

Processes controlling the composition of precipitation at a remote southern hemispheric location: Torres del Paine National Park, Chile

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Abstract. Precipitation composition measured at Torres del Paine National Park, Chile (TdP) ($51^{\circ}10'S$, $71^{\circ}58'W$), between 1984 and 1993 was acidic (volume-weighted-average pH of 4.96) with a dilute seawater component. H^{+} was the dominant non-sea-salt (nss) cation; in decreasing order of abundance, nss anions were $HCOO^{-}$, Cl^{-} , $SO_4^{=}$, CH_3COO^{-} , and NO_3^{-} . Relative to lower latitude, remote locations, concentrations and per-event depositions of nss $SO_4^{=}$, NO_3^{-} , and NH_4^{+} at TdP were lower; those of $HCOO^{-}$ ($HCOO^{-} + HCOOH$) and CH_3COOH , (CH_3COO^{-} and CH_3COOH) were similar; and those of $CH_3SO_3^{-}$ were higher. Concentrations and deposition fluxes of $HCOO^{-}$, CH_3COO^{-} , nss $SO_4^{=}$, $CH_3SO_3^{-}$, and NH_4^{+} varied seasonally with summer maxima and winter minima. Carboxylic acids probably originated from both direct terrestrial emissions and oxidation of hydrocarbons emitted by marine and terrestrial biota. Nss $SO_4^{=}$ and $CH_3SO_3^{-}$ originated primarily from oxidation of biogenic $(CH_3)_2S$ emitted from the southern Pacific Ocean. Direct emissions of NH_3 from upwind terrestrial and marine ecosystems probably accounted for most observed NH_4^{+} . NO_3^{-} concentrations and depositions were highest during the latter part of austral winter and spring suggesting abiotic controls. Transport of precursors from lightning, biomass burning, and fossil-fuel combustion at lower latitudes and possibly transport of reactive N from the stratosphere apparently contributed oxidized N to the southern Patagonian troposphere. Although the ionic strength of precipitation at TdP is currently among the world's lowest, future changes are likely because of increases in local and regional population and energy and food production.

Introduction

Many important tropospheric compounds are produced by terrestrial and marine organisms. Several of these chemical species (or their reaction products) (e.g., $SO_4^{=}$, $CH_3SO_3^{-}$, NO_3^{-} , NH_4^{+} , $HCOOH$, CH_3COOH) have rather short atmospheric lifetimes (e.g., less than 1 week) and are lost from the atmosphere via deposition. For such species, measured concentrations and deposition rates provide important constraints on source strengths associated with the corresponding biological processes. However, the pervasiveness of human influences over most of the globe complicates the assessment of natural linkages between the atmosphere and the biosphere. In extremely remote locations, such as Torres del Paine National Park (TdP) in southern Chile ($51^{\circ}10'S$, $71^{\circ}58'W$) (Figure 1), these relationships can be investigated with reasonable confidence. TdP is downwind of the southern Pacific Ocean and far from human-population and industrial influences.

This paper reports the annual and monthly volume-weighted-average (VWA) concentrations and associated wet-deposition fluxes of major chemical constituents in precipitation at TdP. On the basis of these data and related information, we investigated the major processes controlling tropospheric chemistry in the region with a focus on biosphere-atmosphere interactions. We also assessed the potential impacts that may result from projected increases in anthropogenic emissions over the next few decades.

These data were generated under the auspices of the Global Precipitation Chemistry Project (GPCP). From 1979 to 1994 the GPCP operated a network of stations to determine the processes controlling precipitation composition in regions of the world remote from the influences of human activity thereby establishing a baseline for comparison with more populated regions.

Methods

Site Description

TdP is 400 km north of Punta Arenas (Figure 1). The park covers approximately 240,000 ha and, in 1978, was

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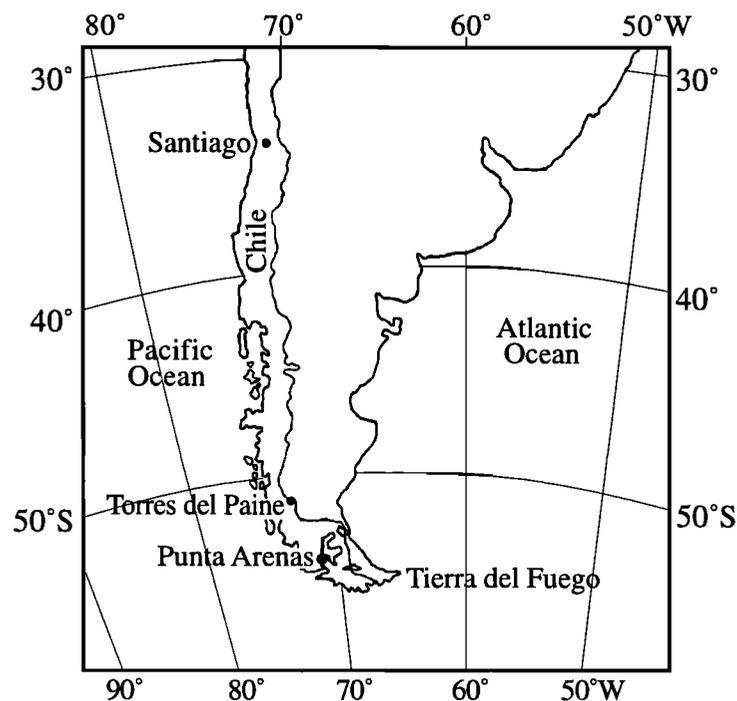


Figure 1. Torres del Paine National Park, Chile, and surrounding areas.

declared a member of the International Network of Biosphere Reserves by the United Nations' Man and the Biosphere program. TdP and its surroundings are formed by a great diversity of landforms, glaciers, snowfields, valleys, lakes, rivers, moraines, plains, and mountains. The water bodies are of glacial origin and some lakes are still connected to glaciers. Mountains with elevations of 3,050 m dominate the landscape. The impact of the Pacific Ocean on precipitation in TdP is diminished by the Andes Mountains, which are between the Pacific Ocean and TdP, creating a continental microclimate [Santana *et al.*, 1992]. Solar radiation varies seasonally driving strong variability in associated meteorological conditions. Average monthly temperatures between 1979 and 1984 ranged from a minimum of 1.9 C° in July to a maximum of 12.1 C° in February (Meteorological Data Report, Torres del Paine National Park). Precipitation is fairly uniformly distributed over the year.

Precipitation Collection and Analysis

Precipitation was sampled by storm event with an Aerograph Metrics collector at two sites in the park between March 23, 1984, and December 19, 1993. From March 23, 1984, to January 30, 1985, precipitation was sampled 2 km north of the Administration Building. After a nearby wildfire, precipitation was sampled at a similar elevation approximately 2 km away where it remained from February 1, 1985, to July 19, 1987. On July 20, 1987, the collection station was moved back to the original site.

After collection, 0.5 mL CHCl₃ was added to 250-mL aliquots (or less for small volume events) to prevent biological activity [Keene *et al.*, 1983; Keene and Galloway, 1984]; samples were subsequently stored on site in a cool, dark location and periodically (within one month of collection) shipped by air to the University of Virginia. Samples were

then analyzed for pH, SO₄⁼, Cl⁻, NO₃⁻, HCOO_i (HCOO⁻ + HCOOH), CH₃COO_i (CH₃COO⁻ + CH₃COOH), NH₄⁺, Na⁺, Mg⁺⁺, Ca⁺⁺, and K⁺. CH₃SO₃⁻ was measured in all samples collected after December 15, 1989. Details of the analytical and quality-assurance procedures are reported by Likens *et al.* [1987], except for CH₃SO₃⁻ which was measured using procedures similar to those of Bardwell *et al.* [1990]. Concentrations of non-sea-salt (nss) SO₄⁼, Cl⁻, Mg⁺⁺, Ca⁺⁺, and K⁺ were calculated as described by Keene *et al.* [1986] using Na⁺ as the reference species and Wilson's [1975] composition of surface seawater. Nine samples were analyzed at the Institute for Ecosystem Studies for orthophosphate using the phosphomolybdenum blue method on an Auto Analyzer II [Murphy and Riley, 1962]. These samples were collected in August, 1990 (1); October, 1990 (1); November, 1990 (2); January, 1991 (1); March, 1991 (2); and April, 1991 (2).

Representativeness of Database

During the study period, 52% of all precipitation was sampled for chemical analysis (Figure 2). The collection efficiencies for individual years typically varied from about 35% to 70%. Because precipitation composition varied greatly over the year and, in some years, seasonal subsampling was not representative, it was impossible to reliably analyze interannual variability. We interpreted only the average compositions and depositions for the entire sampling period and for each month (i.e., compositing data for all Januarys, etc.) assuming that precipitation sampled during each period was a representative subset of all precipitation that fell during that period. During January, February, and October the efficiencies were 27%, 27%, and 35%, respectively, because of problems with site operations usually in the earlier years of the record. Sampling efficiencies in the other months ranged from 42% to 68%.

