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Estimation of the contribution of natural sources to the sulfur oxides deposition in Japan

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Abstract: Air pollution issues are not only based on anthropogenic sources but also natural sources such as volcanoes, marine sources, soil dust and other biological sources. Since Japan has so many volcanoes and surrounded by oceans, the atmospheric condition in Japan is strongly affected by those natural sources. However, very few studies can be found regarding these effects by natural sources.

This study, based on the above-mentioned points, aimed following issues.

- Quantitative estimation of air pollutants and precursors emission from natural sources in Japan,
- Estimation of environmental impacts from them
- Comparison between natural and anthropogenic sources

This paper reports partial results of this study i.e. quantitative estimation of the effects by volcanic and marine sources on the deposition of sulfur species around Japan Islands.

Firstly, the emission data of sulfur species from volcanoes based on several observation studies were compiled. Nine principal volcanoes located in Japan were selected as targets and emission volume of sulfur dioxide and hydrogen sulfide was calculated.

Secondly, the emissions from sulfur species from marine surface were estimated. Dimethylsulfide (DMS) was selected as a representative species because it is well known that DMS occupies major fraction of sulfur species from marine sources. The estimation was carried out using a flux model on the grid bases. The flux model by Liss et al. (1986) was used and the DMS concentration data were estimated using Watanabe et al. (2007).

Finally, the depositions of sulfur oxides were estimated using a three dimensional dispersion model by authors. From the calculation results, the contributions of marine sources and volcanic sources on the deposition of sulfur oxides in Japan were estimated.

As a result, the following points were found.

1) Some pollutants from natural sources have seasonal variations, but others do not have such variations.
2) The depositions of sulfur oxides are varied in wide range, from 8.9mg/m2/month to 451.7mg/m2/month.
3) For the whole of Japan, the contribution of natural sources to sulfur oxides deposition is estimated approximately 35%.

Keywords: *Air pollution, Natural sources, Marine sources, Volcano, Sulfur oxides, DMS*

1. INTRODUCTION

Air pollutants are emitted not solely from anthropogenic sources. Various pollutants and precursors are emitted from natural sources such as volcanoes, marine surfaces, plants, animals, and so on. Although these sources play important roles on atmospheric environment, not so many studies have been carried out based on these sources. Many studies can be found on these natural sources. For example, NATAIR project final report (USTUTT, 2007) gives precise information on natural and biogenic emissions of many species including VOCs, NO_x, PM_{10}, Dimethylsulfide (DMS), and so on. Gross et al. (2007) estimated aerosol formation by DMS emissions. McTaggart et al. (2005) estimated DMS emissions in Antarctic Sea. However, the study area of most of these existing studies is limited. Very few studies can be found whose study area is around Japan or other Asian area. For example, An et al. (2003) estimated the impact of volcano emission from Mt. Oyama (Miyake island) which was erupted in 2000. Nagao et al. (2004) showed the chemical composition of marine aerosols including DMS. The study areas of these papers are also limited. However, it is important for appropriate countermeasures to get enough information on them in regional scale, i.e. quantitative assessment of environmental impacts, comparison with anthropogenic sources, and so on.

Acid deposition is one of the important environmental issues in Japan and East Asia. It is well known that the deposition amounts of acidic species are strongly affected by long range transport of pollutants. Many studies have been reported on this long range transport, for example, Uno et al. (2000) and Katatani et al. (1992). However, almost all of them do not consider the effects of natural sources in spite of their importance based on the topographical feature of Japan Islands which have many volcanoes and are surrounded by oceans.

This study, based on the above-mentioned points, aimed at following issues.

- Quantitative estimation of air pollutants and precursors emission from natural sources in Japan,
- Estimation of environmental impacts from them
- Comparison between natural and anthropogenic sources

This paper reports on the partial results of this study i.e. quantitative estimation of the effects by volcanic and marine sources on the deposition of sulfur species around Japan Islands.

