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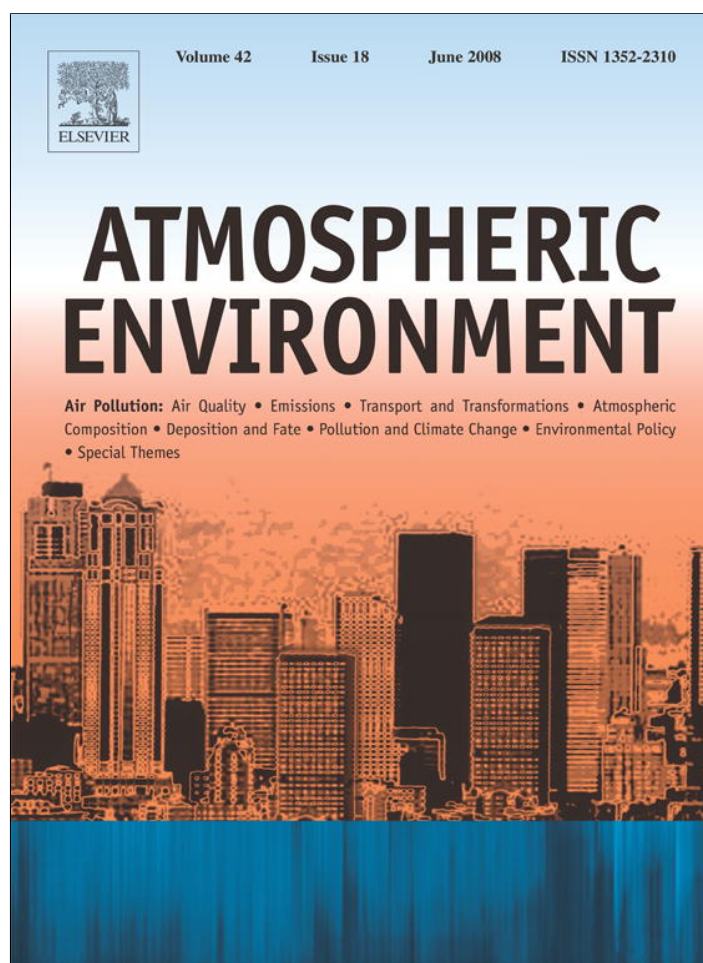


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# Dispersion and photochemical oxidation of reduced sulfur compounds in and around a large industrial complex in Korea

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## Abstract

In this study, the environmental behavior of reduced sulfur compounds (RSCs: H<sub>2</sub>S, DMS, CS<sub>2</sub>, DMDS, and CH<sub>3</sub>SH) was investigated in an area influenced by strong anthropogenic processes based on a numerical modeling approach. The RSC emission concentrations were measured from multiple locations around the Ban-Wall industrial complex (BWIC) in the city of An San (AS), Korea, during a series of field campaigns held between August 2004 and September 2005. These emissions were then used as input for a CALPUFF dispersion model with the 34 dominant chemical reactions for RSCs. The impact of RSC emission on SO<sub>2</sub> concentrations was assessed further in the study areas. The model study indicated the possibility that RSCs emitted in and around the BWIC can exert a direct impact on the ambient SO<sub>2</sub> concentration levels in its surrounding areas with the most prominent effect observed during summer. Our prediction indicated that a significant fraction of SO<sub>2</sub> was produced photochemically in and around the BWIC during the summer (about 30% of total SO<sub>2</sub> concentrations) and fall events (~20%). These photochemical productions of SO<sub>2</sub> were mainly ascribable to H<sub>2</sub>S (~60% of total contributions) and DMDS (~25%) out of all five target RSCs. Meteorological contribution (dispersion) to SO<sub>2</sub> concentration level was also highest during summer.

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**Keywords:** Dispersion; Reduced sulfur; Industrial complex; SO<sub>2</sub>; CALPUFF

## 1. Introduction

Odorous gas emission from the polluted environments has been of increasing concern throughout industrialized countries. Many studies have hence been undertaken to assess the emission characteristics of hazardous odorous pollutants such as reduced

sulfur compounds (RSCs) under various environmental settings (Loizidou and Kapetanios, 1992; Muezzinoglu, 2003; Shon et al., 2005; Kim et al., 2006; Lee et al., 2006). It has been confirmed that exceptionally high concentrations of the odorous pollutants occur in diverse source areas such as an industrial complex (Nunes et al., 2005; Kim et al., 2006) and landfill areas (e.g., Shon et al., 2005; Lee et al., 2006; Wang et al., 2006; Song et al., 2007). These observations accentuate the need for additional studies for odor mitigation and modeling.

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The results of previous studies generally indicate that the distribution of RSCs is spread throughout diverse source environments (e.g., industrial complex, landfills, polluted urban areas, forest, and coastal areas) (Kesselmeier and Hubert, 2002; Muezzinoglu, 2003; Steinbacher et al., 2004; Nunes et al., 2005; Kim et al., 2006; Shon and Kim, 2006; Song et al., 2007). The major RSCs released from polluted environments are identified as: hydrogen sulfide ( $\text{H}_2\text{S}$ ), methyl mercaptan ( $\text{CH}_3\text{SH}$ ), dimethyl sulfide ( $\text{CH}_3\text{SCH}_3$ , DMS), dimethyl disulfide ( $\text{CH}_3\text{SSCH}_3$ , DMDS), and carbon disulfide ( $\text{CS}_2$ ). Of those RSCs released from the urban environment,  $\text{H}_2\text{S}$  is often designated as the most dominant form; it is the primary odor-causing compound produced by diverse industrial activities (Gypsum Association, 1992a,b; Flynn, 1998). In fact, when malodor intensity was compared between different source units, the relative contribution of  $\text{H}_2\text{S}$  and  $\text{CH}_3\text{SH}$  was often the most prominent component in many industrial processes (Kim et al., 2006). It was hence suggested that information on both absolute and relative compositions of RSC emission can be used to assess the significance of different source processes.

