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Trend analyses of sulfur dioxide emissions and sulfate concentrations and their application to global cooling

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RESUMEN

Concentraciones de emisiones de sulfuro y de sulfato en muestras de hielo obtenidas de diferentes profundidades en un lugar del sur de Groenlandia, son usadas para inferir una relación entre las emisiones y los aerosoles de sulfato.

En un modelo teórico se encontró que esta relación es no lineal. La tendencia hacia arriba en las concentraciones de sulfato en los pasados 100 años, está relacionada con un cambio en concentraciones de nubes de gotas de lluvia y su impacto en la temperatura de la superficie global. Se estima que es posible de 1.0 a 2.0°C de enfriamiento.

ABSTRACT

Sulfur emissions and sulfate concentrations in ice samples obtained from different depths at a site in Southern Greenland are used to infer a relationship between the emissions and sulfate aerosols. In a theoretical model, it was found that this relationship is nonlinear. The upward trend in the sulfate concentrations over the past 100 years is related to a change in cloud droplet concentrations and its impact on global surface temperature. It is estimated that 1.0 to 2°C of cooling is possible.

1. Introduction

Sulfur dioxide is one of the major primary pollutants in the atmosphere. However, at typical atmospheric concentrations it is less important than its by products, sulfate aerosols. Sulfate aerosols interfere with normal breathing, reduce visibility, corrode materials and contribute significantly to acid rain. They participate in cloud formation, and for a given cloud, changes in their sizes and/or numbers change the cloud droplet size distribution. Therefore, the relationship between sulfur dioxide emissions and the concentrations of sulfate aerosols on regional and even global scales is one of the major environmental issues. In this note, statistical analyses of published sulfate and sulfur emission data for the last hundred years will be used to infer trends and relationships as they relate to some environmental and climatic change issues. The treatment is not very rigorous because of the many assumptions. However, it does offer a simple approach to a complex problem.

2. Trend analysis

There are no long-term regionally or globally representative atmospheric sulfate measurements to establish any trend. However, there are reported sulfate concentration data in ice samples obtained at different depths from a site in South Greenland. When these later are plotted as a function of time, they show an upward trend since 1890 (Neftel *et al.*, 1985). While the data are reported in terms of sulfate concentrations in ice, they need to be converted to air concentrations. Davidson *et al.* (1985) calculated snow scavenging efficiency of sulfate by analyzing air samples and freshly fallen snow samples. He found that the ratio of mass concentrations per gram of water to the concentrations in air (ng g^{-1} H_2O/ng g^{-1} air) is 180 $\pm$ 120. Using this ratio, and the sulfur concentrations obtained from their figure, the sulfate air concentrations were calculated and are plotted in Figure 1. Anthropogenic emissions of SO_2 over the past one hundred years have been reported by several investigators (Ryaboshapko, 1983). These data are re-plotted and included in Figure 1.

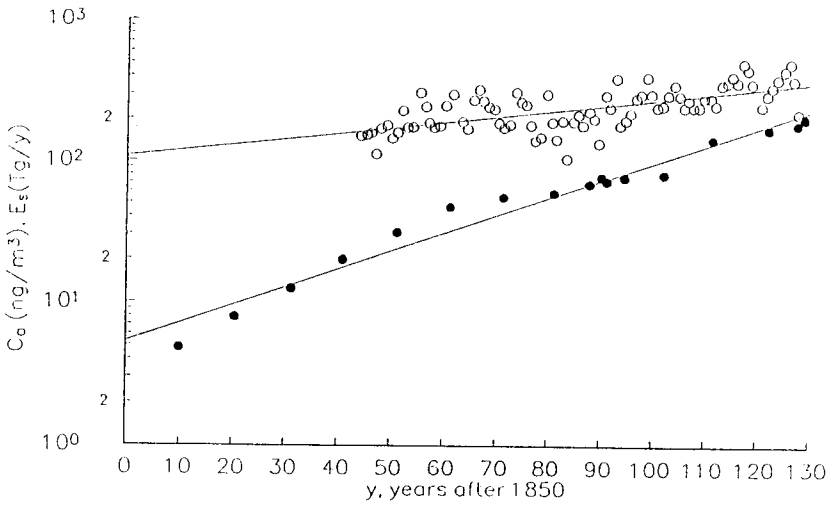

Fig. 1. Trends of global sulfur emissions (Tg/y), solid circles, and sulfate concentrations (ng/m^3), open circles.