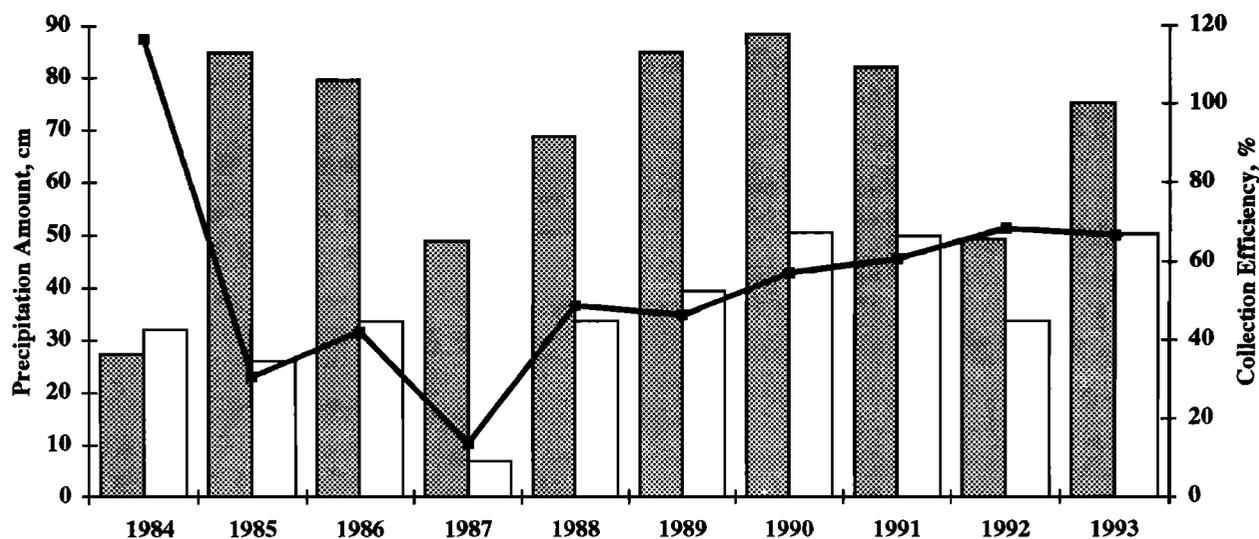


Figure 2. Annual precipitation amounts at Torres del Paine from March 23, 1984, to December 31, 1993, (left axis) for total amounts recorded (grey columns), amounts sampled (open columns), and collection-efficiency percentage (solid line, right axis).

Quality Assurance

Of the 234 precipitation samples collected, 198 met quality-assurance criteria. We excluded data for 36 samples from the analyses: Precipitation gauge data were missing for 4 samples; supporting descriptive data (e.g., date collector installed) were missing for 9; insufficient volume was sampled to allow complete chemical analyses of 7; gross contaminants (e.g., by bird feces) were present in 10; the collector malfunctioned for 3; and 3 were apparently contaminated by Na^+ or Mg^{++} .

In past analyses of GPCP data, we excluded samples that failed to meet criteria involving ionic balances (e.g., samples with ratios of the sum of anions to sum of cations outside a defined limit were excluded). This procedure was appropriate for samples from remote marine regions because the ionic strength of precipitation is dominated by sea salt; thus an ionic imbalance provides insights into the quality of the analysis of sea-salt constituents. However, in remote regions not immediately adjacent to oceans, such as TdP, the overall ionic composition of precipitation is significantly lower and controlled to a greater degree by nss species

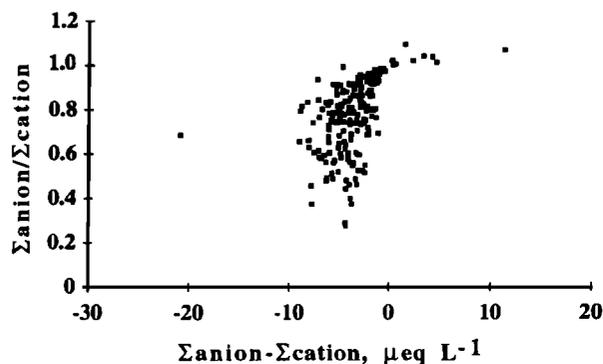


Figure 3. Pattern of $\Sigma_{\text{anion}}/\Sigma_{\text{cation}}$ versus $\Sigma_{\text{anion}}-\Sigma_{\text{cation}}$ in precipitation sampled at Torres del Paine.

(e.g., HCOO^- and $\text{SO}_4^{=}$); unmeasured species can cause significant ionic imbalances. Therefore we did not use ionic balances to assess the data quality, only to investigate patterns in unmeasured ions. Specifically, a plot of the two functions, $\Sigma_{\text{anion}}-\Sigma_{\text{cation}}$ and $\Sigma_{\text{anion}}/\Sigma_{\text{cation}}$, showed that most samples contain unmeasured anions (Figure 3). The median value of $\Sigma_{\text{anion}}/\Sigma_{\text{cation}}$ was 0.80 and the median value of $\Sigma_{\text{anion}}-\Sigma_{\text{cation}}$ was $-3.8 \mu\text{eq L}^{-1}$. Thus the median concentration of unmeasured anions was $3.8 \mu\text{eq L}^{-1}$, corresponding to 20% of total anions. Low concentrations of several species intermittently present probably contributed to this pool of unmeasured anions. Likely candidates included carboxylic anions, such as propionate, oxalate, and pyruvate, and inorganic anions, such as nitrite, bicarbonate, and bisulfite among others.

Results and Discussion

In the following sections we report variability in concentrations and per-event depositions of major chemical constituents in precipitation at TdP and assess the controlling biogeochemical processes. We also compare the TdP data with measured and modeled conditions at other locations within the region and around the globe. Caution is warranted in such comparisons due to regional differences in the frequency, size, and nature of precipitation events; associated water-accumulation rates (i.e., dilution effects); and, for data from snow and ice samples, post-depositional changes in composition. Despite these potential complications, these comparisons do provide useful diagnostic information concerning major biogeochemical interactions in the remote troposphere.

H^+

Precipitation at TdP was slightly acidic and contained both sea-salt (ss) and non-sea-salt components, which averaged $34.0 \mu\text{eq L}^{-1}$ and $22.4 \mu\text{eq L}^{-1}$, respectively. The

Table 1. The Volume-Weighted-Average Concentrations of Chemical Species in Precipitation and Corresponding Annual Rates of Wet Deposition (Based on Annual Precipitation of 0.75 m yr⁻¹) at Torres del Paine

	Concentration, $\mu\text{eq L}^{-1}$		Deposition, $\text{eq ha}^{-1} \text{yr}^{-1}$	
	Total	nss	Total	nss
H ⁺	10.9	10.9	81.8	81.8
Na ⁺	13.2	---	99.0	---
K ⁺	0.4	0.2	3.0	1.4
Mg ⁺⁺	3.2	0.2	24.0	1.5
Ca ⁺⁺	1.1	0.5	8.3	3.8
NH ₄ ⁺	0.6	0.6	4.5	4.5
NO ₃ ⁻	0.5	0.5	3.6	3.6
Cl ⁻	17.0	1.6	128	12.0
SO ₄ ⁼	2.8	1.2	21.3	9.0
CH ₃ SO ₃ ⁻	0.19	0.19	1.5	1.5
HCOO ⁻	4.9	4.9	---	---
CH ₃ COO ⁻	0.5	0.5	---	---

	Concentration, $\mu\text{mol L}^{-1}$		Deposition, $\text{mol ha}^{-1} \text{yr}^{-1}$	
	Total	nss	Total	nss
HCOO _t	5.5	5.5	41.3	41.3
CH ₃ COO _t	1.0	1.0	7.3	7.3
PO ₄	0.06	0.06	0.5	0.5

In table nss is non-sea-salt concentration.

nss component was dominated by H⁺ and HCOO_t with smaller contributions by Cl⁻, SO₄⁼, CH₃COO_t, NH₄⁺, and NO₃⁻. The annual VWA H⁺ expressed as pH was 4.96 (H⁺ = 10.9 $\mu\text{eq L}^{-1}$, Table 1), which was within the range of values reported for precipitation in other remote marine (e.g., Amsterdam Island, 5.1; *Moody et al.* [1991]) and continental regions (e.g., Katherine, Australia, 4.7; *Likens et al.* [1987]). On the basis of ionic ratios, the maximum contributions of HCOOH, HCl, H₂SO₄, CH₃COOH, and HNO₃ to precipitation acidity were 45, 15, 11, 5, and 5%, respectively. When we excluded an early period of record (March 23, 1984, to July 19, 1987) during which HCOOH concentrations were significantly lower (see carboxylic acids section below), the maximum contributions changed slightly (51, 12, 8, 4, and 4%, respectively).