In recent years, a number of modeling studies have been directed toward the assessment of the odorous pollutant levels (especially, the RSCs) and their impact on air quality (Schiffman et al., 2005; Wang et al., 2006; Pringer et al., 2007). According to Mussio et al. (2001), a fluctuating plume dispersion model (FPM) was useful to predict maximum odor levels (within a factor of two of the observed values), which were not affected by stability class or distance from the source, in the receptor regions. At commercial beef cattle feedlots in Texas, the CALPUFF model was employed successfully to estimate average concentrations of odor at downwind positions (i.e., 40 versus 41 odor unit (OU) of field sampled value), compared with those predicted by the ISCST3 model (12 OU; Wang et al., 2006).

Despite recent improvements in measurement techniques and in modeling approaches, the actual volume of data under certain environmental settings (especially the polluted industrial areas) is still limited. Although there were only a limited number of measurements for RSCs distribution in the polluted environments, none of those simultaneously took into consideration both the dispersion of RSCs from the strong source processes and the chemical transformation around them.

In this study, the photochemical oxidation of RSCs was investigated using the data set of RSC emission concentrations measured from a number of urban locations surrounding a large-scale industrial complex during several field campaigns held in 2004–2005 (Choi et al., 2006; Kim et al., 2006). Based on these field measurement data and the abbreviated oxidation mechanisms of RSCs, model calculations for photochemical oxidations of RSCs were conducted in this study. In addition, the dispersion of RSCs emitted from industrial sources was considered using a CALPUFF modeling system. We intended to assess the contribution of RSCs emitted from industrial regions to  $\text{SO}_2$  concentration levels in the surrounding regions. For the reader's reference, the details of our initial effort to characterize the spatial and temporal distributions of RSCs in the same study area have been reported elsewhere (Pal et al., 2008).

## 2. Data and methods

The Ban-Wall industrial complex (BWIC) is a major industrial complex near Korea's capital city, Seoul (Fig. 1). The BWIC consists of a variety of industry types such as chemical product and textile, leather, food, pulp/paper, and waste/sewage (Kim et al., 2006). In order to predict RSC behavior in and around the BWIC in An San (AS), the emission concentration data of five target RSCs (e.g.,  $\text{H}_2\text{S}$ ,  $\text{CS}_2$ , DMS, DMDS, and  $\text{CH}_3\text{SH}$ ) obtained as the result of the field campaigns (for odor research) were employed as the direct input data for the numerical modeling (Kim et al., 2006).

The experimental procedures for the collection and analysis of RSC have been described elsewhere (Kim et al., 2006; Pal et al., 2008). The collection of RSC samples was identically made using a vacuum sampling system to fill up 10 L Tedlar bags (SKC corp., USA) from the sampling sites at the height of 1 m above the ground (Kim, 2005a,b). During the field campaigns, RSC measurements were performed at 14 sampling locations and their emission concentrations in and around the BWIC were estimated from 16 point sources (Fig. 1). Detailed information of the sampling locations for RSCs and their emissions is given by the previous studies (Kim et al., 2006; Pal et al., 2008). Although our measurements were made to cover a total of six independent periods, the use of these experimental data was confined to four periods in the present study: 11 August 2004 (period 1, hereafter period



