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PHOTOCHEMISTRY OF REDUCED SULFUR COMPOUNDS IN A LANDFILL ENVIRONMENT

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ABSTRACT

The photochemical conversions of RSCs compounds (e.g., DMS, CS_2, H_2S, DMDS, and CH_3SH) to a further oxidized form, SO_2 were evaluated in the landfill site in Daegu, Korea during a wintertime period (e.g., 13-16 Jan 2004) using a photochemical box model. The chemical species of RSCs, which may exert influences on the SO_2 production depending on sampling conditions, were found to include DMS, DMDS, and H_2S. RSC contribution to the observed SO_2 levels was insignificant in the sampling sites investigated. The photochemical conversion of the RSCs in the landfill can account for about 15% of the observed SO_2, on average.

Key Words: RSCs; H_2S; SO_2; landfill; Daegu

1. INTRODUCTION

Landfill has been used as a final depository to dispose of most industrial, construction, and municipal wastes in most countries (e.g., US, UK, Mexico, Turkey, etc.) (OECD, 2002). In the landfill, waste degradation takes place under anaerobic conditions, with an initial stage of acidic stabilization and ending in malodorous gas emissions in the surroundings (Vandergheynst et al., 1988). Landfill facilities are considered to be important sources for a wide range of trace gases

including methane (CH_4), volatile organic compounds (VOCs), and reduced sulfur compounds (RSCs).

The major RSCs found in the atmosphere are carbon disulfide (CS_2), dimethyl sulfide (CH_3SCH_3, DMS), and hydrogen sulfide (H_2S) (Berresheim et al., 1995; Watts, 2000). In the case of landfill, other RSCs, which include methyl mercaptan (CH_3SH), dimethyl disulfide (CH_3SSCH_3, DMDS), and so on, also constitute significant portions of trace gas emissions (Kim et al., 2005). The concentrations of RSCs in the landfill sites were significantly higher than those in the ambient air by three orders of magnitude (Kim et al., 2005). However, the data for RSCs in this potential source area are still extremely sparse; thus quantitative knowledge of sulfur gas speciation is lacking. Recently Muezzinoglu (2003) found that ambient SO_2 concentrations were affected closely by both total organic sulfur compounds and certain individual components such as DMS and H_2S emitted from polluted creeks carrying wastewaters from industrial and residential areas. Hence, investigations of the absolute and relative distributions of RSCs and their photochemistry may be highly valuable in evaluating the sulfur gas cycle in strong source environments such as landfills. For instance, acquisition of the SO_2 yield rate from RSC oxidation in landfills can be valuable in assessing their impact on the formation of secondary particles in the urban air.

In this study, the oxidation chemistry of RSCs was investigated using the full scale oxidation mechanisms of RSCs, particularly for DMS and DMDS. In addition, the photochemical conversion of RSCs and their impact on the distribution of stable end-product SO_2 were assessed based on a photochemical box model.

2. METHODS

For the model computation, 5 selected RSCs (e.g., H_2S, DMS, CS_2, CH_3SH, and DMDS) were measured along with SO_2. To better explain their relationships, atmospheric trace gases O_3, NO_X, CO, CH_4, and non-methane hydrocarbons (NMHCs) were also continuously measured concurrently with the meteorological parameters of temperature, relative humidity, solar radiation, and so on. RSC measurements were made 2 times per day (e.g., morning period (10:00-10:45) and afternoon period (16:00-16:45)) from all eight sampling sites in the studied landfill located in Daegu Korea. This study was conducted during a winter period, from January 13-16 2004 (Fig. 1).

The landfill is located in Bangchun district, approximately 10 km west of the central area of Daegu city. Eight sampling locations were chosen for the collection of ambient RSCs samples in the study area as shown in Fig. 1. The studied landfill was built in 1990 and is still in operation, with waste undergoing sanitarization before burial. It is partly covered in its upper part and landfilling is still progressing in the rest of landfill area.

