9-1-1996

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Relationship between continuous aerosol measurements and firn core chemistry over a 10-year period at the South Pole

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Abstract. Before ice core chemistry can be used to estimate past atmospheric chemistry it is necessary to establish an unambiguous link between concentrations of chemical species in the air and snow. For the first time a continuous long-term record of aerosol properties (aerosol light scattering coefficient, σ_{sp}, and Ångström exponent, $\mathring{a}$) at the South Pole are compared with the chemical record from a high resolution firn core (~10 samples per year) covering the period from 1981 to 1991. Seasonal signals in $\mathring{a}$, associated with winter minima due to coarse mode seasalt and summer maxima due to accumulation mode sulfate aerosol, are reflected in the firn core SO_4^{2-}/Na^+ concentration ratio. Summertime ratios of σ_{sp} and aerosol optical depth, τ, to corresponding firn core sulfur concentrations are determined and the 'calibrations' are applied to sulfur concentrations in snowpits from a previous study. Results show that σ_{sp} estimates from snowpit sulfur concentrations are in agreement with atmospheric measurements while τ estimates are significantly different, which is likely due to the lack of understanding of the processes that mix surface air with air aloft.

Introduction

South Pole ice potentially contains a record of aerosol chemistry in the southern hemisphere going back more than 1000 years. Sulfate peaks in South Pole ice cores have already been shown to be related to volcanic aerosols from past eruptions [*Legrand and Delmas*, 1987]. During periods not affected by volcanoes, the sulfur in South Pole snow is believed to be largely biogenic sulfate and methanesulfonic acid (MSA) which originates from the oxidation of dimethylsulfide produced by marine phytoplankton around the Antarctic coast [*Saigne and Legrand*, 1987; *Legrand and Feniet-Siagne*, 1991]. In addition, elevated levels of MSA have been related to aerosol produced during strong El Niño's [*Legrand and Feniet-Saigne*, 1991].

Before these chemical signals can be used to infer atmospheric aerosol properties that influence climate, it is important to establish an unambiguous link between the chemical species in the air and snow. Unfortunately, establishing this link is not straightforward due to a lack of information concerning the deposition processes [*Bergin et al.*, 1995a; *Waddington*, 1996; *Harder et al.*, 1996]. In addition, there has not been a continuous long-term comparison of ice core chemical properties and atmospheric aerosol properties measured at the same location.

Here we present the first comparison between continuous, long-term (~10 year) measurements of the wavelength dependent aerosol light scattering coefficient, σ_{sp}, at the South Pole and chemical concentrations (SO_4^{2-}, MSA, Na^+) in a South Pole firn core over the period 1981-1991. In addition, aerosol optical depth measurements made during Antarctic summers [*Dutton and Christy*, 1992] are compared with both σ_{sp} measurements and firn core chemistry.

Experimental Methods

Aerosol Measurements

Since 1979, continuous measurements of the wavelength dependent aerosol scattering coefficient (λ = 450, 550, 700, 850 nm) have been made at the South Pole at the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory (CMDL) monitoring station [*Bodhaine*, 1996; *Ogren et al.*, 1996] with a four-wavelength nephelometer. There are significant gaps in the scattering coefficient data between 1979 and 1981, therefore data are reported beginning in January 1981. The scattering coefficient measurements are used to estimate the Ångström exponent, $\mathring{a}$, which is the negative slope of the scattering coefficient versus wavelength curve when plotted on a log-log scale. The Ångström exponent gives rough information on the aerosol size distribution [*Thielke et al.*, 1972; *Ogren et al.*, 1996].

Since 1976, direct spectral solar irradiances have been measured with pyrheliometers during the antarctic summertime at the CMDL South Pole station [*Dutton and Christy*, 1992]. The measurements are used along with a simple radiative transfer model to estimate aerosol optical depths for the wavelength band from 0.53 μm to 0.69 μm.

Firn Core Processing and Chemical Analyses

South Pole firn core handling and processing was conducted by the Climate Change Research Center (CCRC) at the University of New Hampshire using ultra-clean sampling techniques as described by *Buck et al.* [1992].

