Monitoring of Atmospheric Reduced Sulfur Compounds and Their Oxidation in Gunsan Landfill Areas

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요 약

이 연구에서 환원성 황 화합물의 시간적, 공간적 분포 패턴들이 매립과정에 크게 영향 받는 지역에서 조사되었다. 이러한 측정 연구에 기초하여 환원성 황 화합물이 이산화황으로 변환되는 광화학적 작용 규모를 광화학적 상 자모델을 이용하여 평가하였다. 이 연구는 2004년 3월에서 12월까지 대기 중 환원성 황 화합물 농도를 군산시의 매립장 내부와 인근에서 평가했다. 환원성 황 화합물의 분포가 일반적으로 H_2S , DMS, 또는 DMDS들이 대부분인 반해, 그 패턴들은 시료채취 지역과 기간에 따라 다양했다. 군산 매립장에서 H_2S , DMS는 연구기간 동안 가장 높은 농도를 나타냈다. 이 지점에서 DMS의 농도는 매립 과정 뿐만 아니라 해양 오염원에 영향을 받는다고 사료되었다. 모든 환원성 황 화합물이 아황산가스의 광화학적 부산물에 대한 상대적 기여도를 비교할 때, 세가지 환원성 황 화합물(DMDS, H_2S , 그리고 DMS)이 가장 중요한 물질로 조사되었다.

Keywords: landfill, source, photochemical oxidation, RSCs, H₂S, SO₂

I. Introduction

The environmental importance of RSCs is wellknown due to their involvement in the production of oxidized pollutants (e.g., sulfuric acid) in the urban air (Berresheim et al., 1995). The major RSCs found at the LF areas include dimethyl sulfide (CH₃SCH₃, DMS), hydrogen sulfide (H₂S), methyl mercaptan (CH₃SH), dimethyl disulfide (CH₃SSCH₃, DMDS), and carbon disulfide (CS₂); they were found to constitute large portions of trace gas emissions in the LF environment (Kim et al., 2005). In this study, the temporal and spatial distributions of RSCs in ambient air were measured from inside and in the surrounding areas of the LF area, Korea during several field campaigns held in 2004. Using these measurement data, the photochemical oxidation of RSCs was investigated in terms of the full scale oxidation mechanisms of RSCs (particularly, DMS and DMDS). In addition, the quantity of RSC converted photochemically to one of their stable end-products, SO₂, in the study

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area was assessed using a photochemical box model (PCBM).

II. Data and Methods

In order to examine the environmental behavior of RSCs in ambient air and their photochemical reactions, the concentrations of four target RSCs (e.g., H₂S, DMS, DMDS, and CH₃SH) were measured at Gunsan coastal LF area in Korea during 2006 campaign periods. To better explain the factors and processes regulating their cycles at the study area, a number of trace gases including carbonyl compounds (e.g., formaldehyde, acetaldehyde, and acrolein) and aromatic VOCs (e.g., benzene and toluene) were also measured concurrently. In addition, the measurements of O₃ and NO₃ were also made simultaneously at the environmental monitoring stations adjacent to LFs (<4 km away from the centers of LF). Information of O₃ and NO_x are essential in this study, because they can react to yield the major oxidants of RSCs, OH and NO₃. Mechanisms governing the interactions between RSC and those oxidants have already been discussed by Shon and Kim (2006).

The general characteristics of the two target LF

areas can be summarized as follows. The LF in the Gunsan city (G-LF: located in the western coastal area of Korea) is nearly 10 km northwest from the center of the city. It has the total area of about 0.28 km² and the volume of 2.6×10^6 m³. Note that the acronyms of G (Gunsan) is assigned below for the simple comparison of both LF sites such as G-LF. These LF facilities have been operated with the pre-sanitary treatment of wastes before burial since their establishment in 1996. The collection of RSCs in both LF facilities was made identically by selecting four sampling sites (Location of sampling areas in Gunsan (35°58'19" and 126°34'19"), Korea. Descriptions of individual sampling sites in Gunsan (G) landfill sites: (1) G-LF: G1 = center of landfill; G2 = residential area; G3 = suburban residential area; G4 = coastal area of landfill.