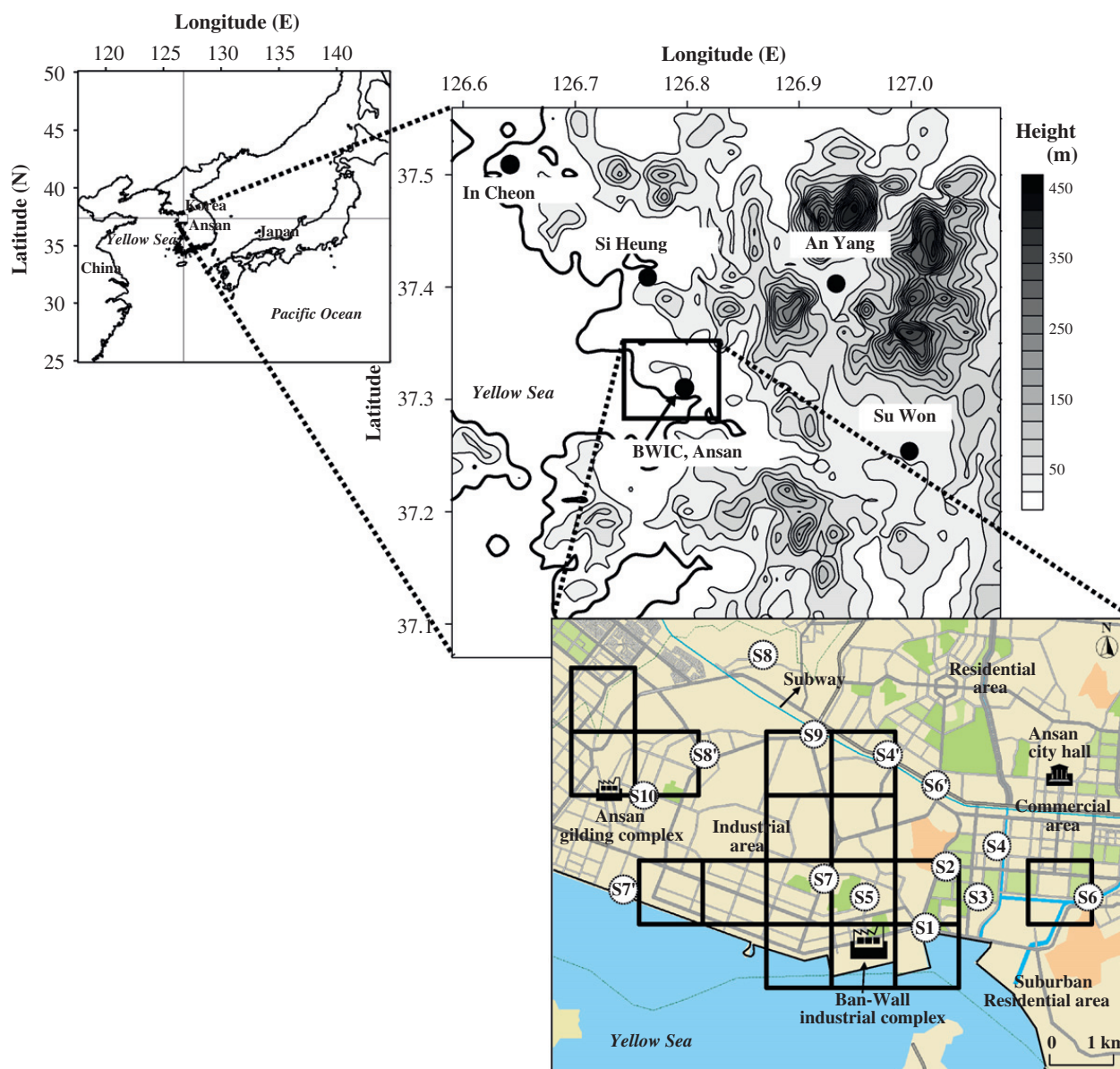


Fig. 1. Study domain including the Ban-Wall industrial complex (BWIC) in the city of An San (AS), Korea ( $37^{\circ}18'10''$  and  $126^{\circ}47'26''$ ). The bold squares within a bottom figure indicate the locations of 16 RSC point sources in the study domain. The sampling locations around the BWIC are assigned as: S1, S2, S4', S5, S7, S7', S8', S9, and S10 = industrial area; S3, S4, and S6 = commercial area; and S6' and S8 = residential area. The locations of some sampling points were changed during P3 and P6 as follows: S4  $\rightarrow$  S4', S6  $\rightarrow$  S6', S7  $\rightarrow$  S7', and S8  $\rightarrow$  S8'.

will simply be referred to as 'P'), 12 August 2004 (P2), 11 January 2005 (P3), and 27 September 2005 (P6) (Pal et al., 2008). The RSC data from two periods (e.g., 27 July (P4) and 4 August 2005 (P5)) were, however, excluded for numerical prediction due to the frequent occurrence of detection limit (e.g.,  $\leq 42\%$  of total data) in possible association with precipitation events that took place one day prior to field sampling (e.g.,  $\leq 30$  mm).

All RSC measurements were principally made on a once-per-day basis (i.e., morning period

(06:50–10:05) for P2 and during the afternoon period (14:10–21:35) for the other periods (i.e., P1, P3, and P6)). Meanwhile, seasonal meteorological conditions (e.g., air temperature, wind direction, and speed) at the sampling sites during the study period were evaluated, which were obtained at a meteorological monitoring station (about 5 km away) adjacent to the BWIC. Mean air temperatures during each period (and season) were observed to be  $32^{\circ}\text{C}$  during P1 and P2 ( $26^{\circ}\text{C}$  in summer),  $1^{\circ}\text{C}$  during P3 ( $-1.1^{\circ}\text{C}$  in winter),  $29^{\circ}\text{C}$  during P6

Table 1

Characteristics of stack emission for five RSCs at 16 CALPUFF grid locations in the study domain

Grid no.	X UTM (km)	Y UTM (km)	Stack height (m)	Stack inner diameter (m)	Exit temp. (K)	Exit velocity (m s <sup>-1</sup> )	Emission rates (g s <sup>-1</sup> ) <sup>a</sup>				
							H <sub>2</sub> S	CH <sub>3</sub> SH	CS <sub>2</sub>	DMS	DMDS
1	300	4133	30.0	4.5	411	20.2	0.234	0.011	0.281	0.126	0.314
2	300	4134	10.7	1.6	307	7.4	0.257	0.067	0.400	0.005	0.017
3	301	4131	9.0	1.3	364	43.0	52.262	0.558	2.847	0.639	0.121
4	301	4133	7.5	1.8	363	6.1	0.010	0.001	0.173	0.019	0.001
5	302	4131	20.0	9.3	305	4.2	2.561	0.165	1.247	0.033	0.030
6	303	4130	20.0	1.0	312	0.1	0.001	0.001	0.001	0.001	0.001
7	303	4131	15.0	3.3	299	2.0	0.049	0.035	0.051	0.025	0.017
8	303	4132	22.0	2.4	311	6.4	0.010	0.001	0.004	0.001	0.004
9	303	4133	21.0	2.6	296	5.0	0.034	0.023	0.104	0.037	0.125
10	304	4130	23.0	1.9	313	3.2	0.108	0.337	0.051	3.288	0.077
11	304	4131	18.0	1.5	317	7.9	0.011	0.001	0.004	0.001	0.003
12	304	4132	18.8	1.8	307	12.0	5.711	0.119	0.442	0.011	0.042
13	304	4133	13.6	2.8	305	3.3	0.088	0.010	0.029	0.039	0.007
14	305	4130	25.0	12.5	328	3.3	0.041	0.003	0.156	0.114	0.010
15	305	4131	13.7	13.4	313	5.4	0.064	0.041	0.880	0.085	0.395
16	307	4131	4.3	1.2	314	6.1	0.001	0.001	0.004	0.001	0.001

<sup>a</sup>Daily mean emission rate for each of the five RSCs was determined with emission concentrations and exit velocity in the 46 emission sources.

(22 °C in fall), respectively. Wind conditions were found to be notably distinguished across seasons: northwesterly (e.g., WNW-NW) and southwesterly (S-SW) in summer (~58%), northwesterly in winter (~70%), and southerly (S) in fall (~51%) with seasonal wind speeds ranging from 1.8 (fall) to 2.6 m s<sup>-1</sup> (winter). During P1 and P2, northwesterly and easterly (E) were dominant (~56%), while northwesterly (~79%) during P3 and southerly and northwesterly (~75%) during P6 were dominant with wind speed ranging from 0.9 (P6) to 2.1 m s<sup>-1</sup> (P3).