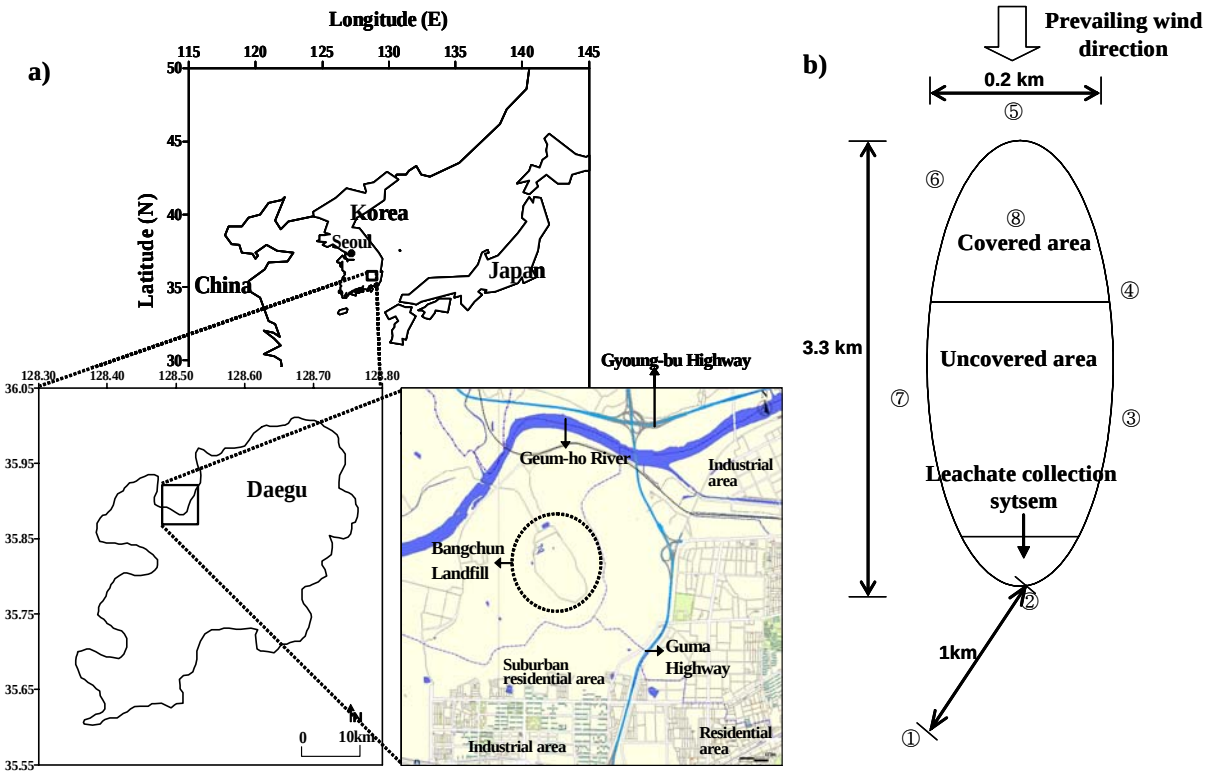

Figure 1. a) Location of sampling area (35°52' 07" and 128°31' 00") in Daegu, Korea and b) characteristics of landfill: site 1=residential area; site 2=near the landfill gate; sites 3-7=circumference of landfill; and site 8=within landfill area; northerly wind is dominant during sampling period; a slope of landfill is 15°; and total area of 596,764 ㎡.

Landfill gas samples were collected by the vacuum sampling method using a 10-liter Tedlar bag sampler (SKC corp. USA). These samples were then brought to the laboratory for analysis within 24 hours to minimize the possibility of RSC loss due to long-term storage. The RSCs were determined by a GC system (Donam Instruments, Model DS 6200) equipped with a pulsed flame photometric detector (O.I. Co., Model 5380).