In the case of G-LF, the selected sites include: (1) the center of the LF (i.e., G1), (2) a residential area (i.e., G2) (about 2 km away from the LF), (3) a suburban residential area (i.e., G3) (about 1 km away from the LF), and (4) a coastal area (i.e., G4) (within 3 km of the LF). RSC measurements at the G-LF sites were made as three individual field campaigns (i.e., 6 May (Period 1, hereafter refer to as P1), 9 August (P2), and 2 December 2004 (P3)). All RSC measurements in the G-LF were made in the morning (i.e., 09:00-11:00). In contrast, sampling locations for the D-LF sites were selected to include one at the center of the LF (i.e., D1) and three at coastal areas (i.e., D2 through D4); the latter 3 sites are all within 3 km east of the LF. The collection of ambient air samples from both LFs was made using a vacuum sampling system to fill up Tedlar bags (SKC corp. USA). For this purpose, a 10-liter Tedlar bag was placed inside the system made of a vacuum container and a vacuum pump. By creating a vacuum inside the container, gas samples were drawn directly into the Tedlar bag. The concentrations of RSCs were then determined by a GC system (Donam Instruments, Model DS 6200) equipped with a pulsed flame photometric detector (PFPD: O.I. Co., Model 5380). The detection limits (DL) for all RSCs were found to be $16.6 \, (H_2S)$, $7.7 \, (CH_3SH)$, $5.7 \, (CH_3SH)$ (DMS), and 4.2 pptv (DMDS). However, because of the cold trap problem that degraded the H₂S detection of the system, the DL for H₂S was found to be as high as 52 pptv during the spring measurements made in Gunsan. To acquire optimum resolution between different RSCs, a BP-1 column $(60 \text{ m} \times 0.32 \text{ mm}, 1.8 \text{ mm ID})$ was used at column flow rate of 1.2 ml min⁻¹ (N₂ carrier gas) with each running cycle ending at 20-min intervals. Detailed information concerning the RSC measurement method has been described elsewhere (Kim, 2005a, b). In addition, a number of trace gases (such as O₃, NO, NO₂, CO, SO₂, CH₄, and NMHCs) were monitored along with meteorological parameters from the environmental monitoring stations adjacent to the LF sites: these measurements were made using a microcomputer controlled system for air quality monitoring (Kimoto MCSAM-6 series) at 1-min intervals. Detailed information on these measurement techniques (i.e., DLs) has been described in Shon et al. (2005).

III. Model Descriptions

The PCBM was chemically constrained with the observed data sets of O₃, NO, NO₂, CO, SO₂, and DMS. Due to the lack of CH₄ measurement data, its concentrations were occasionally extrapolated by an adjustment factor (e.g., 0.85 in G-LF). The concentrations of SO₂ derived from the RSC oxidation were calculated using a mass-balance approach. These procedures are based on Eq. (1).

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

where [SO₂]_{OXD} represents SO₂ concentrations produced from the oxidation of RSCs of interest; P(DMS), P(H₂S), P(DMDS), and P(CH₃SH) are the photochemical production rates of SO₂ from the oxidation of their respective RSC counterparts given in the parenthesis; and L(SO₂) is the frequency of SO₂ photochemical loss. This L(SO₂) term covers a number of processes including (1) gas-phase chemical losses, (2) the physical removal processes defined by the wet/dry deposition to the surface, (3) the scavenging by sea-salt aerosols and the cloud droplets, and (4) the dilution due to the vertical transport. The L(SO₂) values were taken to correspond to SO₂ lifetimes of 6, 12, and

24 h. They were then chosen based on the results of Bae *et al.* (2003), who reported the relative contribution of SO_2 -to-sulfate conversion processes to SO_2 loss in the urban area.

IV. Results and Discussion

1. RSC Distributions at Gunsan Landfill (G-LF)

The individual concentration data of RSCs at the two LF sites and their statistical summary are provided in Tables 1 and 2, respectively. The concentration data from all four sites in the G-LF are shown as a function of the site number. As shown in Fig. 1, G1 is located at the center of LF, G2-G4 are 3 km apart from the center of the LF. Hence, it

is reasonable to expect that the concentrations at G1 may reflect the LF's influence more effectively than the others. In fact, many RSCs measured at the G1 site generally showed much enhanced values relative to other sites, especially during spring and summer (see Table 1).