The data are fitted with linear regression between the common logarithms of the sulfate concentrations (C_a) in ng/m^3 or the sulfur emissions (E_s) in Tg/y and y, year after 1850. The correlation coefficient for the sulfate concentrations is 0.67 and for the emission rates is 0.98. The best fit equations are:

$$\log E_s = 0.013y + 0.7 \tag{1}$$

$$\log C_a = 0.004y + 2.03 \tag{2}$$

From Figure 1 or equation (2), we can see that the predicted present sulfate concentration is less than 0.5 μg/m^3. This value is comparable with others measured in background air. Alkezweeny *et al.* (1982) reported values between 0.6 to 2.0 μg/m^3 over northern Lake Michigan

and southern Lake Superior. Other background measurements include values in the range of 0.2 to 1.6 $\mu g/m^3$ in central Lake Michigan (Alkezweeny and Laulainen, 1981), 1.7 $\mu g/m^3$ in surface air near Boulder, CO. (Georgii, 1970), values of 1.6, 1.7 and 1.2 $\mu g/m^3$ over Antarctic, Subantarctic, and South Pacific Ocean areas, respectively (Cuong *et al.*, 1974), and in the range of 0.1 to 1.0 $\mu g/m^3$ at Townsville, Queensland and Cape Grim Tasmania (Andreae, 1982). A wide range of background sulfate concentrations was reported by Schwartz (1988). The calculated value is on the lower end of the above reported values possibly because of the value used for the scavenging efficiency.

The ratio of the rates of change in the sulfate concentration and the sulfur emission ratio to the concentration and emission are shown below. Note that this ratio for the sulfate concentration is independent of the scavenging efficiency.

$$(\Delta C_a/\Delta y)/C_a = 0.009 \tag{3}$$

$$(\Delta E_s/\Delta y)/E_s = 0.030 \tag{4}$$

3. Result and discussion

If we make the assumption that the emissions of sulfur from non–antropogenic sources have not changed since 1850, and that the sulfate concentrations, used above, are representative of global averages, then the upward trend in the sulfate concentrations shown in Figure 1 is due to the increase in sulfur emissions given in Figure 1. From equations (3) and (4) we can see the rate of fractional increase in the sulfur emission is much larger than the rate of increase in sulfate aerosols. For instance, the sulfur emission from 1930 to 1980 have increased from 55 to 245 Tg/y, an increase of 345%, while the corresponding increase of sulfate aerosols increased from 224 to 355 Tg/y, only 58%. From equations (1) and (2) we get a relationship between the sulfate concentration and sulfur emission in this form:

$$C_a = 65 E_s^{0.31} \tag{5}$$

Clearly, this is not a linear relationship between the two variables. For instance, if we reduce the emission by 50%, the concentration of sulfate will be reduced by only about 20%. This non–linear effect can be explained by the difference in the residence times of the sulfur gases and aerosols; the tropospheric residence times for the major sulfur gases are smaller than that for sulfate aerosols. Slinn (1984) estimated that sulfur dioxide has a residence time of 1 to 3 days compared to one week for aerosols in the size range of 0.1 to 1.0 μm in diameter. Note that nearly all sulfate aerosols are in this size range (Whitby, 1978). The large difference in the residence times means that most of the sulfur dioxide were deposited before being oxidized to sulfate.

Sulfate aerosols, being water soluble, are good cloud condensation nuclei (CCN). They participate in cloud formation and influence the cloud droplet size distributions. Measurements taken in stratiform clouds in Denver, CO and Kansas City, MO show the cloud droplets are smaller in size and large in concentrations in clouds that were impacted by the urban plumes (Alkezweeny *et al.*, 1993). On the other hand, Alkezweeny and Green (1970) and Alkezweeny and Lockhart (1972) show that the CCN concentrations in Los Angeles, CA., can fluctuate over two orders of magnitude; the higher concentrations are associated with higher pollution levels. For clouds

that are common in the Earth's atmosphere (stratiform cloud), a change in cloud droplet size distribution is reflected in a change in cloud albedo. Twomey *et al.* (1984) calculated the mean planetary cloud albedo, a_o, for different droplet concentrations, N, holding the liquid water content constant. Their data can be approximated by the following equation:

$$\Delta a_o = 0.065 \Delta N/N \tag{6}$$

A similar equation was also obtained by Wigley (1989) from calculations made by Charlson *et al.* (1987). Increasing the droplet concentration will increase the cloud albedo and lead to a cooling effect.

The flux radiation reaching the Earth, $Q(W/m^2)$ is:

$$Q = SS(1 - a)/4 \tag{7}$$

where SS is the solar constant (1368 W/m^2) and a is the planetary albedo which is the sum of the albedos from clear and cloud covered regions of the sky. If we denote f_t, and f_o as the average cloud cover for optically thick clouds (clouds that their albedo is independent for optical thickness, Twomey, 1977) and optically thin clouds; a_t, and a_o are the associated albedos, and a_c is the clear sky albedo. Equation (7) becomes:

$$Q = 342[1 - f_t a_t - f_o a_o - (1 - f_t - f_o)a_c] \tag{8}$$

$$\Delta Q = -342[\Delta f_o(a_o - a_c) + f_o \Delta a_o] \tag{9}$$

The first term in the brackets represents the change in the solar flux due to changes in cloud cover, and the second term is due to the changes in cloud albedo resulting from changes in cloud microphysics. We assumed that the albedo and cloud cover for the optically thick clouds are constants. If we further assume that f_o has not changed and has the value of 0.3 (Charlson *et al.*, 1992), and using equation (6) we get:

$$\Delta Q = -6.7 \Delta N/N \tag{10}$$

The relationship between the CCN concentration and the percent supersaturation, S, is frequently approximated by $C = C_o S^k$, where C_o is a constant. Although k has been used by many investigators as a constant, it is actually a function of supersaturation (Alkezweeny and Lockhart, 1972; Hudson, 1980; Laktionov, 1975; Alofs and Liu, 1981; Bigg *et al.*, 1989). Most CCN measurements have been made at supersaturations above 0.1%. Since stratiform clouds have supersaturation well below 0.1%, reported k's values based on these measurements can not be used for this calculation. Alofs and Liu (1981) measured 432 spectra over 10–month period at the ground at Rolla, Missouri and obtained an average value of 3.85 for k in the supersaturation range below 0.05%. This value of k will be used in this calculation. The relation between N and C is given by the following empirical relation (Twomey, 1977):

$$N = BC^{2/(k+2)} \tag{11}$$

where B is a constant. Using the above k's value, and equation (10) we get:

$$\Delta Q = -2.3 \Delta C/C \tag{12}$$

The relationship between CCN and sulfate concentrations can be deduced from field measurements. Alkezweeny and Lockhart (1972) showed that, in Los Angeles, CA. The CCN concentrations active at a Supersaturation of 0.5% can be represented by the following equation:

$$b = \alpha C^{0.84} \tag{13}$$

where b is the aerosol light scattering and α is a constant. On the other hand, several field measurements showed the following relationship between b and sulfate concentrations C_a (Ten Brink *et al.*, 1987):

$$b = \beta C_a \tag{14}$$

where β is a constant. From (13) and (14) we get:

$$C = (\alpha/\beta)^{1.2} C_a^{1.2} \tag{15}$$

Differentiating both sides of the above equation the result is:

$$\Delta C/C = 1.2\Delta C_a/C_a \tag{16}$$

From (3), (12) and (16) we get:

$$\Delta Q = -0.025\Delta y \tag{17}$$

The relationship between changes in solar fluxes and changes in surface temperature, ΔT is given by:

$$\Delta T = \lambda \Delta Q \tag{18}$$

where λ is the global feedback parameter. The variability of λ obtained from several general circulation models is discussed by Cess *et al.* (1989) and Ramanathan *et al.* (1989). Cess *et al.* reported $\lambda = 0.68 \pm 0.24$ °C m^2/W. The change in ΔQ over the last 100 y from (17) is -2.5 W/m^2. This is equivalent to a decrease in global surface temperature due to the increase in sulfate aerosols of about 1.7 °C. The warming due to increases in the greenhouse gases from 1850 to 1985 is 2.2 W/m^2 (Dickinson and Cicerone, 1986). The increase in temperature is about 1.5°C. Clearly, this warming is overwhelmed by the cooling effect of sulfate aerosols. A similar conclusion was researched by Kaufman *et al.* (1991) from analyses of fossil fuel and biomass burning emission impact on global climate change.

The uncertainty in the estimation of ΔQ is largely due to the choice of a value for k. They are not many measurements of k at supersaturations below 0.1%. Alofs and Liu (1981) reviewed the available data and reported a range of 2 to 4. Using these values ΔQ will be approximately -3.0 ± 0.5 W/m^2, and $\Delta t = -1.7 \pm 0.55$°C. ΔQ is inversely proportional to $k + 2$, therefore, smaller values of k will result in lower cooling.

The published temperature trend for the last one hundred years suggests a global warming of about 0.7°C (Schneider, 1989). The warming due to increases in the greenhouse gases is 1.5°C. the difference is 0.8°C of cooling. This model predicted twice the cooling effect of sulfate aerosols. A possible reason for this is that the data used to relate CCN to sulfate concentrations were collected in Los Angeles and do not represent global conditions. As pollutants travel from their

sources, they undergo diffusion, deposition, and chemical reactions. These processes certainly will impact the activation of aerosols as CCN.

4. Conclusion

An attempt was made to use available data to estimate the effect of increasing sulfur emissions of the past 100 years on the production of sulfate earosols. It is shown that the relationship between sulfur emission and sulfate aerosols is not linear. It is also suggests that the increase in the sulfate aerosols of the past one hundred years may have caused the global temperature cooling by about $1.7 \pm 0.55^{\circ}$C. It is recommended that to better understand this effect new measurements are needed. The mass of sulfate and other water soluble aerosols should be measured in the inflow region of stratiform clouds at the same time the CCN and cloud droplet sizes and concentrations are measured. Measurements of sulfate mass concentrations and CCN concentrations at supersaturation below 0.1% also needed. The measurement should be taken at sites far away from the influence of major sulfur sources.

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