Monthly VWA H⁺ concentrations ranged from 6.7 $\mu\text{eq L}^{-1}$ in June to 19.7 $\mu\text{eq L}^{-1}$ in December (Figure 4). By subtracting the concentrations of HCOO⁻ and CH₃COO⁻ from the concentrations of measured H⁺, we estimate that, on a monthly basis, H⁺ contributed primarily by strong mineral acids ranged from 4.2 $\mu\text{eq L}^{-1}$ to 8.2 $\mu\text{eq L}^{-1}$ (Figure 4). By comparison, the acidity from carbonic acid in equilibrium with atmospheric CO₂ is 2.5 $\mu\text{eq L}^{-1}$. The strong seasonality of both organic and mineral acids at TdP suggests that seasonal variability in ecosystem metabolism and productivity led to distinct temporal patterns in emissions of precursor compounds controlling acidity in precipitation. Seasonal variability in oxidative capacity and in other physical processes, such as wind velocity which partially controls sea-air exchange, may also have contributed to the observed patterns. During the austral winter, concentrations of most anions from acids were lower but still measurable suggesting nonbiogenic sources (local or remote), residual local biogenic emissions, or long-distance transport of biogenic material from lower (warmer) latitudes.

Na⁺

The VWA concentration of Na⁺ was 13.2 $\mu\text{eq L}^{-1}$, the annual deposition was 99.0 $\text{eq ha}^{-1} \text{yr}^{-1}$ (Table 1). Na⁺ concentrations and per-event deposition exhibited a modest seasonal pattern (Figure 5a); concentrations were somewhat lower during austral summer and occasional high concentrations and depositions were measured during austral spring when wind speeds are highest [*Santana et al.*, 1992].

Sea salt was relatively less important at TdP than at sites closer to the ocean but still more significant than in regions farther inland. For example, the annual VWA Na⁺ concentration at Amsterdam Island, Indian Ocean, is 269 $\mu\text{eq L}^{-1}$ and annual deposition is 3000 $\text{eq ha}^{-1} \text{yr}^{-1}$ (based on annual VWA concentrations [*Moody et al.*, 1991] and annual precipitation amount [*Miller et al.*, 1993]), about an order of magnitude greater than at TdP (Table 1). In contrast, at Katherine, Australia, a continental GPCP site about 200 km from the ocean, the VWA Na⁺ concentration is 3.3 $\mu\text{eq L}^{-1}$ [*Likens et al.*, 1987], a factor of 4 less than at TdP.

Cl⁻

Annual and monthly VWA concentrations and depositions for Cl⁻ exceeded the contributions expected from seawater by 1.6 $\mu\text{eq L}^{-1}$ and 12.0 $\text{eq ha}^{-1} \text{yr}^{-1}$ (Table 1 and Figure 5b), assuming that Na⁺ was an unbiased reference species for sea salt [*Keene et al.*, 1986]. Although typically referred to as nss Cl⁻, seawater was probably the source of most excess Cl⁻. Poorly understood chemical processes involving sea-salt aerosol in the marine boundary layer (MBL) convert particulate Cl⁻ to one or more inorganic Cl gases including HCl, Cl₂, HOCl, and ClNO₂ [e.g., *Graedel and Keene*, 1995]. The latter three gases are rapidly converted to HCl following photolysis and H-abstraction reactions with hydrocarbons. Assuming that the reacted aerosol and HCl were efficiently scavenged by atmospheric droplets, a shorter atmospheric lifetime against dry deposition for the aerosol relative to HCl would lead to an apparent enrichment in total (ss + nss) Cl⁻ relative to ss-Na⁺ in precipitation [e.g., *Moody et al.*, 1991].

The nss Cl⁻ concentrations and depositions were somewhat more variable from month to month than were other species (Figures 5 and 6). This resulted in part from the relatively greater uncertainties in calculated nss Cl⁻ [e.g., *Keene et al.*, 1986]. A general pattern was evident, however, with higher concentrations and depositions typical during the warmer months and lower values during the

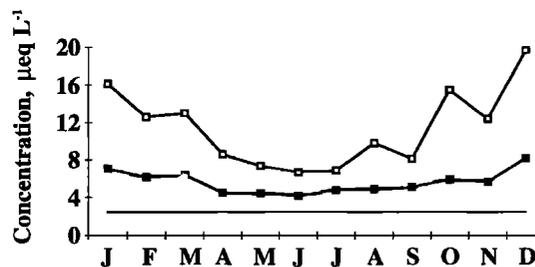


Figure 4. Monthly volume-weighted-average (VWA) H⁺ concentrations for all acids (top line, open squares) and only strong acids (middle line, closed squares) relative to the pH of pure water in equilibrium with atmospheric CO₂ (bottom line, no squares).

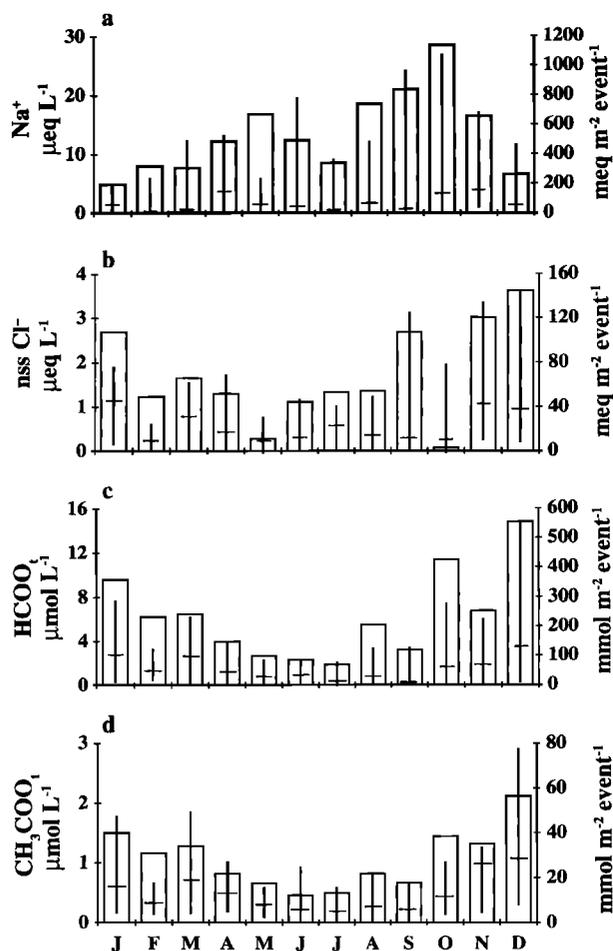


Figure 5. Monthly volume-weighted-average (VWA) concentrations (columns, left axes) and per-event deposition (vertical lines, right axes) of (a) Na⁺, (b) nss Cl⁻, (c) HCOO⁻, and (d) CH₃COO⁻ at Torres del Paine. The vertical lines indicate percentiles (10th at top, 50th at cross bar, 90th at bottom) of per-event deposition. Nine samples were taken in January, 16 in February, 15 in March, 23 in April, 21 in May, 22 in June, 14 in July, 26 in August, 15 in September, 12 in October, 12 in November, and 13 in December.

winter. The seasonal pattern in nss-Cl⁻ was the opposite of that of Na⁺ (Figures 5a and 5b) but the inverse relationship may have been largely fortuitous. The VWA concentrations for Na⁺ suggested that sea salt was transported to the site more efficiently during the colder months (May through October) than during the summer. In contrast, we expect processes that dechlorinate sea-salt aerosol to be more important during the summer when concentrations of reactant species, such as SO₂, N gases, and oxidants (e.g., OH, peroxy radicals, etc.), were presumably higher. Compared to the more remote MBL, elevated concentrations of such species in polluted regions are associated with greater Cl⁻ deficits relative to sea salt [e.g., Martens *et al.*, 1973; Keene *et al.*, 1990]. Assuming that dechlorination was more significant during warmer months, higher concentrations of volatile Cl and differential atmospheric lifetimes against deposition may have contributed to the observed seasonal pattern in nss Cl⁻.