For the analysis of the RSC oxidation pathway, the diurnal profiles of OH and NO_3 were generated by the photochemical box model (PCBM), which includes a full spectrum of $HO_x/NO_x/CH_4$/NMHCs interactions. The PCBM was chemically constrained to the observed input data sets of O_3, NO, NO_2, CO, SO_2, CH_4, (and DMS). In brief, this model contains: 1) 59 HO_X-N_XO_Y-CH_4 gas kinetic/photochemical reactions; 2) 146 NMHC reactions; and 3) 12 heterogeneous processes. Concentrations of SO_2 derived from the RSC oxidation chemistry were calculated using a mass-balance approach. These procedures are based on Eq. (1).

$$\frac{d[SO_2]_{OXD}}{dt} = \{P(DMS) + P(H_2S) + P(CS_2) + P(DMDS) + P(CH_3SH)\} - L(SO_2)[SO_2]_{OXD} \qquad (1)$$

where $[SO_2]_{OXD}$ represents SO_2 concentrations produced from each respective RSC of interest; P(DMS), P(H_2S), P(CS_2), P(DMDS), and P(CH_3SH) are the photochemical production rates of SO_2 from the oxidation of their respective RSC counterpart; and L(SO_2) is the photochemical loss frequency of SO_2. The total first-order loss parameters of SO_2, L(SO_2) include gas-phase chemical losses, the physical removal processes defined by the wet/dry deposition to the surface, the scavenging by aerosols and cloud/fog droplets, and the dilution by vertical transport. Values of L(SO_2) were taken to correspond to SO_2 lifetimes (i.e., $\tau(SO_2)$) of 6, 12, and 24 hours. These L(SO_2) values were chosen based on Bae and Kim (2003), who reported the relative contribution of SO_2-to-sulfate conversion processes (i.e., oxidation by OH, liquid phase oxidation by H_2O_2, O_3, and O_2 in the presence of catalytic metal ions, and absorption of aerosol surface) in the urban area. The full sulfur chemistry model used in this study includes the sum of 88 gas-phase reactions and 9 heterogeneous reactions of sulfur species. The significant fractions of DMS and DMDS oxidation mechanisms were adopted from Yin et al. (1990).

3. RESULTS AND DISCUSSION

3.1 The distribution of RSCs in- and outside landfill site

A statistical summary of all RSCs measured during the study period is provided in Table 1. Comparing the magnitude of RSC concentrations, their values tend to decrease in the order of H_2S, DMS, CS_2, CH_3SH, and DMDS. H_2S varied from 0.01 to 27 ppbv with a mean value of 4 ppbv (a median value of 2 ppbv). Distribution of RSCs in the landfill was somewhat different from that in the ambient air of the Seoul metropolitan area, which was reported by Shon and Kim (2005). For instance, H_2S concentrations in the landfill were significantly higher than those in the ambient air by a factor of more than 10. Mean H_2S concentration in the ambient urban air of Seoul was 0.1 ppbv. However, our H_2S level in the landfill was significantly lower than that measured in polluted creeks in Turkey having a median value of 25 ppmv (Muezzinoglu, 2003). The spatial distribution of RSCs can be used as a clue to explain the impact of strong source processes on the surrounding environment. As shown in Fig. 1, it is reasonable to expect that sites 2 through 8 are more sensitive to the landfill's influence than site 1. In Table 1, the spatial distribution of RSCs is summarized in terms of the site number. In general, most RSC concentration levels in site 1 were significantly lower than those within the landfill boundary (sites 2-8; e.g, up to one order of magnitude for site 8), as those measured in site 8 were significantly higher. However, CH_3SH and DMS concentration levels in site 1 were not notably different from those determined in the landfill boundary (e.g., sites 3-7). In addition, except for H_2S there were no distinct differences in concentrations of most RSCs between morning (e.g., 10:00-10:45 LST) and afternoon (e.g., 16:00-16:45 LST).

Table 1. A summary of RSCs and environmental parameters measured during the field campaign in the Daegu landfill site.