The emission rates of the RSC point sources were estimated for the application of the CALPUFF dispersion model system from various emission sources (e.g., 46 factories) located in the BWIC. The point sources of the five RSCs were aggregated into the 1 × 1 km<sup>2</sup> CALPUFF grids, and their emission rates were assigned to 16 grid locations in the model domain (Fig. 1). The CALPUFF modeling system employed in this study includes three main components: CALMET, CALPUFF, and CALPOST (Earth Tech. Inc., 2000). The CALMET is a meteorological model that develops hourly wind and temperature fields on a 3-D gridded modeling domain. The CALPUFF is a transport and dispersion model that advects “puffs” of material emitted from modeled sources, simulating dispersion and

transformation processes along the way. The CALPOST is used to process the files from CALPUFF, producing a summary of the simulation results in tabulated forms. On the other hand, SO<sub>2</sub> emission rates were also used for the CALPUFF modeling system to assess SO<sub>2</sub> concentrations along the downwind direction and their impact on the surrounding areas (or receptor areas). The point and area sources of SO<sub>2</sub> were obtained from the Clean Air Policy Support System (CAPSS) at National Institute of Environmental Research (NIER), Korea. The CAPSS can be supported by MOBILE6, which is designed by the US Environmental Protection Agency (EPA) to meet a wide variety of air pollution modeling needs (see <http://www.epa.gov/otaq/models.htm>). All emission rates and stack characteristics are listed in Table 1. The daily mean emission rate for each of the five RSCs was determined with emission concentrations and the exit velocity in the 46 emission sources. The largest emission rates for H<sub>2</sub>S, CH<sub>3</sub>SH, CS<sub>2</sub>, DMS, and DMDS were 52.3 (a median of 0.06), 0.6 (0.02), 2.8 (0.13), 3.3 (0.03), and 0.4 (0.02) g s<sup>-1</sup>, respectively. The largest point and area sources of SO<sub>2</sub> exhibited SO<sub>2</sub> emission rates of 155 (a median of 0.07) and 1.2 (0.84) g s<sup>-1</sup>, respectively. Moreover, using the Emissions Modeling Clearinghouse (EMCH) model (<http://www.epa.gov/ttn/chief/emch/temporal/>), temporal allocation

of the emissions was considered to describe the accurate properties of atmospheric dispersion and/or transport processes. The 24 h assignment factors (range of 0.012–0.061) of temporal allocation were applied to convert the daily RSC emissions into their hourly emissions (<http://www.epa.gov/ttn/chief/emch/temporal/>).

### 3. Model descriptions

To assess how SO<sub>2</sub> distribution is affected by RSC emissions in and around the BWIC, the chemical transformation mechanism of the five RSCs was added to the CALPUFF dispersion model system (with RIVAD/ARM3 chemical scheme; Morris et al., 1988). The concentrations of major RSCs oxidants (e.g., hydroxyl (OH) and nitrate (NO<sub>3</sub>) radicals) were estimated by the procedures of Morris et al. (1988). The steady-state equations for O(<sup>1</sup>D) and OH within a puff can be estimated as follows:

$$[O(^1D)] = \frac{J_1[O_3]}{k_2 + k_3[H_2O]}, \quad (1)$$

$$[OH] = \frac{2k_3[H_2O][O(^1D)]}{k_4[SO_2] + k_5[NO_2]}, \quad (2)$$

where  $J_1 = 1.3 \times 10^{-3} (\cos Z_s)^{2.74} \text{ min}^{-1}$ ,  $k_2 = 4.45 \times 10^{10}$ ,  $k_3 = 3.4 \times 10^5$ ,  $k_4 = 2.0 \times 10^3$ , and  $k_5 = 1.4 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$ ; in addition,  $\cos(Z_s)$  is the cosine of the solar zenith angle (Earth Tech. Inc., 2000). The RIVAD/ARM3 chemical scheme includes the conversion process between NO and NO<sub>2</sub> and the transformation processes of NO<sub>2</sub> to total nitrate and SO<sub>2</sub> to sulfate (Morris et al., 1988). For the calculation of radical concentrations, hourly averaged concentrations of O<sub>3</sub> and NO<sub>2</sub> were used, which were observed at an environmental monitoring station adjacent to the BWIC, AS city ( $\leq 4 \text{ km}$  away from the BWIC) during the same study period.

The PSU/NCAR no-hydrostatic meteorological model (i.e., MM5, Grell et al., 1994) was used to simulate a meteorological field together with four-dimensional data assimilation (FDDA) as the initial meteorological field to the CALMET. The FDDA technique was applied to the CALMET based on specific meteorological variables (e.g., air temperature, wind direction, and speed) from 7 Automatic Weather System (AWS) in the entire study area. The computational domain in MM5 consisted of 23 sigma vertical levels and  $55 \times 55$  grid points in a

horizontal grid size resolution of 27 km on the following domain: 24.2–49.5°N, 114.8–140.6°E with the center at 36.8°N, 127.7°E. The whole study area was nested as four domains (i.e.,  $27 \times 27$ ,  $9 \times 9$ ,  $3 \times 3$ , and  $1 \times 1 \text{ km}^2$ ) using the two-way nesting method. The initial field and boundary conditions were extracted from Regional Data Assimilation and Prediction System (RDAPS) data. The RDAPS was produced from the MM5 model simulation with horizontal resolutions of 30 km ( $191 \times 171$  grids) and 33 levels of vertical terrain-influenced coordinates with the center at 38°N, 126°E in East Asia regions. A time step of 90 s was employed for each of the following three durations:

- (1) a 96-h period for P1–P2 (from 00 universal time coordinated (UTC) on 9 to 00 UTC on 13 August 2004);
- (2) a 79-h period for P3 (from 00 UTC on 9 to 09 UTC on 12 January 2005); and
- (3) a 79-h period (from 00 UTC on 25 to 09 UTC on 28 September 2005) for P6.

For our numerical modeling, the abbreviated oxidation mechanisms of RSCs and their emissions were considered and added to the section of chemical transformation. The 34 dominant chemical reactions of RSCs were used in this study to predict the SO<sub>2</sub> concentrations arising from the RSC oxidation mechanisms, as described previously in Shon and Kim (2006). The contribution of the RSC oxidation to SO<sub>2</sub> budget was estimated by simultaneously considering the emission of RSCs and SO<sub>2</sub>. In addition, the value of photochemical loss frequency of SO<sub>2</sub> was taken to correspond to 12 h (SO<sub>2</sub> lifetime) in this study, which was based on the relative contribution of SO<sub>2</sub>-to-sulfate conversion processes to SO<sub>2</sub> loss in the urban area (Bae and Kim, 2003).

