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Photochemical oxidation and dispersion of gaseous sulfur compounds from natural and anthropogenic sources around a coastal location

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ABSTRACT

The photochemical oxidation and dispersion of reduced sulfur compounds (RSCs: H_2S, CH_3SH, DMS, CS_2, and DMDS) emitted from anthropogenic (A) and natural (N) sources were evaluated based on a numerical modeling approach. The anthropogenic emission concentrations of RSCs were measured from several sampling sites at the Donghae landfill (D-LF) (i.e., source type A) in South Korea during a series of field campaigns (May through December 2004). The emissions of natural RSCs in a coastal study area near the D-LF (i.e., source type N) were estimated from sea surface DMS concentrations and transfer velocity during the same study period. These emission data were then used as input to the CALPUFF dispersion model, revised with 34 chemical reactions for RSCs. A significant fraction of sulfur dioxide (SO_2) was produced photochemically during the summer (about 34% of total SO_2 concentrations) followed by fall (21%), spring (15%), and winter (5%). Photochemical production of SO_2 was dominated by H_2S (about 55% of total contributions) and DMS (24%). The largest impact of RSCs from source type A on SO_2 concentrations occurred around the D-LF during summer. The total SO_2 concentrations produced from source type N around the D-LF during the summer (a mean SO_2 concentration of 7.4 ppbv) were significantly higher than those ($\leq$0.3 ppbv) during the other seasons. This may be because of the high RSC and SO_2 emissions and their photochemistry along with the wind convergence.

1. Introduction

A landfill (LF) is one of the largest anthropogenic sources for a number of atmospheric pollutants such as methane (CH_4), volatile organic compounds (VOCs), and reduced sulfur compounds (RSCs) (Davoli et al., 2003; Zou et al., 2003; Shon et al., 2005; Stern et al., 2007). A significant number of researchers in recent decades have focused on assessing the emission characteristics of pollutants from LF environments (Loizidou and Kapetanios, 1992; Flynn, 1998; Ito et al., 2001; Shon et al., 2005; Kim, 2006; Lee et al., 2006; Song et al., 2007).

RSCs constitute the dominant components of trace gas emissions from pollution sources in urban environments (especially in LF or industrial facilities) (Kim et al., 2005b; Nunes et al., 2005; Kim, 2006; Pal et al., 2008). For instance, the LF emission flux of hydrogen sulfide (H_2S) (about 2.0 g m^{-2} y^{-1}) is noticeably higher than that of the other RSCs (e.g., methyl mercaptan (CH_3SH) and dimethyl sulfide (CH_3SCH_3, DMS)) by approximately two orders of magnitude (Kim, 2006). On the other hand, oceanic emissions of DMS are a major component of the natural sulfur budget (about 60% of total natural global sulfur emissions). These emissions contribute to the formation of sulfur dioxide (SO_2) (Bandy et al., 1996; Yvon and Saltzman, 1996; Davis et al., 1999). For instance, DMS alone accounted for ~26% of the total sulfur (SO_2 and non-sea-salt sulfate (nss-SO_4^{2-})) deposited on the eastern Mediterranean coastline in the summer over a 3-y period (1996–1999) (Kouvarakis et al., 2002). Likewise, marine biogenic sulfur emissions (predominantly DMS) constituted ~20% of total oxidized sulfur production (SO_2 and H_2SO_4) during the Mediterranean Intensive Oxidant Study (MINOS) experiment (July–August 2001) (Mihalopoulos et al., 2007). Thus, DMS oxidation is a significant reason for enhanced oxidized sulfur values (Kubilay et al., 2002).