A sampling Interval of 2 cm was used to insure ~10 sample per year resolution over the period of comparison (1981-1991). Cation (Na^+, K^+, Mg^{2+}, Ca^{2+}) concentrations were determined using Ion Chromatography (IC) with a Dionex CS12 column, 20
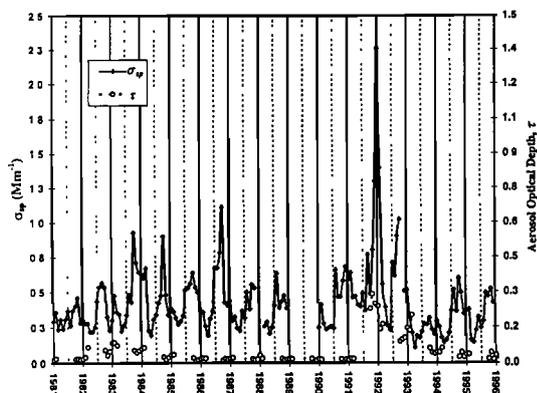

Figure 1. Aerosol light scattering coefficient, σ_{sp}, at 450 nm, and aerosol optical depth, τ, from *Dutton et al.* [1992] versus time.

mM MSA eluant, and a 0.5 mL sample loop. Anion (SO_4^{2-}, NO_3^-, Cl^-) concentrations were determined using IC analysis with a Dionex ASII column, 6.0 mM NaOH eluant, and a 0.25 mL sample loop. Methanesulfonic acid (MSA) concentrations were obtained with IC analysis using a Dionex AS11 column with 0.1 mM NaOH eluant, and a 1.5 mL sample loop.

Results

Aerosol Measurements

Figure 1 shows a time series of the monthly averages of the aerosol scattering coefficient, σ_{sp}, (at a wavelength of 450 nm) as well as the aerosol optical depth taken from *Dutton and Christy* [1992]. The Ångström exponent, å (estimated using scattering coefficients at wavelengths of 450 nm and 550 nm) is shown Figure 2; å supplies rough information on the particle size distribution with higher values representing size distributions having relatively smaller particles. Figure 1 shows a general seasonal cycle in the light scattering coefficient with late winter peaks attributed to seasalt transported from the surrounding oceans and summer minima dominated by sulfur (with contributions from both MSA and sulfate aerosols) light scattering [*Tuncel et al.*, 1989; *Bodhaine*, 1996]. Exceptions to the summer minimum in the aerosol light scattering coefficient are seen in both 1983 and 1992 where the volcanic eruptions of El Chichón and Pinatubo occurred and peaks in the scattering coefficient are seen due to mixing of surface air with stratospheric air containing sulfate aerosol. These events resulted in significant increases in the aerosol optical depth [*Dutton and*
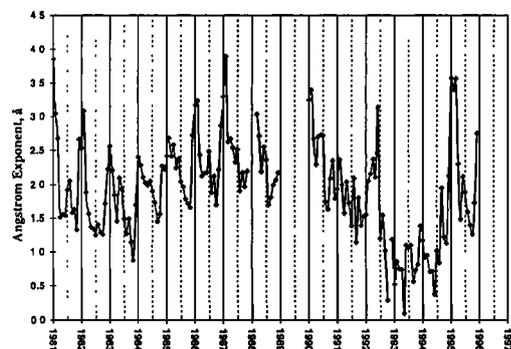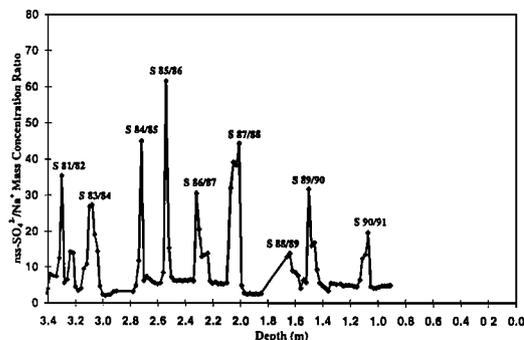

Figure 3. Ice core mass concentration ratio of SO_4^{2-}/Na^+ versus ice core depth.

Christy, 1992], as shown in Figure 1. There is also generally a seasonal cycle in å, as shown in Figure 2, with minimum values occurring during the late winter due to the abundance of coarse mode seasalt aerosol, and maximum values in summer associated with smaller sulfate aerosol.