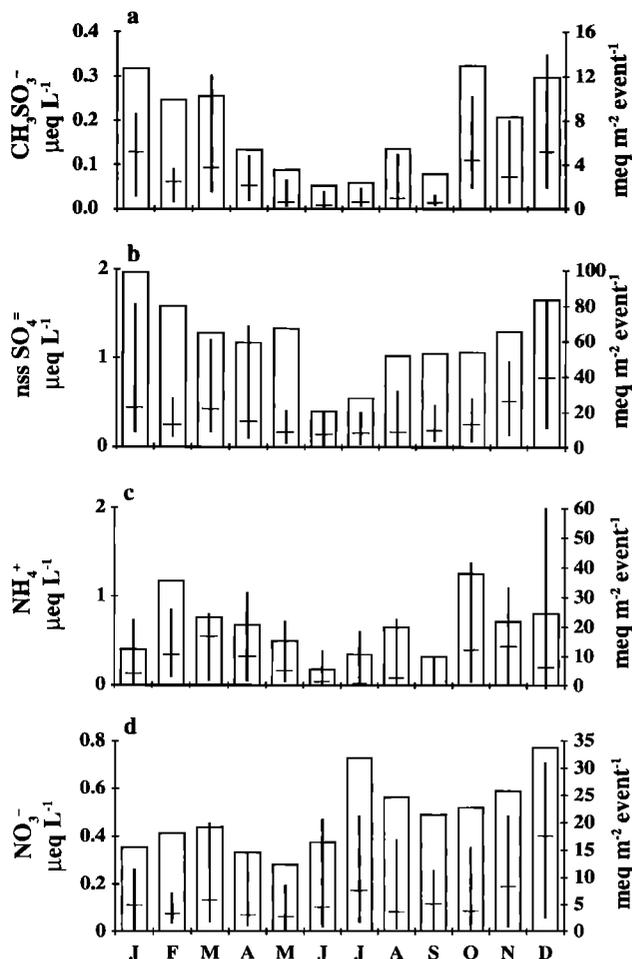


Figure 6. Monthly volume-weighted-average (VWA) concentrations (columns, left axes) and per-event deposition (vertical lines, right axes) of (a) CH₃SO₃⁻, (b) nss SO₄⁼, (c) NH₄⁺, and (d) NO₃⁻ at Torres del Paine. The vertical lines indicate percentiles (10th at top, 50th at cross bar, 90th at bottom) of per-event deposition. For all species except CH₃SO₃⁻, the numbers of samples are the same as in Figure 5: 9 in January, 16 in February, 15 in March, 23 in April, 21 in May, 22 in June, 14 in July, 26 in August, 15 in September, 12 in October, 12 in November, and 13 in December. For CH₃SO₃⁻, 6 samples were taken in January, 15 in February, 12 in March, 16 in April, 9 in May, 7 in July, 19 in August, 7 in September, 8 in October, 5 in November, and 10 in December.

Like the situation on Amsterdam Island [Moody *et al.*, 1991] and at other marine locations [e.g., Graedel and Keene, 1995], substantial concentrations of nss Cl⁻ suggest that HCl may have significantly contributed to the acidity of precipitation at the site (Table 1). The ultimate source of this acidity remains an open question. Acid-displacement reactions involving H₂SO₄ and HNO₃ [e.g., Brimblecombe and Clegg, 1988] do not generate atmospheric acidity. Protons are simply transferred from one class of mineral acids (H₂SO₄ and HNO₃) to another (HCl). If, however, photochemically active Cl gases volatilize from sea-salt aerosol and produce atomic chlorine in significant concentrations [e.g., Keene *et al.*, 1990; Finlayson-Pitts, 1993], subsequent hydrogen abstraction reactions will generate HCl.

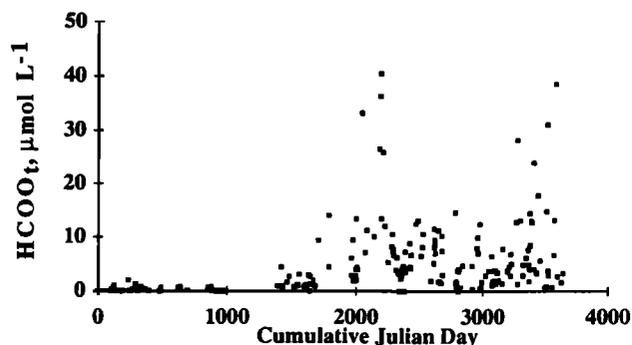


Figure 7. HCOO_t concentrations in individual precipitation events at Torres del Paine for cumulative Julian days from January 1, 1984, to December 19, 1993.

Chemical processes involving sea-salt aerosol could then be an important source for atmospheric acidity in marine regions.

Carboxylic Acids

HCOO_t exhibited an unusual temporal pattern over the course of the study: Significantly lower concentrations and per-event depositions of HCOO_t were measured in samples collected before July, 1987, relative to those collected thereafter (Figure 7). This abrupt and puzzling change suggested one of two possibilities: Either (1) the chemical composition of precipitation changed significantly during the study period or (2) systematic negative (before July, 1987) or positive (after July, 1987) artifacts significantly biased the data. We examined the available information for evidence of artifacts. All plasticware (sample buckets and bottles) used in the GPCP were purchased from the same vendors and washed, quality assured, packaged, and shipped at the University of Virginia using standard, tested procedures [Galloway *et al.*, 1982, 1993]. After receipt, all GPCP samples were analyzed in the central laboratory during mixed analytical runs (i.e., samples from numerous GPCP sites were included) incorporating internal and external quality-assurance procedures. Despite overlapping ranges in concentrations, data for other GPCP sites did not exhibit similar temporal variabilities in HCOO_t over the period in question. This suggests that, if artifacts did occur, they were unique to the Chilean site and must have resulted from some on-site influence. However, available evidence based on both detailed queries of site operators and the operators' notes on forms returned with the samples indicated that standard protocols were followed throughout the entire period of operation. Although clean plasticware and samples were stored at different locations in TdP during the period, the changes in location did not correlate with the variability in the data. In addition, visiting scientists exposed deionized water blanks at storage and sampling locations and subsequent analyses revealed no significant HCOO_t contamination. Finally, other biologically active species (NH_4^+ and CH_3COO_t) did not vary significantly between the early and later periods suggesting that the samples were adequately preserved against microbial degradation. Therefore we conclude that no obvious handling or analytical artifacts caused the abrupt change in HCOO_t ; the measured temporal variability appeared to reflect actual changes in the chemical

composition of incident precipitation during the period of operation.

Alternatively, changes in environmental conditions may have contributed to long-term temporal variability in HCOO_t . As mentioned above, the precipitation collector was reinstalled at the original sampling site during July, 1987, after regrowth of nearby vegetation that had burned in a wildfire two years earlier. This move coincided with the increased HCOO_t . The fire may have led to increases in local emissions of HCOOH or precursor hydrocarbons through changes in flora (e.g., isoprene-emitting vegetation), fauna (e.g., formicine ants; although according to TdP personnel, there were no large ant populations), or soil microbes. As discussed below, however, it is likely, given its close proximity to the ocean, that a portion of HCOO_t deposited at the site originated from marine sources. Therefore local influences such as fires probably did not completely account for the observed temporal pattern. We also used standard linear regression analysis to assess the relationship between variability in HCOO_t and the intensity of El Niño periods (G. Bell, personal communication, 1994) but found no significant relationship. On the basis of the above analysis, we were not able to ascertain the cause of the long-term, temporally variability in HCOO_t .

VWA concentrations and annual depositions of HCOO_t and CH_3COO_t were $5.5 \mu\text{mol L}^{-1}$ and $1.0 \mu\text{mol L}^{-1}$ and $41.3 \text{ mol ha}^{-1} \text{ yr}^{-1}$ and $7.3 \text{ mol ha}^{-1} \text{ yr}^{-1}$, respectively (Table 1). The VWA concentrations and per-event depositions of HCOO_t and CH_3COO_t varied seasonally; highest values were during spring, summer, and autumn when temperature and solar insolation were higher (Figures 5c and 5d). This strong seasonal cycle is typical of carboxylic acids at many remote locations [e.g., Keene and Galloway, 1988] and suggests that biogenic emissions, including both direct emissions [e.g., Graedel and Eisner, 1988; Talbot *et al.*, 1990; Sanhueza and Andreae, 1991] and emissions of precursor hydrocarbons from both marine and terrestrial sources [e.g., Jacob and Wofsy, 1988; Galloway *et al.*, 1989; Madronich and Calvert, 1990] may control atmospheric concentrations. Seasonal variability in the production of photochemical oxidants may also contribute to the seasonality in concentrations. Although the aqueous-phase oxidation of HCHO in clouds had been thought to be a potentially important source of tropospheric HCOOH [e.g., Chameides and Davis, 1983; Jacob, 1986], recent measurements suggest that this mechanism may be relatively unimportant [e.g., Facchini *et al.*, 1992; Sanhueza *et al.*, 1992; Keene *et al.*, 1995a].

