

Dimethylsulfide as a Malodorous Component of a Waste Reclamation Site

Ki-Hyun Kim and Gangwoong Lee¹⁾

Department of Earth Sciences, Sejong University / Sejong Institution

¹⁾*Department of Environmental Sciences, Hankook University of Foreign Studies*

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Abstract

To help identify the potential sources of volatile organic sulfur compounds within the continental environment, we have conducted preliminary measurements of dimethylsulfide (DMS) during field campaigns held from three reference sites. These sampling sites were located within a waste reclamation facility in Won Ju City, Kang Won Province. The results of our measurements showed that DMS levels spanned over 1 to 55 pptv with a mean and 1 standard deviation (1SD) of 12 and 18 pptv (N=13). In a comparison of the data derived from the strongest sources, i.e., oceanic environment, the DMS levels in the reclamation facility were pronouncingly low with high day-to-night concentration ratios. It was noted that a significant difference in DMS levels between daytime and nighttime periods was mainly driven by a few exceptional data measured during daytime. Despite limitations of our measurement data in deriving meaningful interpretations of spatiotemporal distributions of DMS in inland facilities, the existence of extraordinary trends, i.e., especially "lower-than-expected" DMS values, can be explained in terms of mixed effects of several factors. Most importantly, we can infer that the rates of DMS production and of its destruction in the study site are at or near steady-state condition. Another possibility is that DMS is not adequate enough to explain the generally malodorous environment of reclamation sites, of particular in Won Ju area.

Key words : dimethylsulfide (DMS), reclamation, source, sink, malodor

1. INTRODUCTION

Detection of malodor in the vicinity of reclamation site is considered to be the consequence of two factors: 1) production of malodorous compounds from such site and 2) the extent of their dispersion under various meteorological conditions. Most of malodorous compounds monitored from the environments can be classified into combination of various organic components that include: reduced sulfur compounds, nitrous oxid-

es, carboxyl acids, phenols, and others. Coleman *et al.* (1991) pointed out the importance of reduced sulfur compounds as major components of malodor. They are generally produced by microbially mediated reduction of sulfates and/or deterioration of amino acids. The rate with which they are produced, however, is known to depend on such environmental parameters as temperature and water-content of material involved (Kim *et al.*, 1996a).

As stated above, the significance of reduced sulfur compounds have drawn a great deal of attention in the

studies of malodor (Coleman *et al.*, 1991). However, these components have also been recognized as major components of environmental chemistry in the assessment of global atmospheric sulfur cycle (Andreae *et al.*, 1994; Andreae, 1990; Andreae *et al.*, 1985). The sulfur cycle is mainly dominated by dimethylsulfide (DMS) in quantitative sense that is mainly produced from surface waters of the world oceans (Bates *et al.*, 1992; Andreae, 1990). Once being released into the overlying atmosphere, it is readily oxidized by oxidant radicals (like OH or NO₃). The oxidative destruction of DMS can lead to the formation of sulfate aerosol layer that is ultimately capable of affecting the global radiation balance (Charlson *et al.*, 1987).

Previous studies of DMS generally focused on the elucidation of its environmental fate in the oceanic environments, since the oceans represented the predominant sources of DMS. Hence previous database for DMS distribution behavior, while being extensive, is generally confined to the open-ocean environment. By contrast, the continental regions suffer greatly from the lack of database in quantitative analysis of DMS behavior. While most continental regions are expected to have low emission potentials for DMS, the possibility of strong regional sources cannot be excluded yet (Kanda and Minami, 1991; Stuedler and Peterson, 1985; Adams *et al.*, 1981). In an effort to place better limits on the contribution of regional sources to the global atmospheric budgets for DMS, information concerning various point sources may be considered as prerequisite. With an aim of extending DMS database within inland environments, we designed and conducted measurements of DMS from a local reclamation site in Kang Won Province of Korea. Here we present the initial results of our preliminary field campaign measurements that were conducted during March 1997.