Firn Core Chemistry

Figure 3 shows the non-seasalt (nss) SO_4^{2-}/Na^+ ratio in the upper 3.4 m of the South Pole firn core. It is worthwhile to point out that the upper 90 cm of the core are not presented since these layers were disturbed prior to the drilling process and therefore not analyzed. The peaks in the SO_4^{2-}/Na^+ ratio are due to the summer maxima in SO_4^{2-} aerosol and corresponding minima in Na^+. The peaks correspond to the peaks in å shown in Figure 2. The SO_4^{2-}/Na^+ ratio increases by roughly a factor of 10 from winter to summer due to factor of ~2 increases in SO_4^{2-} and factor of ~5 decreases in Na^+ concentrations (Figure 4). This shows that increases in the SO_4^{2-}/Na^+ ratio in the summer are due to a combination of an increase in non-seasalt sulfate aerosol and a decrease in seasalt aerosol during the summer months. Summer dates are attached to each of the SO_4^{2-}/Na^+ peaks in Figure 3. The dating technique is validated by significant MSA peaks during the summers of 1983-1984 and 1986-1987 corresponding to strong and mild El Niño years [*Quinn*, 1992]. These peaks have mass concentrations ratios, R, of MSA/SO_4^{2-} of 0.8 and 0.4 respectively. The values are significantly higher than the mean summer peak values in R of 0.15 for years not having El Niño's.
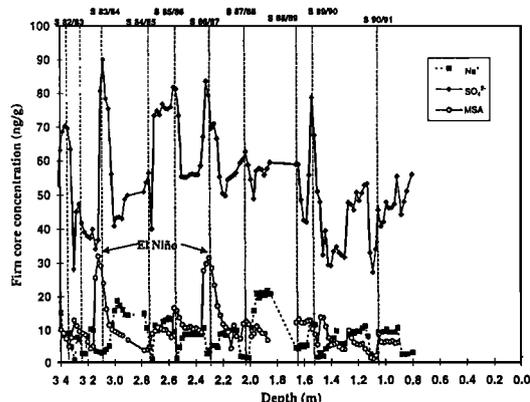

Figure 2. Aerosol Ångström exponent, å, versus time.

Figure 4. Ice core SO_4^{2-}, Na^+ and MSA concentration versus ice core depth.

Relationship Between Aerosol Chemical Species in the Snow and Atmosphere

Theory. The relationship between the concentration of an aerosol chemical species in the air and snow can be written as [Bergin et al., 1995a]:

$$C_{s,i} = C_{a,i}\left(\frac{K_{d,i}}{\rho_s A}\right) \tag{1}$$

where $C_{s,i}$ is the mass concentration of chemical species i in a firn core (g_i g_{snow}^{-1}), $C_{a,i}$ is the mean atmospheric concentration of a chemical species over the time period that a layer has been exposed to the atmosphere (g_i m^{-3}), $K_{d,i}$ is the total deposition velocity of a chemical species (m s^{-1}) which for the South Pole is the sum of the dry deposition and snow deposition velocities, ρ_s the density of snow (g_{snow} m^{-3}), and A the snow accumulation rate (m s^{-1}). The scattering coefficient, $\sigma_{sp,i}$ (m^{-1}), is the product of the aerosol mass concentration, $C_{a,i}$, and the scattering efficiency, α_i (m^2 g_i^{-1}) [Quinn et al., 1996], which when substituted into (1) and rearranged yields:

$$R_{\sigma_{sp}} = \frac{\sigma_{sp,i}}{C_{s,i}} = \alpha_i\left(\frac{K_{d,i}}{\rho_s A}\right)^{-1} \tag{2}$$

In general, (2) states that $R_{\sigma_{sp}}$ is constant given that the parameters on the right hand side of (2) are constant over the periods of deposition. It has been estimated that dry deposition may account for at least 50% of the sulfate concentration in an annual snow layer at the South Pole [Legrand et al., 1987], and that wind pumping of aerosol through the upper layers of snow may influence the dry deposition velocity of aerosols [Waddington et al., 1996; Harder et al., 1996] but this information only allows very rough (order of magnitude at best) estimations of $K_{d,i}$. In addition, estimates of α_i are not available for the South Pole. It is likely that there is seasonal and annual variability in the total deposition velocity at the South Pole. Indeed, Bergin et al. [1995a] show that the dry deposition velocity as well as the snow mass scavenging ratio can vary by as much as a factor of 3 during the summer at Summit, Greenland. Also, (2) does not take into consideration the spatial variability in surface snow chemical concentrations caused by blowing and drifting snow, which adds additional uncertainty in the air snow linkage [Bergin et al., 1995b]. Overall, previous work suggests that there may be seasonal as well as annual variability in $K_{d,i}$ associated with variability in the deposition parameters.