VWA concentrations and median wet depositions at TdP during the warm months were about a factor of 2 greater than those observed at Amsterdam Island in the southern Indian Ocean [Moody *et al.*, 1991] although wintertime values were similar. Thus seasonal excursions in carboxylic species at TdP were relatively more pronounced. Terrestrial regions typically exhibit substantially higher concentrations of tropospheric HCOOH and CH_3COOH relative to marine regions suggesting greater source strengths over continents [Keene and Galloway, 1988]. Differences between Amsterdam Island and TdP may, therefore, indicate significant contributions from terrestrial sources in southern Chile. Alternatively, stronger marine sources for carboxylic acids upwind of TdP relative to those at Amsterdam Island or less efficient removal of marine-derived carboxylics during

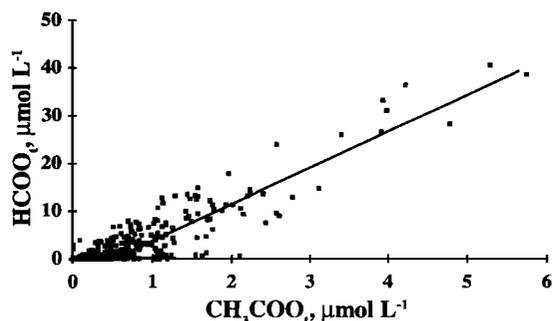


Figure 8. Concentrations of HCOO_t versus CH_3COO_t in individual precipitation events at Torres del Paine from March 23, 1984, to December 19, 1993, showing the reduced major axis regression (solid line).

transport over land may also have contributed to the differences between sites.

Concentrations of carboxylic acids in ice from coastal Antarctica [Legrand and Saigne, 1988] are 2 to 3 orders of magnitude lower than those at TdP. These results are consistent with the lack of significant biogenic sources on the Antarctic continent and suggest that marine sources of precursors upwind of eastern Antarctica are relatively low compared to other regions.

Aqueous- and vapor-phase concentrations of HCOOH and CH_3COOH are usually highly correlated suggesting that both compounds are controlled by similar processes [e.g., Keene et al., 1986; Keene and Galloway, 1988; Talbot et al., 1988, 1995]. A reduced major axis (RMA) regression [Hirsch and Gilroy, 1984] for the TdP data yielded a slope of 7.52 ± 0.24 , an intercept of -2.27 ± 0.34 , and a correlation coefficient of 0.89 (Figure 8). A previously reported slope of 1.01 ± 0.20 for the regression of carboxylic species at TdP [Keene and Galloway, 1986] corresponds to the early record when HCOOH_t concentrations were significantly lower (see above). Although absolute concentrations of HCOO_t and CH_3COO_t in precipitation in TdP were within the range of values at other remote and impacted sites, the slope for the TdP data was higher by factors of 2 to 5 [e.g., Keene and Galloway, 1986]. Since there would probably have been little spatial variability in the relative losses of the two acids through deposition, source strengths of HCOOH upwind of TdP may have been considerably higher than those for CH_3COOH relative to many other regions of the Earth. There has been recurring speculation over the years concerning the biogeochemical

factors leading to the high correlations between HCOOH and CH_3COOH in aqueous and vapor phases [e.g., Keene and Galloway, 1988]. Since both acids appear to be controlled by similar processes (biogenic emissions and photochemical oxidation of precursors, direct biogenic emission, and short lifetimes against deposition), it is not surprising that they are highly correlated. All these processes are driven to greater or lesser extent by seasonal variability in atmospheric physics (radiation, temperature, wind velocity, and precipitation).

Sulfur

$\text{SO}_4^{=}$ and CH_3SO_3^- were the two major S species measured in TdP precipitation. VWA concentrations were $2.8 \mu\text{eq L}^{-1}$ and $0.19 \mu\text{eq L}^{-1}$, respectively, and annual deposition rates were 21.3 eq ha^{-1} and 1.5 eq ha^{-1} , respectively. VWA concentrations of ss and nss $\text{SO}_4^{=}$ were $1.6 \mu\text{eq L}^{-1}$ and $1.2 \mu\text{eq L}^{-1}$, respectively; corresponding deposition rates were 12.3 eq ha^{-1} and 9.0 eq ha^{-1} , respectively (Table 1).

Concentrations of nss $\text{SO}_4^{=}$ in TdP precipitation (Figure 6b) were within the range of those at other high-latitude areas in the southern hemisphere (Table 2, Figure 9). However, nss $\text{SO}_4^{=}$ concentrations in six snow samples from south Patagonia (60 km north) (Table 2) are a factor of 2 lower than at TdP. These differences are probably associated with the closer proximity of TdP to marine sources of $(\text{CH}_3)_2\text{S}$ (see below). In addition, the Patagonian samples correspond to winter snowfall during periods of minimum $(\text{CH}_3)_2\text{S}$ emissions [Bates et al., 1992]. Other factors possibly contributing to these regional differences include orographic influences on precipitation amount, variability in rain- versus snow-scavenging processes, and elevational gradients in precursor gas and aerosol concentrations.

CH_3SO_3^- in precipitation has been measured at only a few high-latitude sites in the southern hemisphere. Concentrations at TdP (Figure 6a; Table 1) were within the range of measurements from coastal Antarctica. Maupetit and Delmas [1992] report that CH_3SO_3^- concentrations in 13 snow samples collected in 1984 at the coastal site of Dumont d'Urville range from below detection to 44 ppb ($0.46 \mu\text{eq L}^{-1}$) with an arithmetic mean of 6.5 ppb ($0.068 \mu\text{eq L}^{-1}$). CH_3SO_3^- in snow deposited during June-December, 1984, on the coast at Mirny-Vostok ranged from about 3 ppb to 23 ppb ($0.03 \mu\text{eq L}^{-1}$ to $0.24 \mu\text{eq L}^{-1}$) [Legrand et al., 1992, Figure 4]. CH_3SO_3^- concentrations in an ice core from Dollerman Island are 1 to $2 \mu\text{eq L}^{-1}$ [Mulvaney et al.,

Table 2. Precipitation Composition at Torres del Paine Compared to Other High-Latitude Sites in the Southern Hemisphere

	nss $\text{SO}_4^{=}$	NO_3^-	NH_4^+	Reference
Antarctica				Delmas [1996]
Median	1.06	0.66	0.06	
Range	0.39-3.94	0.17-3.33	0.04-0.17	
N	34	35	4	
Drake Passage	1.1	0.6	2.6	Pszenny et al. [1989]
Amsterdam Island	3.4	1.3	1.8	Moody et al. [1991]
Patagonia ice cap	0.6	0.3	0.8	Aristarain and Delmas [1993]
Torres del Paine	1.2	0.5	0.6	this paper

Units are $\mu\text{eq L}^{-1}$.

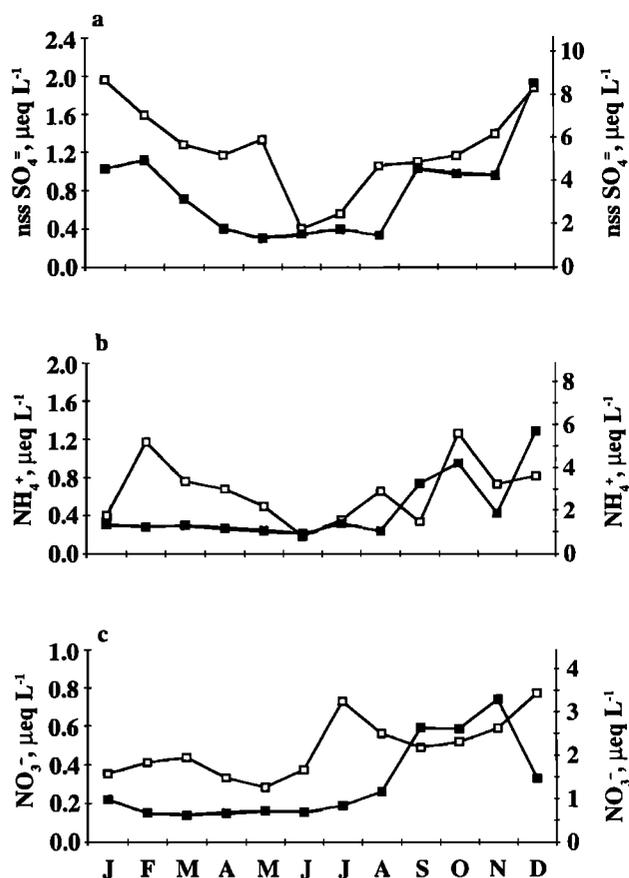


Figure 9. Monthly volume-weighted-average (VWA) concentrations of (a) nss SO₄⁼, (b) NH₄⁺, and (c) NO₃⁻ at Torres del Paine (open squares; left axes) and Amsterdam Island (solid squares; right axes).

1992] (as reviewed by Delmas [1996]). For the Drake Passage, Pszenny *et al.* [1989] report a range from 8 precipitation samples of 0.02 to 0.12 μeq L⁻¹.