2. EXPERIMENTAL

The concentrations of DMS were measured from Sa-je Ri reclamation site with a disposal capacity of 3.14 Mt (megaton = 10⁶ ton) that is placed on the eastern

border area of Won Ju city in Kang Won Province. The site had contained over 2.4 Mts of wastes since the August of 1995 and was still on operation for the waste fill-up. Sampling of atmospheric DMS in the study site was made from the 3rd floor of the waste management office that is located on the site.

The procedures for the collection and analysis of atmospheric DMS generally follow those employed by Lee *et al.* (in submission). Air was drawn into trapping (adsorption) tubes from open-field at height of 2 m altitudes. Samples were taken as replicate at a flow rate of 350 ml min⁻¹ on a 3~4 hr basis (up to four times daily) using replicate vacuum pump line (6 mm-OD, 10-m long plastic tubing). The sampling train for DMS was made up of a KI oxidant scrubber and 6 mm OD quartz glass tube containing adsorbents, either Carbosieve 300 or Molecular sieve 5A (Supelco Inc., PA, USA). The former material was used during the early two experiments and then substituted for the latter due to its low price and high sampling efficiency: both laboratory and field comparison tests showed no systematic bias between the data sets collected using two different materials.

The analysis of DMS samples was made within 2~3 days after their collection. Storage tests revealed no detectable loss of DMS during this period, if sample tubes were stored under dark condition. The tubes were thermally desorbed and analyzed using a SRI GC equipped with a flame photometric detector (FPD). The peak of DMS was attained using a 2-m stainless steel column packed with 10% OV 101 CWHF 80/100 mesh column. The GC/FPD system was calibrated against the sample traps loaded with different levels of DMS whose amounts were regulated by use of a permeation tube controlled under a constant temperature range. The analytical precision of the system was found in the range of ±10% and the absolute detection limit at approximately 1 ng S (DMS).

3. RESULTS AND DISCUSSION

As a preliminary test for characterizing DMS distri-

butions in the surrounding environment of the study site, we conducted measurements of DMS from two other sites within the boundary of Won Ju city (March 1997): reference site 1 as Shin-chon Ri and 2 as Dan-Kye Dong. Although measurements were made for four times from each site, we had to ignore some of the earlier data sets for both rain event and malfunctioning of the system at the beginning stage. The concentrations of DMS for the 1st and 2nd reference sites

were measured as 2 and 13 pptv, respectively. After this initial measurement, we continued measurements from the main study site at Sa-je Ri from 7~10 March 1997. The concentrations of DMS measured during this period are plotted as a function of time in Figure 1. A total of 13 measurements was made, and the DMS concentrations during this campaign spanned at wide range of 1 to 55 pptv (mean and 1 SD of 11.9 ± 18 pptv).

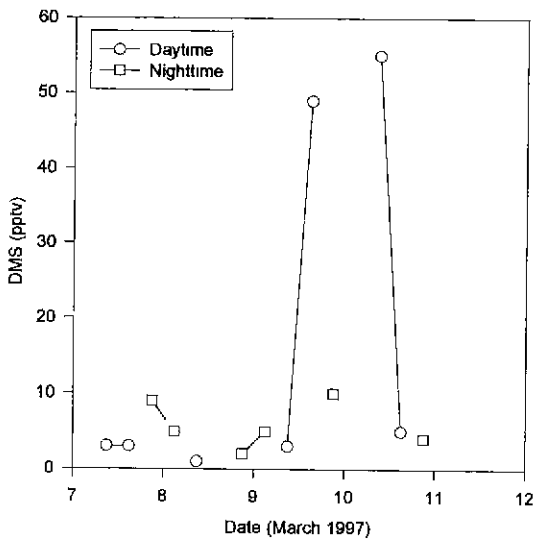


Fig. 1. The concentration of atmospheric DMS measured during 7~10 March 1997 from a reclamation facility located in Won Ju City, Korea.