2. TARGET SPECIES AND SOURCES

This study has been progressed regarding both the sulfur oxides (SO_x) and the nitrogen oxides (NO_x). However, this paper reports the results only on SO_x. Both SO_x and NO_x are well known as principal precursors of the acid deposition issue. This issue, being different from other global environmental issues, has a feature that the distance between source regions and receptor regions is not so long, and hence leads to the importance of spatial and temporal variation of emission of pollutants and precursors.

Various kinds of natural sources of SO_x are existing, however, it can be judged that the emission from volcano gases and marine surface are dominant (NatAir, 2008). Consequently, these two kinds of sources were considered in this study.

3. ESTIMATION PROCEDURE OF EMISSION VOLUME

3.1. Sulfur Species from Volcanoes

It is well known that the sulfur species emitted from volcanoes are dominated by sulfur dioxide (SO_2) and hydrogen sulfide (H_2S). H_2S is oxidized to SO_x in the atmosphere.

Many volcanoes are located and active in Japan. Considering the importance on the environmental effects, volcanoes whose daily exhaust of volcano gases are more than 100t-SO_2/day were selected as target sources. Finally, nine volcanoes shown in Table 1 were selected.

The study period was set from 2002 to 2006, and annual emission volume data were compiled from

Table 1 Selected volcanoes in this study

	Name of volcano	Prefecture
1	Mt.Tokachi	Hokkaido
2	Mt.Asama	Gunma, Nagano
3	Mt.Mihara	Tokyo
4	Mt.Aso	Kumamoto
5	Mt.Unzen	Nagasaki
6	Mt.Sakurajima	Kagoshima
7	Mt.Satsuma-Io	Kagoshima
8	Mt.Suwanose	Kagoshima
9	Mt.Oyama (Miyake Island)	Tokyo

literatures such as Japan Meteorological Agency (2008), Mori et al. (2006, 2008), Kagesawa et al. (2006), and so on. Most of the volcanoes are regularly observed and temporal variation data were available. In the case that year by year variation data were not available, it was assumed constant throughout the study period.

3.2. Sulfur Species from Marine Surfaces

It is known that principal sulfur species emitted from marine surfaces are Dimethylsulfide (DMS) and Carbonylsulfide (OCS) and DMS occupies major fraction of them. Of course, other species including OCS are not fundamentally negligible. However, since this study is at the preliminary stage, DMS was selected as a representative species. DMS is originated in marine creatures, it is transferred to atmosphere, and finally oxidized to aerosols such as SO_4.

The emission volume of DMS was estimated using model calculations. The original model equation to estimate DMS flux used in this study is by Liss (1973) as shown in equation (1) and some modifications were made as follows.

$$Fd_{ij} = K_{ij} \times \left(Cw_{ij} - {Cg_{ij}}/{H} \right) \qquad (1)$$

Where *Fd* is the emission volume of DMS (10^{-6}mol/m^{2}d), *K* is the transfer velocity of gases (m/d), *Cw* is the DMS concentration in marine water (10^{-6}mol/m^3), *Cg* is the atmospheric DMS concentration (10^{-6}mol/m^3), *H* is Henry's constant, *i* is a latitudinal grid number and *j* is a longitudinal grid number.

Here it can be assumed that $Cw >> {Cg}/{H}$, then equation (1) can be replaced by equation (2).

$$Fd_{ij} = K_{ij} \times Cw_{ij} \qquad (2)$$

The value K can be expressed from the relationship between wind velocity and marine water temperature according to Liss and Merlivat (1986)

$$K_{ij} = 0.17\left[A_{ij}(t)\right]^{-2/3} u_{ij} \quad (u \le 3.6) \qquad (3)$$

$$K_{ij} = 0.17\left[A_{ij}(t)\right]^{-2/3} u_{ij} + 2.68\left[A_{ij}(t)\right]^{-1/2}\left(u_{ij} - 3.6\right) \quad (3.6 < u \le 13) \qquad (4)$$

$$K_{ij} = 0.17\left[A_{ij}(t)\right]^{-2/3} u_{ij} + 2.68\left[A_{ij}(t)\right]^{-1/2}\left(u_{ij} - 3.6\right) + 3.05\left[A_{ij}(t)\right]^{-1/2}\left(u_{ij} - 13\right) \quad (u > 13) \qquad (5)$$