At all G-LF sites, DMS and H_2S tend to record the enhanced concentration levels during spring or summer relative to other RSCs or to other seasons (Table 2). The mean DMS concentration $(0.3 \pm 0.3 \text{ ppbv})$ is found to be 50% higher than the mean H_2S concentration $(0.2 \pm 0.5 \text{ ppbv})$. It is also noted that there is a significant difference in H_2S levels between the LF center (G1: $0.6 \pm 0.9 \text{ ppbv}$) and the surrounding areas (G2-G4: $0.09 \pm 0.09 \text{ ppbv}$).

Table 1. A summary of RSC concentrations measured during the field campaign in the G-LF (in pptv)

C:+-	Site	te H ₂ S					CH₃SH				DMS				DMDS			
City	no.	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter	
	G1	< 52**	1683	-	53	44	67	-	7	1090	387	-	87	225	41	-	< 1**	
	G2	< 52**	58	-	297	106	66	-	23	440	215	-	14	36	48	-	42	
Gunsan	G3	< 52**	41	-	109	36	74	-	7	489	293	-	21	59	229	-	69	
	G4	< 52**	168	-	65	19	135	-	14	506	308	-	25	46	70	-	397	

^{*}mean of two-day measurements in spring and summer events.

Table 2. A statistical summary of RSCs measured during the field campaign in the G-LF (in pptv)

G:		Н	$_2$ S	СН	₃SH	DN	MS	DMDS		
City	Season	G1-G4	G2-G4	G1-G4	G2-G4	G1-G4	G2-G4	G1-G4	G2-G4	
	Cia	< 52**	< 52**	51 ± 38 {40}	54 ± 46 {36}	631 ± 307 {498}	478 ± 34 {489}	92 ± 89 {53}	47 ± 12 {46}	
	Spring	(4)	(3)	19~106 (4)	19~106 (3)	440~1090 (4)	440~506 (3)	36~225 (4)	36~59 (3)	
	C	488±799 ^a {113} ^b	89 ± 69 {58}	86 ± 33 {71}	92 ± 38 {74}	301 ± 70 {301}	272 ± 50 {293}	97 ± 89 {59}	116 ± 99 {70}	
	Summer	41~1683° (4) ^d	41~168 (3)	66~135 (4)	66~135 (3)	215~387 (4)	215~308 (3)	41~229 (4)	48~229 (3)	
Gunsan	Fall	-	-	-	-	-	-	<u>-</u>	-	
	Winter	131 ± 113 {87}	157 ± 123 {109}	13 ± 8 {11}	15 ± 8 {14}	37 ± 34 {23}	20 ± 6 {21}	128 ± 182 {56}	169 ± 198 {69}	
	Winter	53~297 (4)	65~297 (3)	7~23 (4)	7~23 (3)	14~87 (4)	14~25 (3)	1~397 (4)	42~397 (3)	
	A 11	215 ± 469 {56}	91 ± 91 {58}	50 ± 41 {40}	53 ± 45 {36}	323 ± 303 {301}	257 ± 201 {293}	105 ± 117 {54}	111 ± 123 {59}	
	All	41~1683 (12)	41~297 (9)	7~135 (12)	7~135 (9)	14~1090 (12)	14~506 (9)	1~397 (12)	36~397 (9)	

^aMean±1σ; ^b{Median}; ^cmin.~max.; ^d(number of data).

^{**}non-detection limit.

^{*}mean of two-day measurements in spring and summer events.

^{**}non-detection limit.

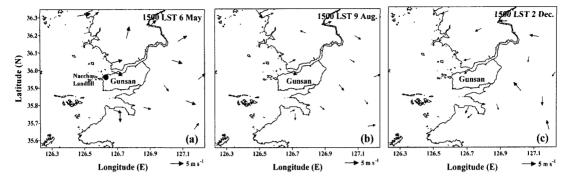


Fig. 1. Characteristics of the observed wind fields during the three (a-c) sampling periods in the G-LF, respectively. Wind field analysis for the sea breeze was carried out based on wind speed and direction data obtained from the ground-based AWS (automatic weather system) located near/in the Gunsan.

