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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: $H_2S$, DMS, $CS_2$, DMDS, and $CH_3SH$) 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 $SO_2$ 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 $SO_2$ concentration levels in its surrounding areas with the most prominent effect observed during summer. Our prediction indicated that a significant fraction of $SO_2$ was produced photochemically in and around the BWIC during the summer (about 30% of total $SO_2$ concentrations) and fall events (~20%). These photochemical productions of $SO_2$ were mainly ascribable to $H_2S$ (~60% of total contributions) and DMDS (~25%) out of all five target RSCs. Meteorological contribution (dispersion) to $SO_2$ concentration level was also highest during summer.


*Keywords:* Dispersion; Reduced sulfur; Industrial complex; $SO_2$; 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 ($H_2S$), methyl mercaptan ($CH_3SH$), dimethyl sulfide ($CH_3SCH_3$, DMS), dimethyl disulfide ($CH_3SSCH_3$, DMDS), and carbon disulfide ($CS_2$). Of those RSCs released from the urban environment, $H_2S$ 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 $H_2S$ and $CH_3SH$ 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 $SO_2$ 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., $H_2S$, $CS_2$, DMS, DMDS, and $CH_3SH$) 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