Where *u* is marine wind velocity (m/s), and [*A*(*t*)] is expressed as equation (6) using Schmidt number *Sc*.

$$\left[A_{ij}(t)\right] = {Sc_{DMS}(t_{ij})}/{Sc_{DMS}(20)} \qquad (6)$$

Where *t* is marine water temperature (deg. centigrade), Sc_{CO2} is determined as 595 by Saltzman et al (1993), $Sc_{DMS(T)}$ is determined using equation (7).

$$Sc_{DMS}(t_{ij}) = 2674 - 147.12 t_{ij} + 3.726 {t_{ij}}^2 - 0.038 {t_{ij}}^3 \qquad (7)$$

The model domain was set as from 24N to 51N and from 120E to 150E. The spatial resolution was one degree by one degree. The temporal resolution was one month.

The basic data used in these calculations are marine water temperature (*t*), marine wind velocity (*u*) and marine DMS concentrations (*Cw*). Water temperature data were available from the Japan Marine Data Center (2008). Wind velocity data were converted in this study from wave height data from the Japan Marine Data Center. Marine DMS concentration data were given by Watanebe et al. (2007) which were estimated using the algorithm shown below.

Watanabe's algorithm shows that the marine DMS concentration is expressed as equation (8). On the contrary, equation (9) can be derived from observed data. Coupling equation (8) and (9), grid by grid DMS concentration can be estimated.

$$\ln DMS = \ln Chl + c \cdot SST + d \cdot \cos(L) + g \qquad (8)$$

$$\ln DMS = 0.06346.SST - 0.1210SSN - 14.11\cos(L) - 6.278 \qquad (9)$$

Where SST is sea surface temperature (K) and SSN is the volume of nitric acid on the sea surface (10^{-6}mol) and L is the latitude (deg).

4. RESULTS AND DISCUSSIONS OF EMISSION ESTIMATIONS

4.1. Sulfur Species from Volcanoes

Figure 1 and Figure 2 show the annual SO_2 and H_2S emission volume from each volcano respectively. Of course these emissions have temporal fluctuations, however, it can be considered that the fluctuations are not strongly affected to the acid deposition. These figures show that Mt. Oyama (Miyake Island) is dominant in both species. This volcano has erupted in 2000 and is still active at present. In 2002, two years after the eruption, it had almost double emission compared to the summation of other eight volcanoes. However, the activity of Mt. Oyama has been getting moderate year by year, and the total emission by all nine volcanoes is clearly decreasing.

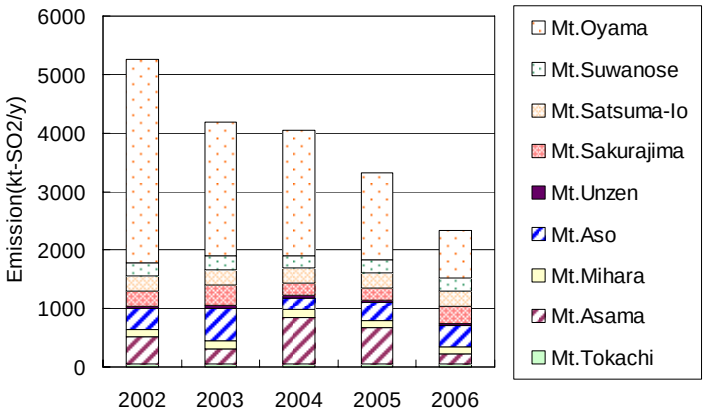

Figure 1 Emission of sulfur dioxide from each volcano.

