory front was on the water 0.5 – 1 km from the shore in front of the factory. Land drive: sampling by driving by a car from around the factory to 4 km east of the factory. Fogs: see section 3.3.