Site No.	H_2S[a]	CH_3SH[a]	CS_2[a]	DMS[a]	DMDS[a]	Temp(°)	NO_2[b]	NO_X[b]	O_3[b]	SO_2[b]	CO[c]	CH_4[c]	NMHC[c]
1	883±815[d] (576)[e] 10-2057[f]	24±18 (22) 6-54	99±58 (70) 48-184	236±193 (148) 89-597	37±71 (9) 4-183	0.2±2.3 (-0.2) -2.8-3.7	16±13 (15) 1-38	26±29 (19) 1-80	24±11 (24) 6-38	8.5±5.5 (8.5) 2.0-15.0	0.3±0.2 (0.3) 0.1-0.6	60±23 (55) 35-97	0.6±0.4 (0.7) 0.1-0.9
2	442±341 (620) 26-760	27±11 (33) 10-36	135±69 (115) 45-215	264±181 (167) 125-542	31±43 (11) 5-107	0.5±2.3 (0.1) -2.7-4.2	17±15 (14) 1–44	29±35 (18) 1-98	24±12 (23) 5-40	7.8±5.5 (7.0) 1.0-15.0	0.3±0.2 (0.3) 0.1-0.5	48±16 (44) 29-73	1.8±1.1 (1.7) 0.8-2.9
3	848±525 (1110) 245-1191	15±8 (14) 7-23	98±10 (104) 87-104	100±14 (99) 87-115	6±2 (7) 4-8	0.1±2.5 (-0.7) -3.0-4.2	17±12 (16) 2–39	26±26 (20) 2-76	23±11 (23) 6-37	7.8±5.3 (6.5) 2.0-14.0	0.3±0.1 (0.3) 0.1-0.5	60±23 (60) 32-98	1.0±1.1 (1.0) 0.2-1.8
4	1282±605 (1111) 782-2333	22±6 (22) 15-31	103±48 (101) 33-158	193±139 (147) 108-437	11±4 (11) 5-15	0.1±2.6 (-0.7) -3.0-4.2	16±12 (14) 2-38	25±26 (18) 2-75	25±12 (25) 6-41	7.8±5.3 (6.5) 2.0-14.0	0.3±0.1 (0.3) 0.1-0.5	65±25 (71) 35-98	0.8±0.1 (0.9) 0.7-1.0
5	3572±2565 (2928) 607-7566	31±23 (27) 8-62	99±43 (101) 47-158	196±150 (139) 108-462	13±7 (11) 7-24	0.1±2.9 (-0.8) -3.5-4.0	16±14 (12) 1-40	25±29 (17) 1-82	24±12 (25) 6-41	8.2±5.1 (7.5) 2.0-15.0	0.4±0.2 (0.4) 0.2-0.5	77±29 (90) 31-102	4.2±3.2 (5.1) 0.6-6.8
6	4989±3615 (4318) 1503-11289	50±60 (22) 18-171	149±89 (119) 65-317	255±227 (138) 98-669	60±73 (20) 5-170	0.7±1.9 (0.4) -1.9-3.6	18±14 (15) 1-40	29±30 (19) 1-83	23±11 (24) 6-36	7.7±5.0 (8.0) 1.0-14.0	0.4±0.2 (0.4) 0.1-0.6	50±16 (48) 29-72	1.7±1.4 (1.2) 0.7-3.3
7	6112±5813 (3384) 427-14485	75±70 (42) 21-183	98±32 (95) 61-151	296±173 (280) 125-608	73±76 (49) 7-200	0.7±2.2 (0.3) -1.9-3.8	18±14 (15) 1-42	30±32 (20) 1-91	24±11 (23) 6-38	8.5±5.3 (9.0) 1.0-14.0	0.3±0.2 (0.3) 0.2-0.5	52±15 (52) 29-68	1.3±0.5 (1.3) 0.8-1.7
8	13169±8944 (9079) 5457-27005	80±93 (47) 17-265	192±96 (179) 71-334	1897±3799 (308) 99-9625	81±137 (28) 9-358	0.1±2.9 (-0.4) -4.0-4.3	15±14 (12) 1-39	24±28 (15) 1-78	25±13 (26) 6-42	7.3±5.8 (6.0) 1.0-14.0	0.3±0.2 (0.3) 0.1-0.5	60±27 (57) 32-97	4.5±2.3 (4.5) 2.9-6.1

a: unit in pptv; b: unit in ppbv; c: unit in ppmv; d: mean ± 1σ; e: (median); and f: min.- max.