The aerosol optical depth is the integral of the aerosol scattering coefficient with height. For a well mixed atmosphere (i.e. constant aerosol scattering coefficient with height) the optical depth is simply the product of the aerosol scattering coefficient and the mixing height. In the case of a constant mixing height, this means that the relationship between the aerosol scattering coefficient and the aerosol optical depth is constant. Assuming a constant relationship between the aerosol optical depth, τ, and the aerosol scattering coefficient at the surface during summer suggests that the ratio $\tau/C_{s,i}$ (R_τ) should also be constant.

Estimating $R_{\sigma_{sp}}$ and R_τ from firn core sulfur chemistry and summertime aerosol measurements

The ratios $R_{\sigma_{sp}}$ and R_τ can be estimated for sulfur species in the firn core by comparing the ratios of τ and σ_{sp} to ice core summertime sulfur concentrations, $C_{s,s}$ (MSA + SO$_4^{2-}$), for each of the SO$_4^{2-}$/Na$^+$ peaks in the ice core corresponding to å peaks in the aerosol. This assumes that MSA and SO$_4^{2-}$ are the aerosol chemical species responsible for all of the light scattering at the surface during the summer. The mean summertime MSA/SO$_4^{2-}$ firn core mass concentration ratio is 0.15, suggesting

that sulfate is the dominant sulfur species responsible for light scattering during the summer. However, during the summer of 1983/1984 the ratio is 0.8 which shows that during strong El Niño years the light scattering by MSA aerosol may be comparable to that of sulfate. The estimated mean and standard deviation values (n = 8) for $R_{\sigma_{sp}}$ and R_τ are $25.8 \times 10^{-3} \pm 14.0 \times 10^{-3}$ Mm^{-1}ngs^{-1}g and $19.3 \times 10^{-4} \pm 14.0 \times 10^{-4}$ ngs^{-1}g, respectively. The square of the correlation coefficients (r^2) for the linear regressions of σ_{sp} and τ versus $C_{s,s}$ are 0.12 and 0.05, respectively. The low r^2 values show that there is not a linear trend in the data. This is likely due to the fact that there is not a great deal of variability in the σ_{sp}, τ, and $C_{s,s}$ values used in the regression. Indeed, the upper and lower limits of the values for σ_{sp}, τ, and $C_{s,s}$ vary by less than a factor of 3, which is within the expected variability in $K_{d,i}$. For $R_{\sigma_{sp}}$ there is an uncertainty of roughly 50% which is most likely due to year-to-year variability in the parameters on the right-hand side of (2). For the aerosol optical depth there is nearly a factor of 2 uncertainty. This uncertainty likely arises from the assumption of a well mixed atmosphere with a constant mixing height, as well as from variability in the parameters in (2).

The validity of using the estimated $R_{\sigma_{sp}}$ and R_τ values to estimate the summertime values of σ_{sp} and τ can be tested using sulfate concentrations from snowpits corresponding to layers attributed to the eruption of Pinatubo. Unfortunately, the firn core discussed in this paper does not include snow layers associated with Pinatubo since the uppermost layers were discarded during the drilling process. Dibb and Whitlow [1996] retrieved several snowpits at the South Pole during November of 1994 dating back to roughly 1988. They report relatively high values of sulfur in South Pole snow pit layers (~80 ng$_s$ g^{-1}) associated with sulfate from Pinatubo. Table 1 compares estimates of σ_{sp} and τ based on mean summertime peak concentrations in $C_{s,s}$ from the snow pits reported by Dibb and Whitlow [1996] by showing the measured means and standard deviations of the summertime values (December-February) for both σ_{sp} and τ, as well as the mean value and uncertainties (one standard deviation) in the estimates of σ_{sp} and τ. For σ_{sp}, the estimated summertime values are similar to the measured values. In addition, the estimated scattering coefficient for the summer impacted by Pinatubo (1991-1992) is statistically different (based on uncertainties represented by one standard deviation of the means) than the scattering coefficient for the summer prior to Pinatubo as well as for the 1993-1994 summer when the influence of Pinatubo became negligible. For τ, the estimated aerosol optical depth during the summer of 1991-1992 is a factor of 2 lower than the measured value. In addition, the estimated aerosol optical depth for the summer of 1991-1992 is not significantly different than the optical depths prior to and after