Possible sources of precursors for nss SO₄⁼ in precipitation at TdP include biogenic emissions of reduced sulfur gases (primarily (CH₃)₂S from the upwind ocean); the long-distance transport of combustion-derived SO₂ from remote, primarily anthropogenic sources; and volcanic emissions of SO₂. CH₃SO₃⁻ is thought to originate almost exclusively from the oxidation of biogenic (CH₃)₂S. Since there was no major volcanic activity upwind of the site during the study period, volcanic emissions were probably an insignificant regional source of S (although we cannot discount the possibility of nonexplosive venting of S). Thus the following analysis will focus on assessing the biogenic-versus-anthropogenic sources of nss S in precipitation at TdP. At the latitude of TdP, (CH₃)₂S is the most important reduced S gas emitted to the atmosphere and marine ecosystems are substantially stronger sources than terrestrial ecosystems [Bates *et al.*, 1992]. The oxidation of (CH₃)₂S by OH produces both H₂SO₄ and CH₃SO₃H [Yin *et al.*, 1990]. Relative production appears to be strongly temperature dependent; CH₃SO₃H is produced in greater abundance at lower temperatures [Hynes *et al.*, 1986].

CH₃SO₃⁻ and nss SO₄⁼ relationships. Aqueous- and particulate-phase concentrations of CH₃SO₃⁻ and nss SO₄⁼

typically covary over marked seasonal cycles at high-latitude, marine-influenced sites in the southern hemisphere including TdP (Figure 10a), Amsterdam Island (Figure 10b) [Nguyen *et al.*, 1992], Cape Grim, Tasmania [Ayers *et al.*, 1991], and Antarctica [Legrand *et al.*, 1992; Savoie *et al.*, 1993]. Such relationships support the hypothesis that seasonally varying emissions of biogenic (CH₃)₂S from the southern oceans are major sources for CH₃SO₃H and H₂SO₄ in the overlying MBL. The equivalent ratio for VWA concentrations of CH₃SO₃⁻ to nss SO₄⁼ at TdP during the period when both species were measured was 0.17 (Figure 10c), within the range of 0.05–0.4 reported for coastal Antarctica [Berresheim, 1987; Pszenny *et al.*, 1989; Legrand *et al.*, 1992; Delmas, 1996] but substantially higher than that for Amsterdam Island (0.04, calculated from Table 3). Monthly equivalent ratios (based on VWA concentrations) at TdP were lower during the austral summer and higher during the winter (Figure 10c); that is, relative seasonal variability in CH₃SO₃⁻ was greater than that of nss SO₄⁼. Ratios at Amsterdam Island exhibited somewhat less seasonal variability (Figure 10c). Since CH₃SO₃H appears to be more efficiently produced from (CH₃)₂S oxidation by OH at colder temperatures [e.g., Hynes *et al.*, 1986], we expected a relatively more pronounced seasonal excursion in nss SO₄⁼ at TdP assuming both species originated exclusively from (CH₃)₂S and had similar atmospheric lifetimes. The greater seasonal variability in CH₃SO₃⁻ suggests the possibility of a significant anthropogenic contribution to nss

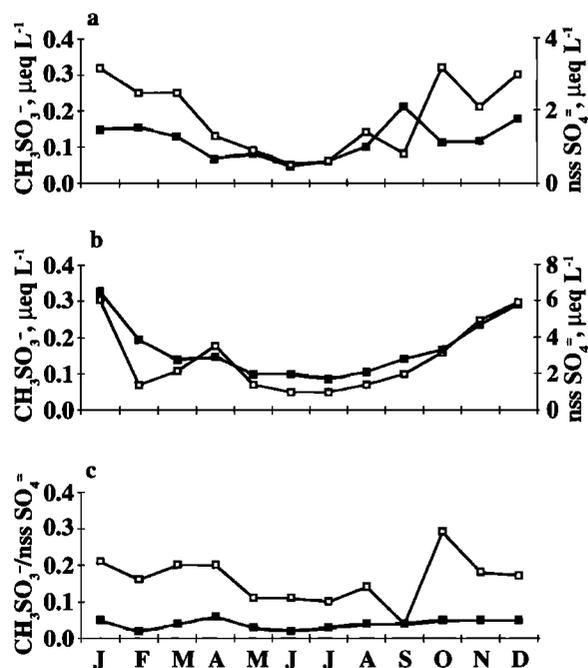


Figure 10. Monthly volume-weighted-average (VWA) concentrations at (a) Torres del Paine and (b) Amsterdam Island of CH₃SO₃⁻ (open squares, left axes) and nss SO₄⁼ (solid squares, right axes); (c) the CH₃SO₃⁻/nss SO₄⁼ ratios at Torres del Paine (open squares) and Amsterdam Island (closed squares). The Amsterdam Island data are for paired measurements (*n*=198) from July 31, 1989, to March 28, 1994 (J. N. Galloway and W. C. Keene, University of Virginia, Global Precipitation Chemistry Project unpublished data, 1995).

$\text{SO}_4^{=}$ in precipitation at the site. A complicating factor may involve differential seasonal variabilities in atmospheric lifetimes for CH_3SO_3^- and nss $\text{SO}_4^{=}$. Relative to nss $\text{SO}_4^{=}$, CH_3SO_3^- is associated with coarser aerosol (e.g., *Pszenny* [1992] among others). Thus seasonal variability in physical processes, such as sea-salt aerosol production, associated scavenging, and subsequent dry deposition, could lead to relative differences in the seasonality of removal rates for the two species.

Cl chemistry may also complicate interpretation of sources for nss S in the MBL based on presumed ratios of sulfonated products from the oxidation of biogenic $(\text{CH}_3)_2\text{S}$. In contrast to OH, there is no evidence that oxidation by atomic Cl leads to the production of $\text{CH}_3\text{SO}_3\text{H}$ [*Keene et al.*, 1996]. Thus latitudinal or seasonal variability in the relative importance of Cl versus OH oxidation of $(\text{CH}_3)_2\text{S}$ may contribute to observed patterns in tropospheric CH_3SO_3^- and nss $\text{SO}_4^{=}$. Since the spatial and temporal distributions of Cl-atom concentrations in the MBL are very poorly constrained [e.g., *Graedel and Keene*, 1995], it is impossible, at present, to critically assess the potential importance of this chemical process in the tropospheric S cycle.

CH_3SO_3^- is enriched relative to nss $\text{SO}_4^{=}$ in coastal Antarctic ice during strong El Niño Southern Oscillation events suggesting that increased $(\text{CH}_3)_2\text{S}$ emissions during El Niño periods may contribute to interannual variability in absolute and relative concentrations of sulfonated products [*Legrand and Feniet-Saigne*, 1991]. We investigated the relationship between El Niño and S species in precipitation

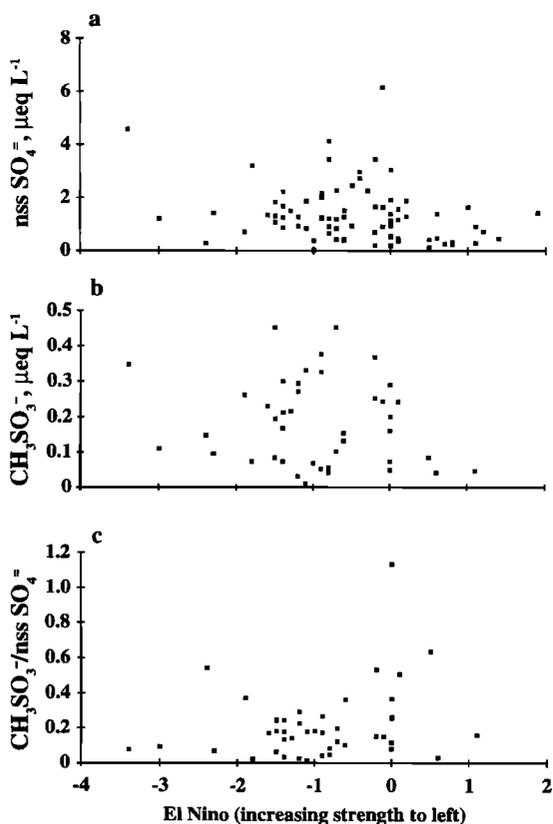


Figure 11. The relationship between the El Niño index and the monthly volume-weighted-average (VWA) concentrations of (a) nss $\text{SO}_4^{=}$, (b) CH_3SO_3^- , and (c) $\text{CH}_3\text{SO}_3^-/\text{nss SO}_4^{=}$ ratio.