In recent years, RSC emission measurements taken in polluted urban areas have shown that long- and short-distance dispersion of RSCs from anthropogenic activities (e.g., LF and composting facilities, and wastewater treatment plants) can lead to serious malodorous problems in surrounding communities (Song et al., 2008 and references therein). Thus, the necessity for specific studies centering on the impact of RSCs on air quality has been accentuated through modeling results supported by observation data. Model studies have assessed RSC levels and their impact on SO_2 production

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under different environmental conditions (Sarkar et al., 2003; Wang et al., 2006; Pringer et al., 2007; Song et al., 2008). Although there have been numerous modeling studies on RSCs, quantitative information on RSCs is still so scarce that it is impossible to provide a proper evaluation of their environmental behavior when impacted simultaneously by anthropogenic (A) and natural (N) sources.

The objective of this study is to characterize the behavior of gaseous sulfur compounds (e.g., RSCs and SO_2), using anthropogenic RSC emission concentrations measured from several coastal locations within the LF in Donghae (D-LF) (i.e., source type A) and natural DMS emissions estimated from its adjoining sea surface (i.e., source type N). Note that only emissions of DMS alone were considered for the source type N as DMS (out of RSCs) is known to be the dominant sulfur component in seawater. For the purpose of this study, the distributions of SO_2 and surface winds were simulated to show the relationship between RSC (and DMS) emissions from the D-LF (and its adjacent sea surface) and SO_2 production utilizing a CALPUFF modeling system (based on field measurement data and the oxidation mechanisms of RSCs). The contribution of RSCs' oxidation to SO_2 concentration levels from A sources was compared with the N source.

2. Materials and methods

2.1. Study area and periods

The D-LF is approximately 5 km east from the central area of Donghae city located near the eastern coast of Korea (Fig. 1). It has a total area of about 0.035 km^2 (e.g., about 300 m × 100 m) with a landfilling capacity of 0.3×10^6 m^3 at the time of the field study. The D-LF is composed of a variety of wastes such as coal ash, paper, plastic, and glass. In order to predict the RSC behavior of the source types A and N, the emission concentration data of five RSCs were obtained from the field campaigns in the D-LF. In addition, DMS emissions were calculated from the estimated DMS concentration and transfer velocity in its adjacent sea surface and employed as the input data for numerical modeling. Detailed descriptions estimating the DMS concentration and transfer velocity are given in Section 2.2. The RSCs measured in this study area include H_2S, CH_3SH, DMS, carbon disulfide (CS_2), and dimethyl disulfide (CH_3SSCH_3, DMDS).

The collection of RSC samples at the D-LF was done identically using a vacuum sampling system to fill 10-L Tedlar bags (SKC corp. USA) at a height of 1 m above ground (Kim, 2005a,b). The RSC measurements were made from 8 sampling sites in the D-LF area during four field campaigns (i.e., 15–16 May (Period 1 (P1)), 14–15 July (P2), 6–7 November (P3), and 20–21 December 2004 (P4)). DMS emissions from the sea surface near the D-LF were estimated from 8 area sources (Fig. 1). These area sources included the Donghae and Samcheok coasts (within 10 km east from the D-LF) which covers 37.5–37.6°N and 129.0–129.1°E. Detailed descriptions on the measurement methods and the concentration distribution of RSCs have been reported elsewhere (Kim, 2006).

2.2. The estimates of A and/or N emission rates of RSCs and SO_2

Numerical modeling with the use of emission rates of point and area sources was performed for five RSCs and SO_2 to assess the contribution of RSC oxidation to SO_2 formation and its impact on ambient air quality surrounding the D-LF. Daily mean emission rates for the five RSCs were calculated with emission concentrations and exit velocity at the 8 sampling sites at the D-LF, while those rates for DMS were estimated from sea surface DMS concentrations and transfer velocity from sea to air. Because seawater is highly supersaturated with respect to DMS, DMS flux can be expressed as the product of surface DMS concentrations and its transfer velocity in the air–sea interface. In this study, sea surface DMS concentrations were estimated from a DMS empirical algorithm constructed with chlorophyll-a (Chl-a) concentrations and mixed layer depths (MLDs) (Kettle et al., 1999; Simó and Dachs, 2002; Cropp et al., 2004; Gabric et al., 2004). Monthly mean concentrations of Chl-a measured in 8 oceanic source sites closest to the D-LF (i.e., 8 area sources) during the entire study period were obtained from the marine environment data center at the National Fisheries Research & Development Institute (NFRDI) in South Korea (see http://portal.nfrdi.re.kr/envirodata). MLD data obtained from hydrographic observations near a buoy station in the East Sea varied from 20 to 40 m during the observational period (Kim et al., 2005a). Estimated DMS concentrations at 30 m MLD were used because they were not significantly distinguishable from those of 20 (1.2 times higher) or 40 m (0.8 times lower).