Although the DMS data obtained from reference sites 1 and 2 are limited, the magnitude of these data is quite consistent with the range of concentrations found from the Sa-je Ri site. Hence, simple comparison of data sets from different sites suggests that the concentrations of DMS in most regions of the city may fall within the comparable range. Similarly to the case of DMS measurement data, the concentrations of criteria pollutants measured concurrently from each site again showed comparable results among different sites (Table 1). Since measurement data for the reclamation site are abundant relative to two other reference sites, temporal distribution pattern of DMS may be assessed for the Sa-je Ri site. If the concentrations between day and night periods are compared, the daytime concentrations appear to be higher than the nighttime ones (e.g., by about three times) despite the shift of trend due to two exceptionally high concentration values found during the daytime: the mean concentration for

Table 1. The concentrations of major atmospheric pollutants determined from the three comparative sites in Won Ju City. Other than TSP, these pollutant levels were measured separately from each study site but within similar time of the day on the 5th of March 1997. The TSP data were obtained from daily measurements during 5 to 10 March 1997.

Pollutant (unit)	Site No. 1 (Shin-chon Ri)	Site No. 2 (Dan-kye Dong)	Main Site (Sa-je Ri)
O ₃ (ppb)	27.4 ± 1 (R=26~28.8, N=5)	20.5 ± 4.8 (R=13.6~27.3, N=6)	25.8 ± 2 (R=22.1~28, N=11)
SO ₂ (ppb)	22 ± 3 (R=19~28, N=8)	21 ± 3 (R=19~27, N=6)	20 ± 1 (R=19~22, N=11)
CO (ppm)	1.131 ± 0.164 (R=26~28.8, N=5)	0.901 ± 0.091 (R=13.6~27.3, N=6)	0.860 ± 0.029 (R=22.1~28, N=11)
NO ₂ (ppb)	11.5 ± 1.2 (R=10.6~12.3, N=2)	16.6 ± 0.6 (R=16.1~17, N=2)	10.6 ± 0.2 (R=10.4~10.7, N=2)
TSP (µg m ⁻³)	168 (N=1)	60 (N=1)	114 ± 45 (R=69~172, N=4)

* R and N denote the concentration range and a total number of measurements, respectively.

daytime is computed to be 17 ± 24 pptv (range = 1 ~ 55 pptv, N = 7), and that for nighttime is 5.8 ± 3.1 pptv (range = 2 ~ 10 pptv, N = 6). If differences of these data sets are checked using students' t-test, their differences are found out to be significant statistically ($P \sim 0.073$). Results of this comparison hence suggest the possibility that the production of malodorous compounds may occur more efficiently during daytime than nighttime.

To understand emission potential of DMS for the reclamation site, it may be important to have comparative knowledge of its distribution characteristics in relation with other sites. Since quantitative data for DMS distributions in other reclamation sites are rarely found, we made comparison of our DMS data with those measured recently from coastal regions of the Korean Peninsula (Kim *et al.*, 1996, 1997). For the case of the Masan Bay area where measurements of DMS were made for the first time in the Korean Peninsula (Kim *et al.*, 1996), its concentrations were excessively high with mean and maximum values of 600 and 4000 pptv, respectively. However, when those measured from Kosan district of Cheju Island are concerned, the concentrations of atmospheric DMS were found at 127 ± 94 pptv (N = 42; Kim *et al.*, 1997). While the Masan data were obtained during highly productive seasons for DMS, the Cheju data were made during less productive winter periods. Regardless of large differences between two coastal regions, the data from coastal regions appear to be significantly higher than those measured from the inland reclamation site. This comparison hence indicates the fact that the emission potential for the reclamation site may still be uncomparably low relative to the major source like the oceanic regions. The limited data sets from our study may not be used to represent the typical distribution pattern for the reclamation site. Nonetheless, our results indicate that DMS may not necessarily be suitable for explaining the behavior of malodorous compounds under certain circumstances.

4. SUMMARY

For the purpose of investigating the production and distribution of DMS under various circumstances, we undertook the measurements of DMS from a reclamation site located in Sa-je ri of Won Ju city. Although we were not able to describe the factors affecting DMS distributions due to data limitation, the findings of notably low DMS levels in the study area suggest the following possibilities. First of all, the DMS production rate of the study area during the actual measurement periods was in fact low. If this is the case, DMS may not be used to represent the environmental behavior of malodorous compounds. As another possibility, we may assume that oxidant radicals that can destruct DMS may be produced effectively in the study area. To critically evaluate the factors associated with the production and destruction of DMS in the reclamation area, further research is strongly desired.

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