## 4. Results and discussion

### 4.1. The role of RSC on the formation of SO<sub>2</sub> in and outside of the BWIC

The impact of RSCs emission on SO<sub>2</sub> formation was assessed with the chemical transformation of the RSCs and their dispersion in the industrial environments. The temporal and spatial distributions of SO<sub>2</sub> in and outside the BWIC were investigated using the numerical modeling approach (e.g., CALPUFF modeling system). For the pur-



pose of this study, a 24 h simulation run of SO<sub>2</sub> concentration levels with surface wind vectors was conducted to describe the influence of five RSCs (emitted in and around the BWIC) on SO<sub>2</sub> production during the entire study period. Thereafter, SO<sub>2</sub> concentrations were estimated by considering both the chemical transformation (and atmospheric dispersion) of the RSCs and the direct emissions of SO<sub>2</sub> in and around the BWIC. Note that the model estimates of SO<sub>2</sub> in the entire study area (including AS) were underestimated significantly relative to SO<sub>2</sub> observations; this is probably due to the lack of information concerning RSCs and SO<sub>2</sub> emission outside the BWIC. Nonetheless, the current estimates of SO<sub>2</sub> can still be used to provide information concerning the relative contribution of RSC oxidations to SO<sub>2</sub> observation.

Changes in meteorological conditions (such as wind pattern) in regional/local scales can affect RSCs/SO<sub>2</sub> distribution in the study area. Fig. 2 shows the simulated SO<sub>2</sub> contribution from BWIC with mostly northwesterly and easterly surface winds of approximately 1–10 m s<sup>-1</sup>. The SO<sub>2</sub> concentrations at the surface level hence depend on the wind speed and direction of the inflow of winds. A land-sea breeze circulation was dominant during summer and fall (i.e., a strong sea breeze in the afternoon and a weak land breeze in the early morning), whereas synoptic-scale winds were prominent during winter (i.e., a very weak land-sea breeze circulation). During summer (Fig. 2a), high SO<sub>2</sub> concentrations converged into the source regions (i.e., the BWIC) in the early morning (i.e., at 09:00 local standard time (LST)); it was, however, found to move into the southeastern areas from the BWIC in the afternoon (i.e., at 15:00 LST). In particular, SO<sub>2</sub> concentration levels at 09:00 LST reached significantly high levels of approximately 100 ppbv in the central BWIC along with the convergence of wind at low wind speed (e.g.,  $\leq 2$  m s<sup>-1</sup>). During winter (Fig. 2b), a relatively low SO<sub>2</sub> concentration (a maximum concentration of 20 ppbv) was simulated persistently in down-stream regions (the southeastern area from the BWIC) at both 09:00 and 15:00 LST due to the dilution effect predominated by the strong synoptic-scale winds (e.g., northwesterly) at approximately 10 m s<sup>-1</sup>. During fall, SO<sub>2</sub> concentration levels of  $\leq 30$  ppbv were dominant in downwind regions (the northwestern and northeastern areas from the BWIC at 09:00 and 15:00 LST, respectively) with

the inflow of southerly and/or southeasterly winds (Fig. 2c).

In order to assess the photochemical conversion of the five RSCs (to SO<sub>2</sub>) and their atmospheric dispersion to the surrounding cities, the 24-h model estimates of SO<sub>2</sub> concentrations were simulated by the CALPUFF modeling system. These results were then compared with the SO<sub>2</sub> concentrations simulated in surrounding cities such as In Cheon (acronym, IC), Si Heung (SH), and Su Won (SW) for the matching period (Fig. 3). The impact of the photochemical oxidation of RSCs on air quality in the surrounding cities was also evaluated by two sets of scenarios: the estimation of SO<sub>2</sub> concentrations (1) with and (2) without the photochemical oxidation of the five RSCs. The SO<sub>2</sub> concentrations for these contrasting situations were estimated as CHEM and BASE Case, respectively. Comparison of SO<sub>2</sub> concentrations between CHEM and BASE cases showed that SO<sub>2</sub> can be produced significantly by RSCs' photochemistry during the daytime of the whole study period. (For instance, a maximum SO<sub>2</sub> level of 8 ppbv can occur at 14:00 LST during summer.)

The movement patterns of air flow from the adjacent cities to the sampling sites (during each study period) are shown in Fig. 2. Based on the analysis of airflow patterns, the spatial distribution of SO<sub>2</sub> was estimated between different cities: (1) AS and IC (summer), (2) AS and SW (winter), and (3) AS and SH (fall) (Fig. 3). During summer, an increase in SO<sub>2</sub> concentrations clearly occurred at AS in the early morning with the peak value exceeding 20 ppbv (10:00 LST). This might be caused by the convergence of the surface winds in AS (and its surrounding areas) at 09:00 LST (see Fig. 2a). A few hours later, the peak concentration of SO<sub>2</sub> (about 10 ppbv) occurred at 1400 LST in IC along the air flow pathway. In the meantime, the daytime SO<sub>2</sub> concentrations in the CHEM Case (e.g., a mean of 14 ppbv from 06:00 to 19:00 LST) in AS were found to be 1.3 times higher than the BASE counterpart (e.g., 11 ppbv). However, in IC, the former (e.g., 4.6 ppbv) was 1.9 times higher than the latter (e.g., 2.4 ppbv). The difference in SO<sub>2</sub> concentration ratio between CHEM and BASE Case (i.e., [SO<sub>2</sub>]<sub>CHEM</sub>/[SO<sub>2</sub>]<sub>BASE</sub>) in the downwind region (i.e., IC (1.9)) somewhat increased (32%) compared with the source region (i.e., AS (1.3)). This ratio increase in IC was caused by the dispersion of SO<sub>2</sub> released from AS because SO<sub>2</sub> simulation in IC does not include RSCs and/or SO<sub>2</sub> emissions and