Typically, n=6 in each site for each RSC; n=96 (e.g., 4 days × 24 (hourly mean)) in each site for meteorological parameters and trace gases (NO_x, O_3 etc.)

3.2 Contribution of the RSC oxidation to SO_2 levels in landfill sites

Contribution of the oxidation of individual RSCs (e.g., $[SO_2]_{DMS}$, $[SO_2]_{DMDS}$, $[SO_2]_{CH3SH}$, $[SO_2]_{CS2}$, and $[SO_2]_{H2S}$) to the observed SO_2 levels is given in Fig. 2. Overall, the proportion of SO_2 concentrations, total $[SO_2]_{OXD}$, converted from the oxidation of 5 RSCs, was episodic depending on the sampling period, ranging from <1 to 80% with a mean value of 13%. The total $[SO_2]_{OXD}$ during the first two days (e.g., Jan 13-14) was significantly higher than that during Jan 15-16, by a factor of 15 on average. In addition, the major compounds of RSCs which make significant contributions to total $[SO_2]_{OXD}$ were DMS, DMDS, and H_2S. As shown in Fig. 2, the significant contribution of RSC oxidation to observed SO_2 levels occurred on Jan 13, ranging from 30 to 80% with a mean value of 45%, based on our standard model runs (23% for the minimum case). The significant fraction of total $[SO_2]_{OXD}$ was derived by DMDS oxidation on that day. However, the RSC contribution in most sites on the other days was insignificant (e.g., <10%), except for sites 5-8 (15-50%) on Jan 14, based on our standard model runs as well as the maximum case runs.

In order to identify the source contribution of SO_2 in the landfill, the correlation patterns between RSCs and SO_2 were examined. In most cases, there were no clear correlations between them. However, there was a case with a clear correlation (e.g., r^2=0.53) between DMS and SO_2 during the study period. The strong negative correlation between the RSC and SO_2 may be expected with a sampling resolution significantly less than 1 day if the following conditions are met: (1) the oxidations of RSCs are the significant source of SO_2 in ambient air and (2) SO_2 production from non-chemical sources (i.e., anthropogenic sources or transport) is not significantly larger than that by RSC oxidation. In field experiments, there have also been some reports for the strong negative correlation between DMS and SO_2 in the clean marine boundary layer (MBL) (Bandy et al., 1996; Davis et al., 1999). In contrast, there was no strong correlation in the MBL on Jeju Island, Korea, which was occasionally influenced by the long range transport of air mass from China and/or the Korean peninsula, according to our previous study (Shon et al., 2004). The atmospheric SO_2 levels on Jeju Island during the sampling period could not be explained solely in terms of DMS oxidation. A clear correlation between these two sulfur species was not noticed previously in the anthropogenically influenced regions such as a coastal site in Brittany, France (Putaud et al., 1999), the Western North Atlantic Ocean (Berresheim et al., 1991), and the Arctic BL (Leck and Persson, 1996)). Meanwhile, there was a weak negative correlation between DMDS and SO_2, although the relative contribution of DMDS oxidation to the total $[SO_2]_{OXD}$ is higher than that of DMS oxidation.

The contribution of DMS oxidation, $[SO_2]_{DMS}$, ranged from 5 to 37% of oxidized SO_2 levels from total RSC (i.e., total $[SO_2]_{OXD}$) with a mean value of 16%, depending on measurement points and the time period. There were significant temporal variations in relative contribution of

DMS oxidation. In other words, although the absolute levels of total $[SO_2]_{OXD}$ on Jan 13 were relatively higher, the relative DMS contribution, $[SO_2]_{DMS}$, was significantly lower than those on the other days (e.g., Jan 14-16) by a factor of 3. For spatial distribution of $[SO_2]_{DMS}$ at the sampling sites, sites 1-4 showed similarity in $[SO_2]_{DMS}$ levels; however, sites 5-8 showed slightly lower levels by a factor of 2.5.