From all sampling sites (G1-G4), high H_2S levels $(0.5 \pm 0.8 \text{ ppbv})$ were observed in the summer (i.e., P2) due probably to the high microbial activity. In contrast, the distribution patterns of DMS were distinguished from those of H_2S . High concentrations of DMS $(0.6 \pm 0.3 \text{ ppbv})$ were generally observed in the spring (i.e., P1), especially at the G1 site. Comparison of the DMS concentration data with those of surrounding sites indicated enhanced concentration levels at the site (G4), which is the closest to the coast, regardless of seasons. Our DMS values measured at the coastal sampling

sites (G2-G4) (e.g., 0.2 to 0.3 ppbv) during the summer event were compatible with those measured at a bay area of Masan in southern sea of Korea (e.g., 0.01 to 6 ppbv with a mean of 0.2 ppbv) (Lee *et al.*, 2004). CH₃SH concentration (0.05 \pm 0.05 ppbv) at the surrounding areas (G2-G4) was found to be 1.4 times higher than that at the G1 site. Similar to H₂S, the relatively enhanced concentrations of CH₃SH (0.09 \pm 0.03 ppbv) were observed in the summer. However, DMDS values tend to peak in the winter (0.1 \pm 0.2 ppbv) (see Tables 1 and 2).

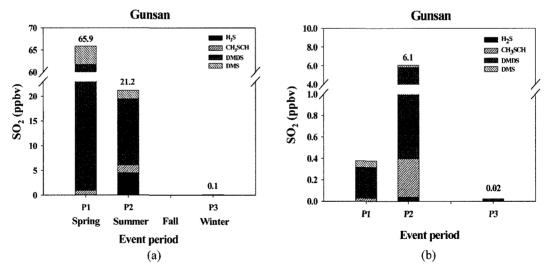


Fig. 2. Contribution of RSC oxidation to SO₂ concentrations at (a) the center of LF site (i.e., G1) and (b) the circumference of LF (i.e., G2-G4) during the entire study periods. P1-P3 and P1'-P4' represent the numbers of events in the G-LF. The bar for each event represents the contribution of individual RSC to SO₂ ([SO₂]_{H2S}, [SO₂]_{CH3SH}, [SO₂]_{DMDS}, and [SO₂]_{DMS}).

In this study, the findings of relatively enhanced DMS levels at G1 (the spring event) or G4 (during all sampling seasons) suggest the potential influence of an oceanic source transport by a sea breeze blowing from sea to land (see Fig. 2). In the surface seawater, DMS is produced from its precursor, dimethylsulfonium propionate (DMSP), which is a metabolic byproduct of phytoplankton. Once released into the water column, DMS undergoes degradation and is emitted into the overlying atmosphere. Therefore, many researches were able to find fairly good correlations between DMS and chlorophyll-a concentration (or phytoplankton cell concentration) in many previous studies (Kettle et al., 1999 and references therein). In this study, it is thus suspected that high DMS levels at the coastal areas during the spring event are affected by phytoplankton blooms; such phenomena are commonly observed in the springtime along the coastal areas in the southern sea (Chung and Yang, 1991). On a local scale, a sea breeze in Gunsan and its surrounding areas was prominent during P1 and P2 (i.e., a strong sea breeze (4-5 m s⁻¹) at 1500 LST), whereas a synoptic-scale wind was dominant during P3 (i.e., no sea breeze) (see Figs. 2(a)-(c)).

2. Comparison of RSCs Data between the Present and Previous Studies

The concentration levels of RSCs at the two LFs are distinguished fairly clearly from those of previous sites such as Daegu LF (Shon *et al.*, 2005). For instance, H₂S concentrations at the G-LF (range of 0.05 to 1.7 ppbv with a seasonal mean of 0.9 ppbv) were about four times lower than those at the Daegu LF; those values are also approximately two times lower than that at the D-LF. CH₃SH were observed to be a minor component of RSCs regardless of sites from both LF sites

during the whole study period; it ranged from < 0.01 to 0.2 ppbv (seasonal means of the G- and D-LF to be 0.04 and 0.09 ppbv, respectively). DMDS concentration levels in this study (seasonal means of the G- and D-LF to be 0.1 and 1.4 ppbv, respectively) were significantly higher than those found at other inland LF areas such as Daegu (< 0.08 ppbv, see Shon et al. (2005)). Recently, Muezzinoglu (2003) reported the concentrations of RSCs including DMS and H₂S at the polluted creeks and an urban LF in Izmir, Turkey in summer 2001. They were found to be strongly correlated with ambient SO₂ concentrations. Their DMS concentration showed a significantly higher level (e.g., 5.5 ppbv) compared to our LFs but 3 times lower than those of the creeks. Nunes et al. (2005) measured the atmospheric concentrations of several RSCs at a number of coastal locations in Brazil. They found that the areas without direct industrial activities maintained low RSC concentrations (e.g., <0.3 ppbv), while the areas affected by the anthropogenic influences had relatively high values of H2S, DMS, and CH₃SH in the winter (<1.4, 0.6, and 1.5 ppbv, respectively). Compared with the D-LF results seen in this study, the concentration levels of most RSCs measured at the industrial areas of Brazil (except for DMS) were moderately low. However, most RSC values in the areas with low industrial influences were relatively high compared to the surrounding sites of the D-LF (i.e., D2-D4) (See Table 4).