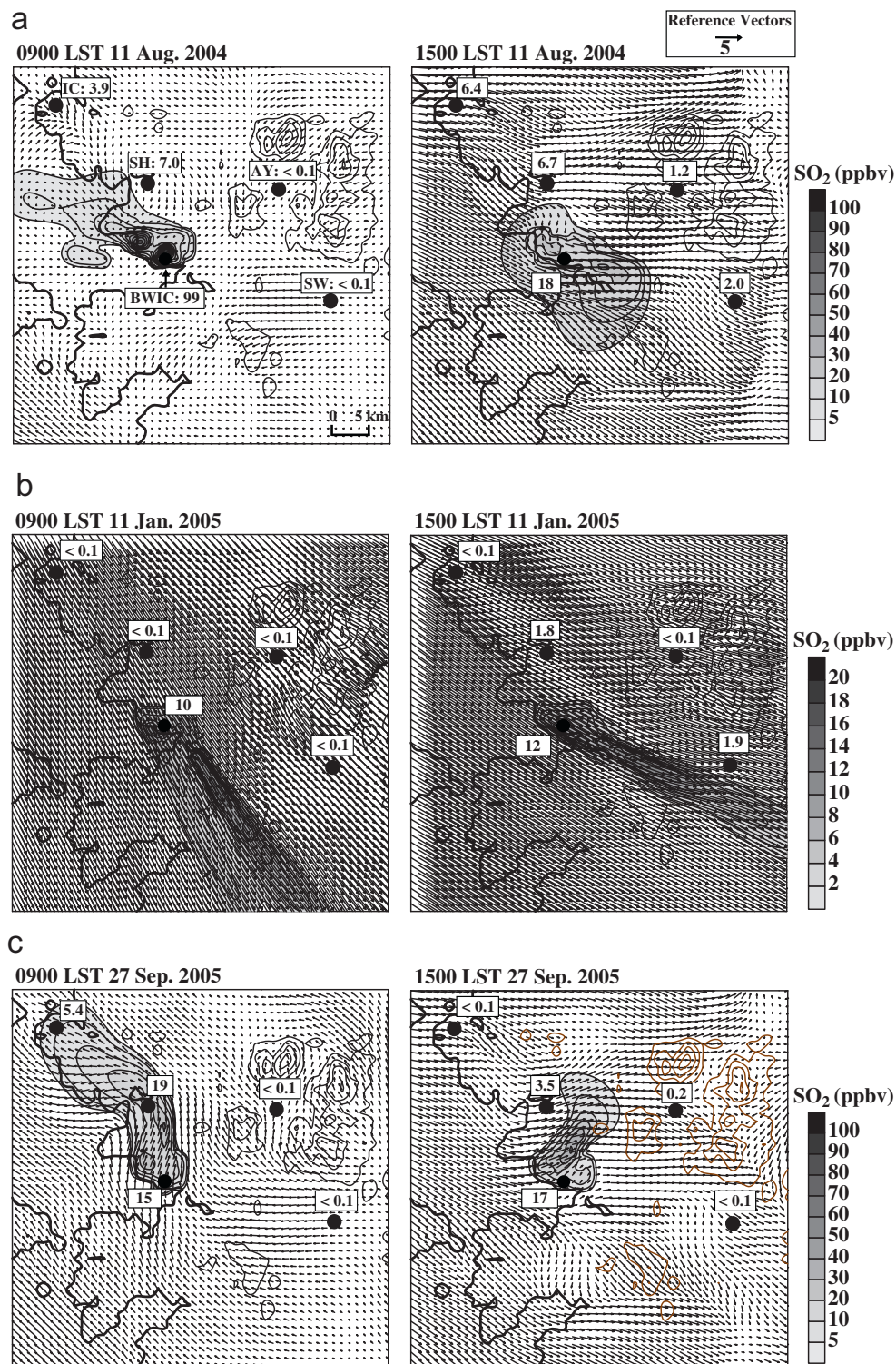


Fig. 2. Horizontal distributions of the simulated wind vectors ( $\text{m s}^{-1}$ ) and SO<sub>2</sub> concentrations (ppbv) at 09:00 and 15:00 LST during (a) summer, (b) winter, and (c) fall study period. The names of city shown in the figure are abbreviated as follows: IC = In Cheon, SH = Si Heung, AY = An Yang, and SW = Su Won. The values within rectangle indicate the simulated SO<sub>2</sub> concentrations in four cities.

environmental conditions in AS and IC were not quite different. Thus, the dispersion of SO<sub>2</sub> from the source region can play a significant role in SO<sub>2</sub> concentration level in the downwind region.

During winter, the dominant northwesterly winds (from AS to SW) were accompanied by strong synoptic-scale flows (or weak local-scale circulation) throughout the day (see Fig. 2b). There were no