In the mean time, the contributions of DMS oxidation by the major oxidants, OH and NO_3 during the study period ranged from 32-62 and 38-68%, respectively. For DMS oxidation by OH, the addition channel during the study period was dominated by cold temperatures. The branching ratios of abstraction and addition channels were 35 and 65%, respectively. Our model simulation indicated that the significant fractions of SO_2 converted from DMS oxidation by OH were produced by the abstraction channel under high NO_x conditions, although the addition channel favors cold temperature.

For DMDS, its contribution to the oxidation pathway (e.g, the ratio of $[SO_2]_{DMDS}$ to total $[SO_2]_{OXD}$) was highly variable, ranging from 12 to 91% with a mean value of 42%. The higher contribution of its oxidation to both total $[SO_2]_{OXD}$ and observed SO_2 levels occurred only during the first day of the sampling period. On the other days, the contribution of its oxidation to total $[SO_2]_{OXD}$ was high, but its contribution to the observed SO_2 levels was insignificant (e.g., <10%). For CS_2, the contribution of its oxidation, $[SO_2]_{CS2}$, to total $[SO_2]_{OXD}$ was negligible (e.g. <4%). In addition, the contribution of CH_3SH oxidation, $[SO_2]_{CH3SH}$, to total $[SO_2]_{OXD}$ was insignificant, ranging from 1 to 11% with a mean value of 4%. In contrast, the contribution of H_2S oxidation, $[SO_2]_{H2S}$, to total $[SO_2]_{OXD}$ fell in a wide range from <1 to 78% with a mean value of 37%. A high contribution of its oxidation to both total $[SO_2]_{OXD}$ (e.g., 78%) and observed SO_2 levels (e.g., 40%) existed only in site 8 on Jan 14. Its contribution to the total $[SO_2]_{OXD}$ was relatively high (e.g., 43% on average) during most study periods, except for the day of Jan 13 (e.g., 5%), but that to the observed SO_2 levels was insignificant (e.g., <4%) .

4. CONCLUSION

In this study, the environmental behavior of RSCs in landfill conditions was investigated in terms of their temporal and spatial distributions and through their oxidation pathways. The results of the ambient measurements indicated that the distribution patterns of RSCs in the landfill were clearly different from those commonly observed in the ambient air (i.e., significantly higher H_2S levels in the landfill). In addition, the photochemical conversions of RSCs of DMS, CS_2, H_2S, DMDS, and CH_3SH to SO_2 were examined using a photochemical box model with the data collected at the landfill site during the winter period. At the end of the study, it was found that the ratio of the SO_2 in the air obtained from the oxidation of the 5 selected

RSCs to the overall SO_2 concentration measured directly in the air was not uniform. Rather, it was dependent on the environmental conditions of the day such as the magnitude of each RSC level. In general, the RSC contribution to SO_2 observations was insignificant in most sites. DMDS and H_2S may also exert influences on the SO_2 production depending on sampling conditions, but there were no clear correlations between these RSCs and SO_2.