In general, the transfer velocity is commonly parameterized with wind speed and molecular diffusivity (Schmidt number). To this end, two types of its parameterizations (Liss and Merlivat (1986) and Wanninkhof (1992) (henceforth referred to as LM86 and W92, respectively)) are commonly used in the literature. The former parameterized the transfer velocity (for the three regimes of wind speed) separately with the first order equation (Liss and Merlivat, 1986), while the latter utilized the second order equation (Wanninkhof, 1992). In this study, both the LM86 and W92 approaches for transfer velocity were applied to calculate DMS emissions due to potential uncertainties (e.g., by a factor of two) in their flux estimates (Andreae and Crutzen, 1997; Jones et al., 2001). The wind speed data for this computation were provided by the Korea Oceanographic Data Center (KODC) (see http://kodc.nfrdi.re.kr/home/eng/near-goos/step1.php). The dependence of the Schmidt number (for DMS flux) on sea surface temperatures was experimentally derived by Saltzman et al. (1993). Detailed information on the calculation of transfer velocity and the associated DMS flux has been described in previous studies (Liss and Merlivat, 1986; Wanninkhof, 1992; Cropp et al., 2004; Gabric et al., 2004; Kettle and Merchant, 2005).

The point sources of five target RSCs at the 8 sampling sites were aggregated into the 1 × 1 km CALPUFF grids, and their emission rates were assigned to two grid locations in the model domain (Fig. 1). The oceanic sources of DMS close to the D-LF (i.e., 8 area sources) were also assembled into the same CALPUFF grids by assigning the emission rate to 8 grid locations (Fig. 1). Note that the 8 grid locations were selected to assess DMS contribution to SO_2 production at the sea surface close to the D-LF. On the other hand, the point and area sources of SO_2 in the study area were estimated by the Clean Air Policy Support System (CAPSS) at the National Institute of Environmental Research (NIER) in South Korea. Moreover, by using the Emissions Modeling Clearinghouse (EMCH) model, the 24-h assignment factors (range of 0.012–0.061) for temporal allocation of SO_2 emissions were utilized to convert the RSC emissions from daily to hourly intervals (http://www.epa.gov/ttn/chief/emch/temporal/). Detailed information on the CAPSS for SO_2 emissions and their temporal allocation has been previously described (Song et al., 2008 and see also http://www.epa.gov/ttn/chief/emch/temporal/).

The five RSC emission rates at the D-LF are listed along with LF vent pipe characteristics (Table 1). The mean emission rates for H_2S, CH_3SH, DMS, CS_2, and DMDS at the D-LF were 1900 (a median of 400), 11 (0.19), 11 (0.49), 4.0 (0.27), and 3.7 (0.18) $g\,h^{-1}$, respectively. The values for DMS for W92 and LM86 in the sea (near D-LF) during the entire study period were 10.3 (a median of 8.2) and 5.3 (4.4) $g\,h^{-1}$, respectively. The difference in DMS emission rates were caused by the potential uncertainties (by a factor of two) between the LM86 and W92 approaches. The mean summertime emission rates of SO_2 from point and area sources were estimated to be 3.9×10^4 (a median of 1.1×10^3) and 1.5×10^{-3} (2.5×10^{-4}) $g\,h^{-1}$, respectively.