3. Contribution of the RSC Oxidation to SO₂ Concentrations at LF Areas

Photochemical conversion of RSCs to SO_2 has been examined due to their potential role as the source of SO_2 and secondary aerosol formation (Shon *et al.*, 2001, 2004). For instance, it was

Table 3. SO₂ concentrations converted from the oxidation of four selected RSCs in the G-LF (in ppty)

	Site		[SO ₂]		[SO ₂] _C	H3SH		$[SO_2]_{DMS}$				$[SO_2]_{DMDS}$				[SO ₂] _{OXD}					
City	no.	Spring	Sum- mer	Fall	Win- ter	Spring	Sum- mer	Fall	Win- ter	Spring	Sum- mer	Fall	Win- ter	Spring	Sum-mer	Fall	Win- ter	Spring	Sum- mer	Fall	Win- ter
	Gl	114	4581	-	2	827	1520	-	27	4115	1663	-	64	60 796	13 429	-	12	65 852	21 193	-	105
Gun-	G2	3	103	-	< 1	47	857	-	< 1	49	534	-	< 1	203	8881	-	4	302	10 375	-	< 7
san	G3	3	13	-	< 1	14	168	-	< 1	51	116	-	1	289	7167	-	7	357	7464	-	< 10
	G4	5	8	-	< 1	12	43	-	< 1	73	17	-	1	383	266	-	54	473	334	-	< 57

^{*}mean of two-day measurements in spring and summer events.

Table 4. Comparison of RSC concentrations with other studies (in pptv)

Compound	Site	Concentration	Reference		
H ₂ S	G-LF*	581 ± 954 (≤1683)	This study		
	Creeks in Izmir, Turkey	$1.7 \times 10^5 \pm 3.9 \times 10^5 $ (504~1.1 × 10 ⁶)	Muezzinoglu, 2003		
	Daegu inland LF	3912 ± 4298 (442~13 169)	Shon et al., 2005		
	Industrial areas in Bahia, Brazil	(≤1350)	Nunes et al., 2005		
	Saint Bay in Bahia, Brazil	(≤250)	Nunes et al., 2005		
CH ₃ SH	G-LF*	39 ± 31 (7~67)	This study		
	Daegu inland LF	41 ± 25 (15~80)	Shon et al., 2005		
	Industrial areas in Bahia, Brazil	(≤1500)	Nunes et al., 2005		
DMS	G-LF*	521 ± 515 (87~1090)	This study		
	Creeks in Izmir, Turkey	16 399 ± 8566 (4663~23 394)	Muezzinoglu, 2003		
	Izmir LF, Turkey	5493	Muezzinoglu, 2003		
	Masan Bay, Korea	188 (10~6000)	Lee et al., 2004		
	Daegu inland LF	430 ± 596 (100~1897)	Shon et al., 2005		
	Industrial areas in Bahia, Brazil	(≤550)	Nunes et al., 2005		
	Saint Bay in Bahia, Brazil	(≤70)	Nunes et al., 2005		
DMDS	G-LF*	89 ± 119 (≤225)	This study		
	Daegu inland LF, Korea	39 ± 29 (6~81)	Shon et al., 2005		
	Izmir LF, Turkey	5493	Muezzinoglu, 2003		
	Industrial complex, Korea	700 ± 2800	Kim et al., 2006		
	Urban monitoring station in Seoul, Korea	ı 17-44	Shon & Kim, 2006		
CS2	Daegu inland LF, Korea	98-192	Shon et al., 2005		
	Industrial complex, Korea	15000 ± 110000	Kim et al., 2006		
	Urban monitoring station in Seoul, Korea	13-2322	Shon & Kim, 2006		
	Marine air	(<20)	Berresheim et al., 199		

^{*}RSC concentrations measured at the centers (G1) in the G-LF.

reported that the major gas-phase products of DMS and DMDS oxidations by hydroxyl (OH) and nitrate (NO₃) radicals included SO₂ as well as other intermediate products (Berresheim *et al.*, 1995; Sørensen *et al.*, 1996). CH₃SH is also oxidized by OH and NO₃, leading to the formation of SO₂ and/or MSA as stable end-products (Berresheim *et al.*, 1995; Sander *et al.*, 2002; Wallington *et al.*, 1986). In addition, H₂S is also known to be oxidized by OH during the day.