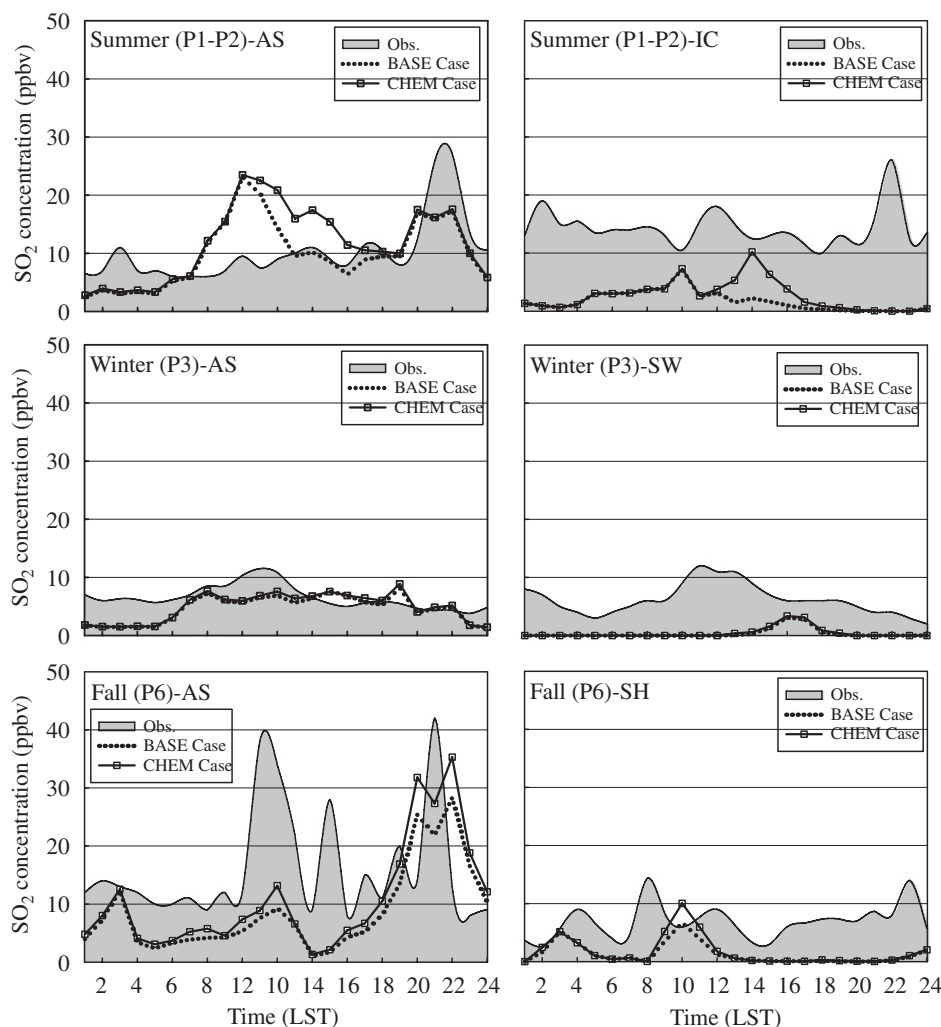


Fig. 3. Time series plot of simulated versus observed  $\text{SO}_2$  concentrations (at cities of AS, IC, SW, and SH) during the entire study period. Legends, Obs. (■), CHEM (—□—), and BASE Case (·····) in the figure indicate the observed  $\text{SO}_2$  concentrations and  $\text{SO}_2$  concentrations simulated with and without the photochemical oxidation of the five RSCs, respectively.

significant differences in  $\text{SO}_2$  concentration levels between CHEM and BASE Case, because of very strong atmospheric dispersion ( $10 \text{ m s}^{-1}$ ). The low  $\text{SO}_2$  concentrations, shown consistently from both the model estimates and observations, remained persistently during this period, except for a sudden increase at 16:00 LST in SW. In AS, the daytime  $\text{SO}_2$  concentrations in the CHEM Case (e.g., a mean of 6.8 ppbv from 08:00 to 17:00 LST) were found to be similar (e.g., 1.1 times higher) to the BASE counterpart (e.g., 6.4 ppbv). However, in SW city, the magnitude of the former (e.g., 0.9 ppbv) was slightly higher (1.3 times) than the latter (e.g., 0.7 ppbv). The  $[\text{SO}_2]_{\text{CHEM}}/[\text{SO}_2]_{\text{BASE}}$  ratio in SW slightly increased (15%) compared with AS (e.g., 1.1). The effect of dispersion of  $\text{SO}_2$  in SW during winter was smaller than that in IC during summer. On the other hand, compared to IC, the low

concentration ratio of  $\text{SO}_2$  in the CHEM Case (relative to the BASE Case in SW) may have resulted from a number of factors. For instance, winds actually moved to the southern part of SW, while the monitoring sites in SW did not exactly coincide with the model grids.

During fall, there was no significant difference in  $\text{SO}_2$  concentration levels between AS and SH, except for the slight increases in the CHEM Case between 20:00 and 22:00 LST in AS and at 1000 LST in SH. In the meantime, the daytime  $\text{SO}_2$  concentration levels in the CHEM Case (e.g., a mean of 6.5 ppbv from 07:00 to 18:00 LST) in AS were found to be slightly different (e.g., 1.2 times higher) from those of BASE Case (e.g., 5.4 ppbv). In SH, the former (e.g., 2.1 ppbv) was 1.5 times higher than the latter (e.g., 1.4 ppbv). The  $[\text{SO}_2]_{\text{CHEM}}/[\text{SO}_2]_{\text{BASE}}$  ratio in SH increased (20%) compared

with AS. On the other hand, during the day (07:00–18:00 LST), the difference (e.g. 1.2 times) in the fall-term  $\text{SO}_2$  concentration in AS between CHEM (e.g., a mean of 6.5 ppbv) and BASE Cases (e.g., 5.4 ppbv) was very similar to the summer-term counterpart.

As to observed  $\text{SO}_2$  concentrations, the pattern of  $\text{SO}_2$  concentrations in the source and downwind regions was different across the seasons. There was significant difference (e.g., 1.5 times) in  $\text{SO}_2$  concentrations between AS (e.g., a mean of 8.5 ppbv at 06:00–19:00 LST) and IC (e.g., 13 ppbv) during summer. In contrast, there were no distinct concentration differences between AS (a mean of 8 ppbv) and SW (8.3) during winter and between AS (7.3) and SH (7.0) during fall.

#### 4.2. Contribution of RSC oxidation to $\text{SO}_2$ concentrations

The extent of photochemical conversion from RSCs to  $\text{SO}_2$  has been examined in light of the potential role of RSCs as the source of  $\text{SO}_2$  and secondary aerosol (Shon et al., 2001, 2004). For instance,  $\text{H}_2\text{S}$  and  $\text{CS}_2$  are known to be oxidized by hydroxyl (OH) in the daytime, while  $\text{CH}_3\text{SH}$  is oxidized by OH (during the day) and nitrate ( $\text{NO}_3$ ) radicals at night. Both of these reactions can lead to the formation of  $\text{SO}_2$  and/or methanesulfonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ : MSA) as stable end-products (Berresheim et al., 1995; Sander et al., 2002). It is well-known that DMS and DMDS released into the atmosphere can be oxidized by OH and  $\text{NO}_3$  radical (Yin et al., 1990). If DMS is oxidized by those radicals, the major form of its gas-phase products includes  $\text{SO}_2$  and other intermediate products (Berresheim et al., 1995; Sørensen et al., 1996).

The relative contribution of individual RSCs to the production of  $\text{SO}_2$  averaged from 16 grid locations (including the BWIC) within the study domain is plotted and compared in Fig. 4. This was highly variable between different periods: 28% (P1–P2), 0.2% (P3), and 4% (P6). In addition, there were strong diurnal differences in their contribution to  $\text{SO}_2$  formation in each period. The total daytime  $\text{SO}_2$  concentrations (i.e., RSC oxidation and  $\text{SO}_2$  emissions) varied significantly across seasons as well as five RSC species with the median values of 400 (range: 30–2100 pptv in summer), 1 (0.04–5 pptv in winter), and 20 pptv (2–200 pptv in fall). As such, the maximum value of total  $\text{SO}_2$  concentrations was estimated to occur in summer