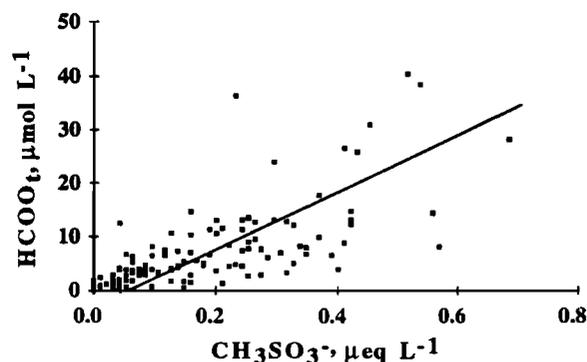


Figure 12. Concentrations of HCOO_t versus CH_3SO_3^- in individual precipitation events at Torres del Paine from December 16, 1989, to December 19, 1993, showing the reduced major axis regression (solid line).

at TdP using standard linear regression of measured concentrations versus an index of El Niño intensity (G. Bell, Climate Analysis Center, National Weather Service, NOAA, unpublished data, 1994). Although concentrations of both nss $\text{SO}_4^{=}$ and CH_3SO_3^- appeared to be greater during El Niño periods (Figures 11a and 11b), only nss $\text{SO}_4^{=}$ was statistically significant. In addition, the ratios of the two species showed no apparent trend (Figure 11c). A similar analysis of precipitation amount at TdP versus the index of El Niño intensity revealed no significant relationship. Although our results are not completely consistent with variability in CH_3SO_3^- and nss $\text{SO}_4^{=}$ measured in Antarctic ice [*Legrand and Feniet-Saigne*, 1991], they do support the hypothesis that fluxes of $(\text{CH}_3)_2\text{S}$ from the southern ocean to the atmosphere increase during strong El Niño periods. Such variability may have important implications for the direct and indirect effects of S aerosol on the Earth's radiative balance and climate [e.g., *Charlson et al.*, 1992]. Spatial heterogeneity in ecosystems, their responses to El Niño, atmospheric oxidation processes, or atmospheric lifetimes may contribute to regional variability in tropospheric CH_3SO_3^- and nss $\text{SO}_4^{=}$ relative to El Niño events. A possible explanation for the lack of consistency between our data and those of *Legrand and Feniet-Saigne* [1991] is that our data spanned only 10 years whereas their analysis corresponds to a longer period (1922 to 1984).

HCOO_t and CH_3SO_3^- relationships. HCOO_t and CH_3SO_3^- in precipitation at TDP were also significantly correlated (Figure 12). A RMA regression yielded a slope of 53.1 ± 3.4 , an intercept of -2.35 ± 0.79 , and a correlation coefficient of 0.70 suggesting a possible direct chemical link between the cycling of S and HCOOH. The oxidation of $(\text{CH}_3)_2\text{S}$ produces both HCHO and CH_3SO_3^- [*Yin et al.*, 1990]; the subsequent vapor- or aqueous-phase oxidation of HCHO generates HCOOH [e.g., *Jacob*, 1986]. However, much of the HCHO in the rural and remote troposphere is thought to originate from the oxidation of CH_4 [e.g., *Logan et al.*, 1981; *Duce et al.*, 1983] and isoprene [e.g., *Shepson et al.*, 1991; *Munger et al.*, 1995]; thus, the relatively minor contribution from $(\text{CH}_3)_2\text{S}$ oxidation would not be expected to result in strong correlations between CH_3SO_3^- and HCOOH via this pathway alone. The major precursors for HCOOH in marine air are probably other hydrocarbons emitted from the ocean surface. It is likely that the observed

correlation between CH_3SO_3^- and HCOO_i reflects the common influence of physical processes on essentially independent biogenic sources, the subsequent photochemical oxidation of precursor compounds, and deposition. Like HCOOH , CH_3SO_3^- is produced from the photo-oxidation of a biogenic precursor and is lost from the atmosphere via deposition to the surface.

Sulfur budget. Estimating the annual budget for nss sulfur requires information on emissions of $(\text{CH}_3)_2\text{S}$, wet-deposition rates of CH_3SO_3^- and nss $\text{SO}_4^{=}$, and dry-deposition rates of CH_3SO_3^- , SO_2 , and nss $\text{SO}_4^{=}$. The annual wet-deposition rates of CH_3SO_3^- and nss $\text{SO}_4^{=}$ at TdP were $1.5 \text{ eq ha}^{-1} \text{ yr}^{-1}$ and $9.0 \text{ eq ha}^{-1} \text{ yr}^{-1}$, respectively ($1.5 \text{ mol ha}^{-1} \text{ yr}^{-1}$ and $4.5 \text{ mol ha}^{-1} \text{ yr}^{-1}$, respectively) (Table 1).

Estimates of wet-deposition rates for nss sulfur in polar and marine regions range from about $1 \text{ mol ha}^{-1} \text{ yr}^{-1}$ to $30 \text{ mol ha}^{-1} \text{ yr}^{-1}$ [Galloway, 1985]; wet-deposition rates at TdP fell within this range. On the basis of eight precipitation samples collected in the austral fall on a cruise in the Drake Passage, Pszenny *et al.* [1989] estimate a wet-deposition rate for CH_3SO_3^- and nss $\text{SO}_4^{=}$ of $0.26 \mu\text{mol m}^{-2} \text{ d}^{-1}$ and $1.7 \mu\text{mol m}^{-2} \text{ d}^{-1}$, respectively. These scale up to $0.9 \text{ mol ha}^{-1} \text{ yr}^{-1}$ and $6.3 \text{ mol ha}^{-1} \text{ yr}^{-1}$, respectively, which are similar to the TdP data. Pszenny *et al.* [1989] and Galloway [1985] estimate that dry deposition of nss sulfur ($\text{SO}_2 + \text{nss SO}_4^{=}$) is about one quarter and less than one half of the wet-deposition flux of nss $\text{SO}_4^{=}$, respectively. Assuming that dry-deposition rates for SO_2 and nss $\text{SO}_4^{=}$ at TdP were one third of the nss $\text{SO}_4^{=}$ wet-deposition rate, we calculate a flux of $1.5 \text{ mol ha}^{-1} \text{ yr}^{-1}$. Total (wet plus dry) deposition of nss $\text{SO}_4^{=}$ was thus estimated to be $6.0 \text{ mol ha}^{-1} \text{ yr}^{-1}$. Pszenny *et al.* [1989] estimate that the dry-deposition rate of CH_3SO_3^- is about one third of wet deposition, which, at TdP, would have yielded a dry deposition of $0.5 \text{ mol ha}^{-1} \text{ yr}^{-1}$. Therefore the total deposition of nss sulfur to TdP was about $8 \text{ mol ha}^{-1} \text{ yr}^{-1}$, with CH_3SO_3^- providing about 25% of the total with SO_2 and nss $\text{SO}_4^{=}$ providing the balance.

Berresheim [1987] estimates that $(\text{CH}_3)_2\text{S}$ emissions from the Southern Ocean average $4.9 \mu\text{mol m}^{-2} \text{ d}^{-1}$ over a year. Bates *et al.* [1992] estimate $(\text{CH}_3)_2\text{S}$ emissions from marine ecosystems in the same latitude range as Torres del Paine are about $2.21 \mu\text{mol S m}^{-2} \text{ d}^{-1}$ in winter and $4.96 \mu\text{mol S m}^{-2} \text{ d}^{-1}$ in summer. The annual marine fluxes of Berresheim and Bates *et al.* are about $18 \text{ mol ha}^{-1} \text{ yr}^{-1}$ and $13 \text{ mol ha}^{-1} \text{ yr}^{-1}$, respectively, or about a factor of 2 greater than our estimated deposition flux of $8 \text{ mol ha}^{-1} \text{ yr}^{-1}$. However, TdP is not surrounded by ocean; it is 50 km inland and separated from the ocean by a significant mountain chain. Thus we expect S deposition at TdP was influenced by both marine and terrestrial emissions and by S deposition in the overland fetch. Bates *et al.* [1992] estimate S emissions from terrestrial ecosystems in the same latitude as TdP are $0.02 \mu\text{mol S m}^{-2} \text{ d}^{-1}$ and $0.19 \mu\text{mol S m}^{-2} \text{ d}^{-1}$ in winter and summer, respectively. The annual rates would be about $0.4 \text{ mol ha}^{-1} \text{ yr}^{-1}$, significantly less than our estimated S deposition rates at TdP. Our estimated total deposition of nss S at TdP falls between the estimated biogenic S emissions in upwind marine and terrestrial ecosystems; the consistency of these estimates provides independent corroboration of their reliability.

Nitrogen

NH_4^+ . The VWA concentration of NH_4^+ in TdP was $0.6 \mu\text{eq L}^{-1}$ (Table 1). This value is greater than the range observed in Antarctica (0.04 to $0.17 \mu\text{eq L}^{-1}$) but less than that for other high-latitude, non-Antarctic sites (Table 2).

A pronounced seasonal cycle of NH_4^+ concentrations and per-event depositions had maxima during spring and fall and a minimum during winter (Figure 6c). The seasonal pattern at Amsterdam Island [Moody *et al.*, 1991] also peaks during spring but absolute values are substantially higher, suggesting greater sources in that region (Figure 9b). Strong seasonal patterns in NH_4^+ wet deposition are consistent with biological sources. Both terrestrial and marine ecosystems emit NH_3 [Dentener and Crutzen, 1994]. Given the similarity of natural emissions from the marine and terrestrial systems ($15 \text{ mol ha}^{-1} \text{ yr}^{-1}$ and $36 \text{ mol ha}^{-1} \text{ yr}^{-1}$, respectively) [after Dentener and Crutzen, 1994], we expect that both contributed to NH_4^+ in TdP precipitation. Agricultural materials (fertilizer, animal waste) can also be important sources of NH_3 [Galloway *et al.*, 1995]. The primary terrestrial ecosystem at TdP is grassland, some of which is used to raise sheep whose waste emits NH_3 [Schlesinger and Hartley, 1992].