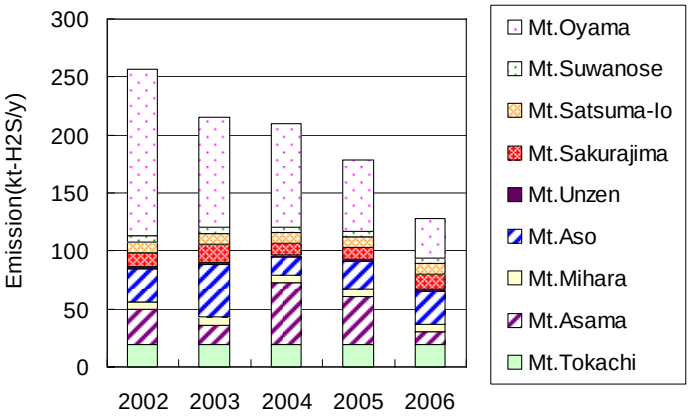

Figure 2 Emission of hydrogen sulfide from each volcano.

4.2. Sulfur Species from Marine Surfaces

Figure 3 shows monthly DMS emissions from whole marine surface in the model domain. Clear seasonal variation can be seen from this figure. It increases in summer and decreases in winter. This variation seems to be mainly caused by the activity and number of individuals of microbes as sources of DMS. These factors may strongly affected by marine water temperature.

Figure 4 and Figure 5 show the DMS flux from marine surface in February and August, respectively. These values are expressed as per unit area basis. In February, the flux are generally small, however, some regions show relatively higher value such as northern Japan, southeast direction of Japan, and so on. On the contrary, in August, generally larger value can be found, especially in northern direction of Japan and east direction of Japan. High values are shown in the northern area near Asian continent, which can be understood as a result of eutrophication. The spatial variation of DMS emission is very large, where the

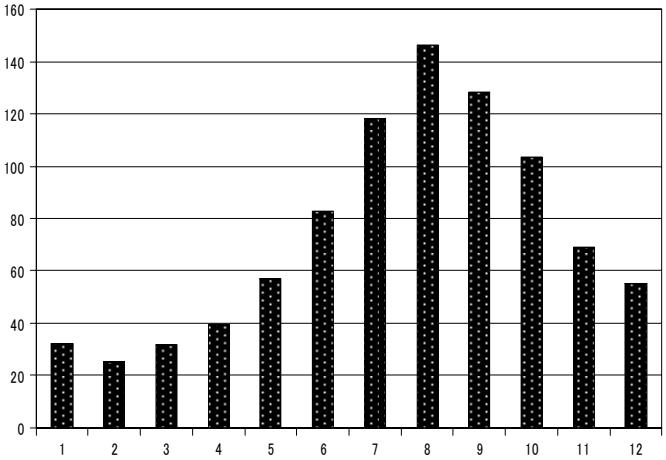

Figure 3 Monthly variation of DMS emission from marine sources. (GgS/month)

difference between maximum and minimum is more than two orders of magnitude.

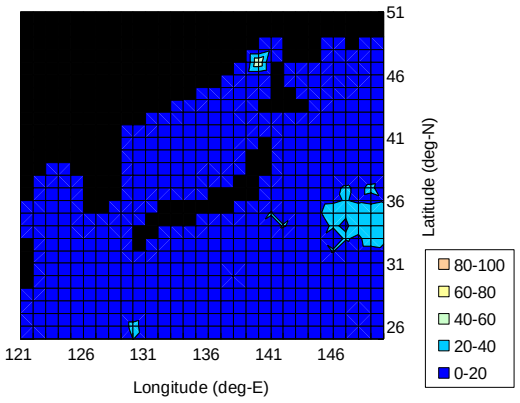

Figure 4 Estimated DMS flux from marine sources in February, 2000 (10^{-6}mol/m^2/d) (Black zone indicates land area)

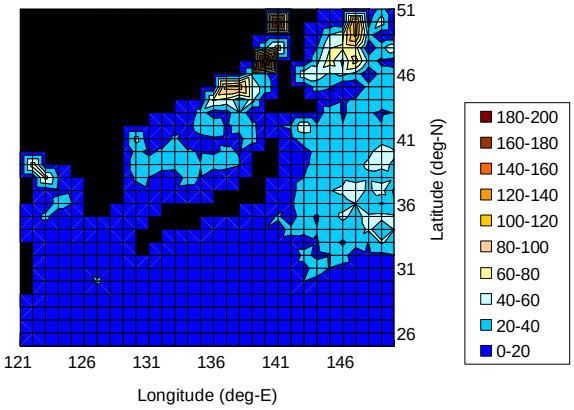

Figure 5 Estimated DMS flux from marine sources in August, 2000 (10^{-6}mol/m^2/d) (Black zone indicates land area)

5. MODEL SIMULATION OF SULFUR OXIDES DEPOSITION USING A NUMERICAL MODEL

In order to estimate the effect of natural source emissions on the acid deposition around Japan, some model calculations were carried out using a numerical model.