The contribution of the oxidation of individual RSCs (e.g., $[SO_2]_{DMS}$, $[SO_2]_{DMDS}$, $[SO_2]_{CH3SH}$, and $[SO_2]_{H2S}$) to SO_2 is given in Table 3. At the centers of the G-LF, total SO_2 concentrations ($[SO_2]_{OXD}$)

converted from the RSC oxidation varied significantly across the seasons with median values of 21 (range: 0.1 to 66 ppbv) and 2.9 ppbv (1.6 to 264 ppbv), respectively. The maximum concentration of $[SO_2]_{OXD}$ at the G-LF site was observed in the spring (P1). The observed pattern of relative contribution is thus likely to be influenced by such factor as the DMDS distribution (Table 1).

In the surrounding area of the G-LF, the seasonal variation of $[SO_2]_{OXD}$ (ranging from 0.01 to 10 ppbv) was significant to low levels of all RSCs in the winter (P3) and relatively high DMDS levels (with the high conversion efficiency) in the summer (P2). For instance, $[SO_2]_{OXD}$ during P2 was

^aMean±1σ; ^b(min.~max).

significantly higher than those during P1 and P3 by more than an order of magnitude. However, the median values of [SO₂]_{OXD} (e.g., 0.3-0.4 ppbv) at three sites (G2-G4) were similar. Compared to the G-LF. [SO₂]_{OXD} during P4' was higher than those during P1'-P3', due to significantly high DMDS levels. It thus appears that RSC photochemistry can be important even during the winter (e.g., P4') in the LF. Therefore, the proportion of SO₂ converted from the oxidation of four RSCs was highly variable, depending on the sampling site and period. The concentrations of SO2 in the ambient air ranged from 2 to 35 ppbv (a mean of 7 ppbv) at the rural area of Gunsan during the study periods; its highest value was generally seen in the summer (Korean Ministry of Environment, 2005), coinciding with the maximum [SO₂]_{OXD} in the surrounding area of the LF. The major RSCs contributing to the formation of [SO₂]_{OXD} were found to include DMDS, H₂S, and DMS for both LF areas. In particular, a significant fraction of [SO₂]_{OXD} was estimated to come from DMDS oxidation in the present study. However, the RSC contribution during P3 and P2' was found to be insignificant (e.g., < 0.5 ppbv) at both the center and surrounding area of the LFs. In the meantime, the relative contribution of photochemical conversion of RSCs (to SO₂) in the current study was different from those at the Daegu LF (Shon et al., 2005) and in the urban area (Shon and Kim, 2006).

V. Conclusions

The environmental behavior of RSCs at two LF environments was investigated using their concentration data and through the estimation of their oxidation mechanism. For the purpose of this study, the extent of photochemical conversion from reduced sulfur compounds (RSCs: DMS, H₂S, DMDS, and CH₃SH) to SO₂ was examined using a PCBM at the coastal LFs during the study period.

For the purpose of our study, each RSC measurement was taken at the center and the surrounding areas of the LF sites in the Gunsan (G), Korea during three (e.g., 6 May, 9 August, and 2 December 2004) and four field campaigns (e.g., 15-16 May, 14-15 July, 9 October, and 22 December 2004),

respectively. It was found that DMS and H_2S were more dominant than the others in the G-LF sites during the study periods. When compared in LF, the concentration levels of most RSCs (except for DMS) was higher at the centers of LF than its at the surrounding sites.