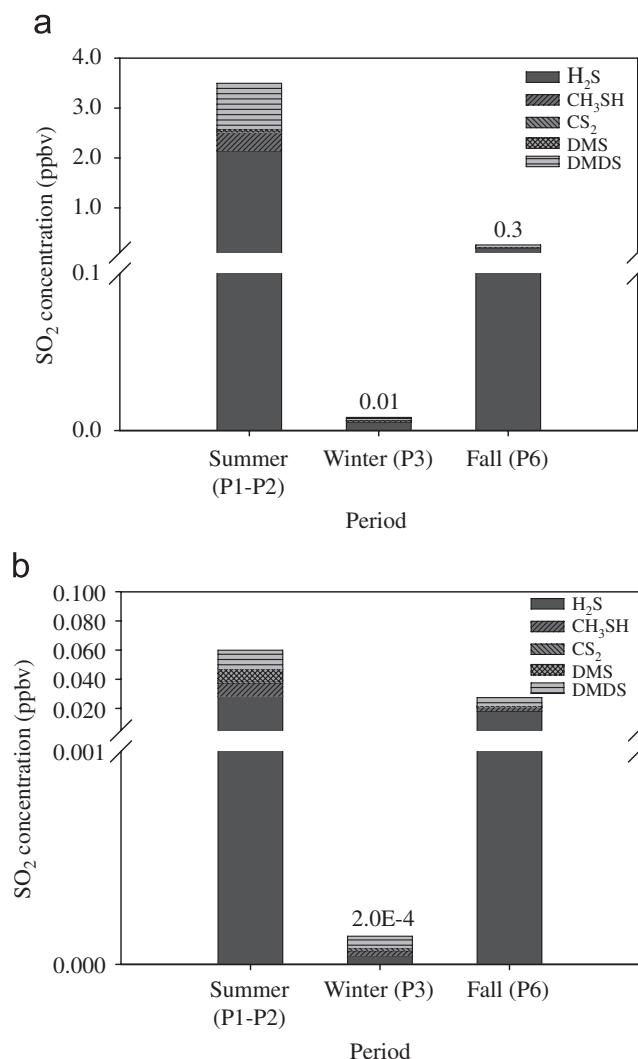


Fig. 4. The relative contribution of RSC oxidation to the formation of  $\text{SO}_2$  averaged from 16 grid locations within the study domain during (a) the day and (b) night periods. The bar for each period represents the relative contribution of each individual RSC to  $\text{SO}_2$  formation.

(Fig. 4a). Evaluation of the relative contribution between different RSCs indicated that the formation of  $\text{SO}_2$  was influenced most sensitively by the distribution of  $\text{H}_2\text{S}$ . The nighttime patterns of total  $\text{SO}_2$  concentrations (ranging from 0.2 to 60 pptv) were highly variable across the seasons due to low RSC levels in winter (i.e., P3) and relatively enhanced  $\text{H}_2\text{S}$  levels (with the high conversion efficiency) in summer. For instance, the total nighttime  $\text{SO}_2$  concentrations (e.g., 0.2 pptv) in winter were significantly smaller than those in summer (e.g., 60 pptv) and fall (e.g., 30 pptv) (Fig. 4b).

As shown in Fig. 4, the formation of total  $\text{SO}_2$  was generally dominated by  $\text{H}_2\text{S}$  and DMDS during



the study period. A significant fraction of total SO<sub>2</sub> concentrations was estimated to result from H<sub>2</sub>S oxidation, especially summer and fall. However, the SO<sub>2</sub> conversion during winter was fairly insignificant (e.g.,  $\leq 0.01$  ppbv) in the study areas. This suggests that RSC photochemistry in the study area is very important only during summer. When the relative contribution of photochemical conversion was compared between different studies, the results of the current study were quite different from those in the urban area (Shon and Kim, 2006) and/or in the landfill sites (Song et al., 2007). Although H<sub>2</sub>S exhibited the predominant role in SO<sub>2</sub> formation in this study, DMDS was found to the leading role in the urban and landfill area (Shon and Kim, 2006; Song et al., 2007).

## 5. Summary and conclusions

The contribution of photochemical conversion in which RSCs are oxidized into SO<sub>2</sub> was examined using a CALPUFF modeling system coupled with information of the chemical transformation of RSCs. For the purpose of this study, RSC emission concentrations measured from the surroundings of the industrial complex during four field campaigns (August 2004 through September 2005) were used as input data for numerical prediction.

The model study indicated that the seasonal variations of simulated SO<sub>2</sub> concentration occurred in accordance with changes in the wind direction and speed of the air flows. It was found that high SO<sub>2</sub> concentrations around the BWIC occurred during summer due to the convergence of weak winds (e.g.,  $\leq 2 \text{ m s}^{-1}$ ) as well as a strong sea breeze. In contrast, relatively low SO<sub>2</sub> concentrations were shown in downwind regions from the BWIC during fall and winter, due to their dispersion along the sea breeze (fall) and the strong synoptic-scale flows ( $\sim 10 \text{ m s}^{-1}$ ) (winter). SO<sub>2</sub> concentrations for CHEM Case in their source area (AS) during summer were remarkably higher (about 30% of total SO<sub>2</sub> concentrations) than those without photochemical oxidation of RSCs (BASE Case), compared with the other seasons ( $\sim 10\%$  during winter and  $\sim 20\%$  during fall). On the other hand, the [SO<sub>2</sub>]<sub>CHEM</sub>/[SO<sub>2</sub>]<sub>BASE</sub> ratio difference between source and downwind regions was highest during summer (32%), indicating strong dispersion of SO<sub>2</sub> during summer compared with the other seasons (15–20%).

The total photochemical production of SO<sub>2</sub>, when compared between different RSCs, was generally dominated by H<sub>2</sub>S (approximately 60% of total contributions) and DMDS (25%) during the entire study period. A comparison of the daytime SO<sub>2</sub> concentrations indicated that the values varied significantly across study periods: from 30 to 2100 (P1–P2), 0.04–5 (P3), and 2–200 pptv (P6). However, the variation of their nighttime counterpart was found to be less significant, ranging from 0.2 to 60 pptv. In conclusion, the major components of RSCs in the photochemical production of SO<sub>2</sub> were identified to be H<sub>2</sub>S and DMDS in this selected industrial environment. This study hence confirms the possibility that SO<sub>2</sub> concentration levels in air can be affected mainly by both photochemical oxidation of RSCs and partly by meteorological contribution (dispersion) from urban sources.

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