5.1. Model Description

The model used in this study is by authors (Katatani et al, 1992). It is a general three dimensional Eulerian type model. The model domain was set in East Asia including Japan, Korea, Taiwang, middle-east part of China, Far-east of Russia. Meteorological data were processed using ECMWF data. Emission inventory from anthropogenic sources was estimated based on Akimoto et al. (1994) and expanded to the value in 2000 according to Kannari et al. (2008).

Calculation condition was varied by combination of anthropogenic source data, marine source data and volcanoes source data. Since the anthropogenic source data year was 2000, volcanoes data year was set to 2002 which is the closest year in the study period in this study. February was selected as the target month because it is known that the deposition amount of sulfur species shows its peak in winter (Katatani et al., 1992).

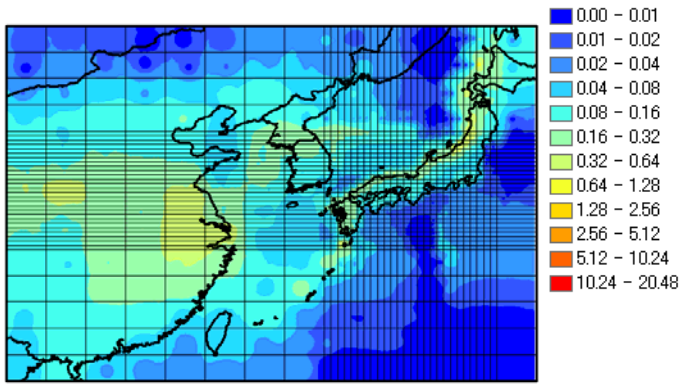

Figure 6 SOx deposition by only anthropogenic sources in Feb.2002 (mg/m^2/month)

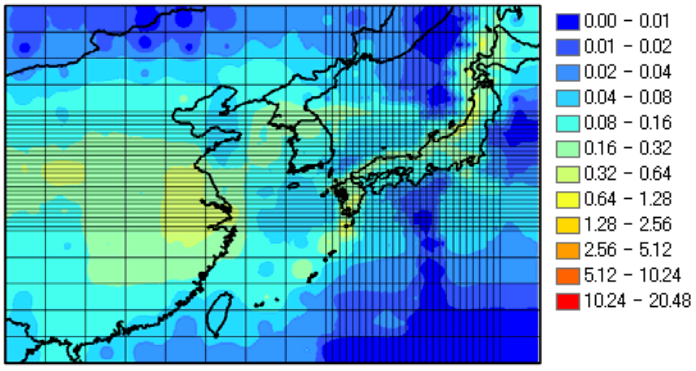

Figure 7 SOx deposition by anthropogenic and volcanic sources in Feb.2002 (mg/m^2/month)

The following three scenarios were assumed for calculations.

1) Anthropogenic sources only.
2) Anthropogenic and volcanoes sources.
3) Anthropogenic, marine and volcanic sources.

5.2. Result for Each Scenario

Figure 6 through Figure 8 show the results for above-mentioned three scenarios.

In Figure 7, the increase of deposition can be seen in Kanto area (eastern Japan) and Kyushu area (western Japan). Kanto is strongly affected by large volcanoes, i.e. Mt.Oyama and Mt.Asama. Kyushu is also affected by Mt.Aso, Mt.Unzen and others. Figure 8, in comparison with Figure 6, shows that the deposition is slightly increased in the ocean in the south part of Sea of Japan, however, the difference is not so remarkable.