The results of the model study indicated that photochemical production of SO₂ from RSC oxidation mainly resulted from DMDS in the LF. Total SO₂ concentrations ([SO₂]_{OXD}) converted from the RSC oxidation showed a complicated signal of seasonal variations (less variation in the D-LF). The maximum concentration of [SO₂]_{OXD} at the center of the G-LF was observed in the spring event. The observations of the highest SO₂ concentrations in the ambient air of the rural areas of Gunsan coincided with those of maximum [SO₂]_{OXD} values in the surrounding area of LFs during the study periods. This observation thus suggests that SO₂ concentration levels can be affected by photochemical oxidation of RSCs emitted from the LF.

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References

- Bae, G.-N., Kim, M. C., Lim, D.-Y., Moon, K.-C. and Baik, N. J.: Characteristics of urban aerosol number size distribution in Seoul during winter season of 2001. *Journal of Korean Society for Atmo*spheric Environment, 19, 167-177, 2003.
- Berresheim, H., Wine, P. H. and Davis, D. D.: Sulfur in the atmosphere, in Composition, Chemistry, Climate of the Atmosphere. edited by H.B. Singh, Van Nostrand Reinhold, New York, pp. 252-307, 1995
- Chung, C. S. and Yang, D. B.: On the primary productivity in the southern sea of Korea. *The Korean Society of Oceanography*, 26, 242-254, 1991.
- Kettle, A. J. et al.: A global database of sea surface dimethylsulfide (DMS) measurements and a procedure to predict sea surface DMS as a function of latitude, longitude and month. Global Biogeochemical Cycles, 13, 399-444, 1999.
- Kim, K.-H.: Performance characterization of the GC/PFPD for H₂S, CH₃SH, DMS, and DMDS in air. Atmospheric Environment, 39, 2235-2242, 2005a.

- Kim, K.-H.: Some insights into the gas chromatographic determination of reduced sulfur compounds (RSC) in air. Environ. Science and Technology, 39, 6765-6769, 2005b.
- Korean Ministry of Environment, 2005. Annual Report of Ambient Air Quality in Korea, 2004.
- Lee, G., Kahng, S.-H., Oh, J.-R., Kim, K.-R. and Lee, M.: Biogenic emission of dimethylsulfide from a highly eutrophicated coastal region, Masan Bay, South Korea. *Atmospheric Environment*, 38, 2927-2937, 2004.
- Muezzinoglu, A.: A study of volatile organic sulfur emissions causing urban odors. *Chemosphere*, 51, 245-252, 2003.
- Nunes, L. S. S., Tavares, T. M., Dippel, J. and Jaeschke, W.: Measurements of atmospheric concentrations of reduced sulphur compounds in the All Saints Bay area in Bahia, Brazil. Journal of Atmospheric Chemistry, 50, 79-100, 2005.
- Sander, S. P., Friedl, R. R., Golden, D. M., Kurylo, M. J., Moortgat, G. K., Ravishankara, A. R., Kolb, C. E., Molina, M. J. and Finalyson-Pitts, B. J.: Chemical kinetics and photochemical data for use in stratospheric modeling. Jet Propulsion Laboratory Publication 02-25, Jet Propulsion Laboratory, Pasadena, California, 2002.

- Shon, Z.-H., Kim, K.-H., Bower, K., Lee, G. and Kim, J.: Assessment of the photochemistry of OH and NO₃ on Jeju Island during the Asian Dust-Storm Period in the Spring of 2001. *Chemosphere* 55, 1127-1142, 2004.
- Shon, Z.-H., Kim, K.-H., Jeon, E.-C., Kim, M.-Y., Kim, Y.-K. and Song, S.-K.: Photochemistry of reduced sulfur compounds in a landfill environment. *Atmospheric Environment*, 39, 4803-4814, 2005.
- Shon, Z.-H. and Kim, K.-H.: Photochemical oxidation of reduced sulfur compounds in the atmosphere of Seoul metropolitan city, chemosphere, 2006. in press
- Sørensen, S., Falbe-Hansen, H., Mangoni, M., Hjorth, J. and Jensen, N. R.: Observation of DMSO and CH₃S(O)OH from the gas phase reaction between DMS and OH. *Journal of Atmo*spheric Chemistry, 24, 299-315, 1996.
- Wallington, T. J., Atkinson, R., Winer, A. M. and Pitts Jr., J. N.: Absolute rate constants for the gasphase reactions of the NO₃ radical with CH₃SH, CH₃SCH₃, CH₃SSCH₃, H₂S, SO₂, and CH₃OCH₃ over the temperature range 280-350K. *Journal of Physical Chemistry* 90, 5393-5396, 1986.