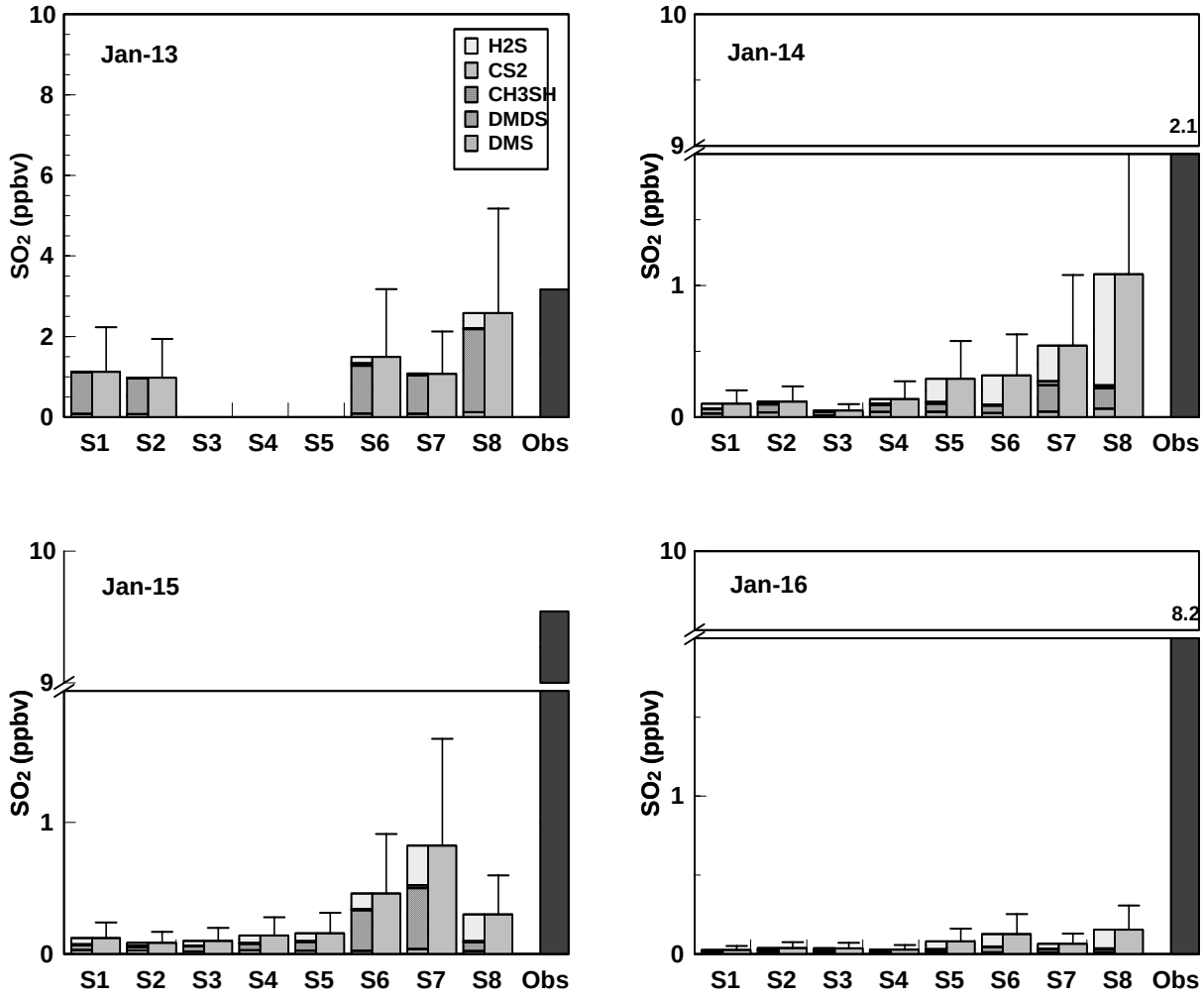

Figure 2. Comparison of observed SO_2 with model simulated values ($[SO_2]_{OXD}$). S1-S8 represent site numbers and Obs (the last bar in black) represents the mixing ratio of observed SO_2. The first bar represents the contribution of individual RSC to observed SO_2 ($[SO_2]_{DMS}$, $[SO_2]_{DMDS}$, $[SO_2]_{CH3SH}$, $[SO_2]_{CS2}$, and $[SO_2]_{H2S}$). The best estimate for $[SO_2]_{OXD}$ (our standard model run, sum of $[SO_2]_{DMS}$, $[SO_2]_{DMDS}$, $[SO_2]_{CH3SH}$, $[SO_2]_{CS2}$, and $[SO_2]_{H2S}$) is defined by the second solid bar with a vertical line and corresponds to $\tau(SO_2)$=0.5d. The top of the vertical lines within each second bar defines the upper limit of model estimates (corresponding to $\tau(SO_2)$=1d) for the mixing ratio of SO_2 when produced from RSC oxidation.

5. ACKNOWLEDGMENTS

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