Table 1. Estimated Values of σ_{sp} and τ for Several Summers Based on Sulfate Concentrations in Summertime Snowpit Layers Reported by Dibb and Whitlow [1996]

Summer	Measured	Estimated
	σ_{sp} (Mm^{-1})	
1990-1991	0.65 (0.04)	0.44 (0.24)
1991-1992	1.63 (0.40)	1.81 (0.98)
1992-1993	0.70 (0.20)	1.03 (0.56)
1993-1994	0.40 (0.10)	0.41 (0.22)
	τ	
1990-1991	0.02 (0.01)	0.03 (0.02)
1991-1992	0.26 (0.03)	0.13 (0.09)
1992-1993	0.12 (0.03)	0.07 (0.05)
1993-1994	0.05 (0.02)	0.03 (0.02)

the impact of Pinatubo. This is due to the approximate factor of 2 uncertainty in τ estimates based on the uncertainty in R_τ.

The close agreement between the estimated and measured σ_{sp} values is likely due to the fact that dry deposition is the dominant deposition process at the South Pole. Unfortunately, there is a great deal of uncertainty in estimating τ, which is based on the uncertainty in R_τ. It is likely that the uncertainty in R_τ is due to our general lack of understanding of the processes which are responsible for the mixing of surface air with air aloft. Overall, the agreement between the estimated and measured σ_{sp} values for the summer of 1991-1992 suggest that $R_{\sigma sp}$ is a firn core calibration for the summertime aerosol scattering coefficient at the South Pole.

Conclusion

In this paper, for the first time continuous measurements of aerosol properties (scattering coefficient, σ_{sp}, and Ångström exponent, å) measured at the South Pole are compared with firn core chemical concentrations from a South Pole firn core for a 10-year period of overlapping data. The aerosol scattering coefficient generally has a seasonal cycle with maxima during winter associated with seasalt aerosol and minima during the summer related to sulfate aerosol believed to be from primarily biogenic sources. Exceptions to this cycle occur during the summers of 1982-1983 and 1991-1992 where peaks occur in the aerosol scattering coefficient due to downward mixing of stratospheric air containing volcanic aerosols from the eruptions of El Chichón and Pinatubo, respectively. In addition, there is a seasonal cycle in å with summertime peak values associated with smaller sulfate aerosols and winter troughs corresponding to coarse mode seasalt aerosols.

Annual å peaks are reflected as peaks in the firn core SO_4^{2-}/Na^+ ratio as a function of depth. The peaks in the SO_4^{2-}/Na^+ ratio occur due to elevated levels of sulfate aerosol during the summer which correspond to minimum concentrations in seasalt aerosol. The peaks in the firn core SO_4^{2-}/Na^+ ratios as a function of depth suggest that seasonal aerosol signals are archived in South Pole firn cores. Peaks in SO_4^{2-}/Na^+ are used to date the firn core annual layers, and the dating is verified by elevated MSA concentrations which correspond to years during which El Niño's occurred.

The ratios of the summertime aerosol scattering coefficients (corresponding to each summertime å peak) to summertime firn core sulfur (SO_4^{2-} + MSA) concentrations (related to each SO_4^{2-}/Na^+ peak), $R_{\sigma sp}$, as well as each corresponding ratio of the aerosol optical depth to firn core sulfur concentration, R_τ, are estimated to be $25.8 \times 10^{-3} \pm 14.0 \times 10^{-3}$ $Mm^{-1}ngs^{-1}g$ and $19.3 \times 10^{-4} \pm 14.0 \times 10^{-4}$ $ngs^{-1}g$, respectively. Using these values along with summertime sulfur concentrations in South Pole snowpits associated with a several year time period that covers the eruption of Pinatubo [Dibb and Whitlow, 1996] yields estimates of σ_{sp} that are in agreement with measured values. Estimated values of τ are not statistically different measurements due to the roughly factor of 2 uncertainty associated with R_τ. The uncertainty in R_τ is most likely associated with the general lack of understanding of the atmospheric processes responsible for the mixing of surface air with air aloft. Results suggest that summertime sulfur concentrations in South Pole ice cores can be used to estimate past values of the aerosol scattering coefficient at South Pole with a roughly 50% uncertainty.

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