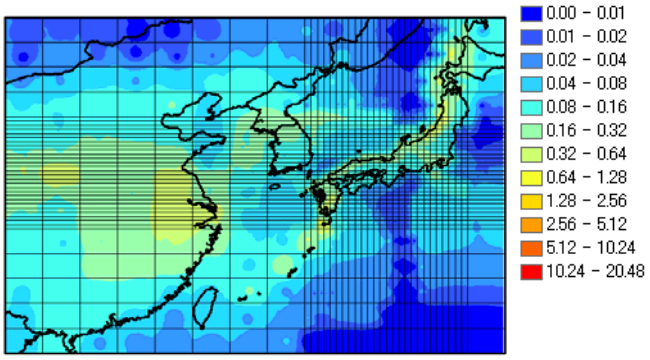

Figure 8 SOx deposition by anthropogenic, marine and volcanic sources in Feb.2002 (mg/m^2/month)

5.3. Comparison with Anthropogenic Sources

Figure 9 show the contribution of each source, anthropogenic, marine and volcanic, in the sulfur oxides deposition amount on entire Japan. Volcanic sources has 32% and marine sources has 3%. Of course, these values are not negligible, however, the contribution of volcanic sources are not very large despite its emission amount is larger than anthropogenic sources. It can be considered that this difference is principally due to the location of large volcanoes. Most of these are located in the coastal area. Since the wind system around Japan is mostly west to east, the major fraction sulfur species from volcanoes are transported to Pacific Ocean area and are deposited onto the marine surface. Of course, it is important to analyze this anthropogenic contribution into sector by sector basis, it could not be achieved because emission inventory used in this study did not have enough information.

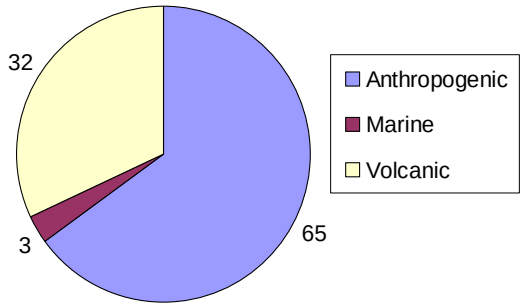

Figure 9 Contribution of each source type on sulfur oxides deposition in Japan (%)

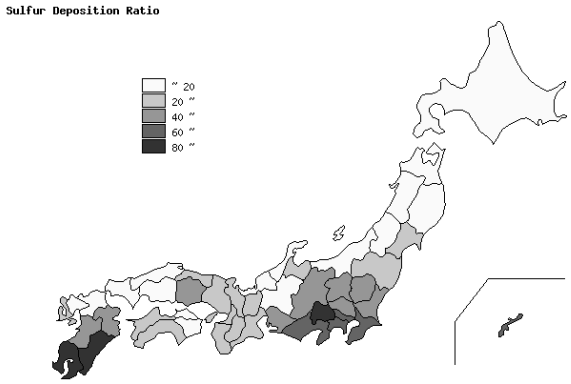

Figure 10 Contribution of natural sources on sulfur oxides deposition in Japan for each prefecture (%)

Figure 10 shows the contribution of natural sources on the sulfur oxides deposition in Japan on the prefecture by prefecture basis. As shown here, in Kyushu area (south-western part of Japan) and Kanto area (eastern part of Japan), the contribution is remarkably high. On the contrary, in the northern part of Japan, the contribution is low. These contributions varies in very wide range such as from less than 20% to more than 80%. When we discuss the contribution of natural sources, it is important to consider these spatial variations.

6. CONCLUDING REMARKS

In this paper, the estimation of sulfur species emission from natural sources and the quantitative assessment of the contribution by natural sources on the deposition of sulfur species were carried out. The following points were found out from this study.

- Some kinds of air pollutants from natural sources have strong seasonal and temporal variations, others do not have remarkable variations.

- Sulfur oxides depositions caused by natural sources varies by prefectures in vary wide range such as from 8.9 to 451.7 mg/m^2/month.
- The contribution of natural sources on the deposition of sulfur oxides in the entire Japan was estimated approximately to be about 35%. This means that natural sources have environmental effects in the same order as anthropogenic sources.

Since this study is still at the first stage, further study should be necessary for more precise estimation and expansion of target species.

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