The wet-deposition rate of NH_4^+ at TdP was $4.5 \text{ eq ha}^{-1} \text{ yr}^{-1}$ (Table 1). Dentener and Crutzen [1994] use a three-dimensional, chemical-transport model to calculate global distributions of NH_x emissions and depositions. For the southwest coast of Chile, they estimate emissions to be approximately 20 to $50 \text{ mg N m}^{-2} \text{ yr}^{-1}$ (14 to $36 \text{ eq ha}^{-1} \text{ yr}^{-1}$). Their estimated wet-deposition rates are of the same magnitude, or about 3 to 8 times higher than our measurements. There are several possible explanations for these differences: Dentener and Crutzen's model may overestimate NH_3 emissions; NH_x might have been scavenged and deposited upwind of TdP; or there might have been substantial dry deposition of NH_3 . Langford *et al.* [1992] note a rapid uptake of emitted NH_3 within the grassland canopy and thus little net NH_3 emission to the atmosphere above the canopy. Such rapid recycling could possibly account for some apparent differences between the measured and modeled fluxes. In another study, Quinn *et al.* [1988] estimate an NH_3 flux from the northeastern Pacific Ocean during spring of $7 \mu\text{mol m}^{-2} \text{ d}^{-1}$ or about $25 \text{ mol ha}^{-1} \text{ yr}^{-1}$. This flux is also substantially higher than our measurements. However, spatial and temporal variabilities in emissions and associated uncertainties in extrapolations compromise the reliability of direct comparisons between Quinn's estimates and our measurements.

NO_3^- . The VWA concentration of NO_3^- at TdP was $0.5 \mu\text{eq L}^{-1}$ (Table 1), slightly higher than at the Patagonian ice cap ($0.3 \mu\text{eq L}^{-1}$, Table 2) [Aristarain and Delmas, 1993]. NO_3^- concentrations at other southern high-latitude sites fall within the range of Delmas' [1996] estimates of 0.17 – $3.33 \mu\text{eq L}^{-1}$, with a median of $0.66 \mu\text{eq L}^{-1}$ similar to that at TdP (Table 2). NO_3^- in precipitation at TdP (Figure 9c) and at Amsterdam Island [Moody *et al.*, 1991] exhibit similar seasonal patterns. However, long-distance transport of pollutant NO_3^- from southern Africa to Amsterdam Island contributes to the springtime peak and larger annual VWA NO_3^- concentration of $1.3 \mu\text{eq L}^{-1}$ [Galloway and Gaudry, 1984; Moody *et al.*, 1991].

The seasonality in VWA concentration and per-event deposition of NO_3^- at TdP are different from those of NH_4^+ , HCOO_i , CH_3COO_i , nss $\text{SO}_4^{=}$ and CH_3SO_3^- . NO_3^- peaks during austral winter through late spring, the others peak during the austral summer (Figures 5 and 6). The different pattern of NO_3^- suggests abiotic controls. Several processes (fossil-fuel combustion, biomass burning, transport from the stratosphere, or lightning) could have been responsible. Given the long fetch over the Pacific and modest upwind emissions from fossil-fuel combustion, it is unlikely that the long-distance transport of anthropogenic NO_y was a major contributor to NO_3^- measured in precipitation at TdP. However, under conditions of cold temperatures and low $[\text{NO}]/[\text{NO}_2]$ ratios typical of the high-latitude, southern Pacific during the austral winter and spring, peroxyacetyl nitrate (PAN; a reservoir species for NO_x produced in more polluted regions) is sufficiently stable to be transported long distances [e.g., Crutzen, 1979; Singh and Hanst, 1981; Singh et al., 1985]. Pollutant N oxides transported as PAN may, therefore, have contributed to the higher NO_3^- concentrations in precipitation and associated wet-deposition fluxes at TdP during this period. NO produced by regional biomass burning was a possible source [Fishman et al., 1991] (H. Levy II, personal communication, 1995). In the winter when wind speeds decrease, burning is prevalent across southern Chile (D. Soto, personal communication, 1994) although the concentrations of nss K^+ (a tracer of biomass burning; Andreae [1983]) at TdP were low (annual VWA nss K^+ was $0.2 \mu\text{eq L}^{-1}$, Table 1) and showed no seasonal signal. Transport of NO_y from the stratosphere may have been important. Mayewski and Legrand [1990] report higher NO_3^- concentrations at Dome C and Vostok in Antarctica during the austral spring possibly because of transport from the lower stratosphere associated with formation of polar stratospheric clouds and, therefore, connected with the Antarctic ozone hole. Long-range transport of NO_x (and its reaction products) produced by lightning in the low-latitude troposphere and lower stratosphere and NO_x produced by N_2O oxidation within the lower stratosphere may also be important sources for NO_3^- in precipitation in high-latitude regions of the southern hemisphere [Legrand and Kirchner, 1990]. However, Likens et al. [1987] report no correlation between the frequency of local lightning and NO_3^- in rainfall at Katherine, Australia. Seasonal variability in NO_3^- over the high-latitude southern oceans is caused by multiple factors of unknown magnitude (see also, Savoie et al. [1993]). Relative to other species (e.g., nss $\text{SO}_4^{=}$, CH_3SO_3^- , HCOO_i , CH_3COO_i), biological processes appeared to be less important sources for NO_3^- in TdP precipitation.

The annual wet-deposition rate of NO_3^- at TdP was $3.6 \text{ eq ha}^{-1} \text{ yr}^{-1}$ ($3.6 \text{ mol ha}^{-1} \text{ yr}^{-1}$) (Table 1). This flux was somewhat lower than Levy et al.'s recent model estimate (H. Levy II et al., NOAA's Geophysical Fluid Dynamics Laboratory, Princeton University, Global deposition and distribution of reactive nitrogen in the troposphere, manuscript in preparation) of $6 \text{ mol ha}^{-1} \text{ yr}^{-1}$. However, when we accounted for the differences in precipitation amounts (Levy et al. use 100 cm yr^{-1} ; we used 75 cm yr^{-1}), the Levy et al. estimate dropped to $4.5 \text{ mol ha}^{-1} \text{ yr}^{-1}$, similar to our measured value. Levy et al. estimate a total NO_y deposition of $14.5 \text{ mol ha}^{-1} \text{ yr}^{-1}$; wet and dry fluxes are approximately

equal. Because of the diverse and poorly quantified sources of oxidized N species, it was difficult to compare our results to estimated emissions as we did for nss $\text{SO}_4^{=}$, and NH_4^+ . However, these estimates provided a useful constraint for the combined sources of oxidized N upwind of TdP.

Phosphorus

The VWA concentration of the nine samples analyzed for orthophosphate (PO_4) was $0.06 \mu\text{mol L}^{-1}$ (Table 1), with a range of $0.02 \mu\text{mol L}^{-1}$ to $0.10 \mu\text{mol L}^{-1}$. Phosphorus data for other regions are limited. At Lago Yelcho near Puerto Monte, Chile, the concentrations of orthophosphate and total phosphorus in six precipitation samples ranged from below detection limits to $0.08 \mu\text{mol L}^{-1}$ and from 0.1 to $0.2 \mu\text{mol L}^{-1}$, respectively (D. Soto, unpublished data, Universidad Austral de Chile, 1994). At Katherine, Australia, the VWA concentration for PO_4 in ten samples collected during 1990 was $0.10 \mu\text{mol L}^{-1}$, with a range of $0.08 \mu\text{mol L}^{-1}$ to $0.14 \mu\text{mol L}^{-1}$ (K. Weathers, unpublished data, Institute of Ecosystem Studies, 1994).

Atmosphere-Biosphere Interactions

The atmosphere and biosphere are integrally linked. Ecological processes in terrestrial and aquatic systems control, to varying degrees, emissions of nitrogen and sulfur compounds to the atmosphere. For instance, seasonal relationships in our data suggest that the biosphere exerted considerable control over atmospheric concentrations of NH_4^+ , nss $\text{SO}_4^{=}$, CH_3SO_3^- , HCOO_i , and CH_3COO_i at TdP. In addition, atmospheric deposition is a major source of water, nutrients, and toxic substances for aquatic and terrestrial ecosystems [e.g., Gorham, 1961; Likens et al., 1977]. Atmospheric deposition may be an important N source for freshwater ecosystems in the TdP region. Preliminary information suggests that freshwater systems in TdP are oligotrophic and perhaps N limited [Soto et al., 1994]. For example, Lago Toro, the largest lake in TdP, has a water volume of 30.2 km^3 with a theoretical turnover time of approximately 13 years. The dominant cations are Ca^{++} and Na^+ ; the dominant anions are HCO_3^- and $\text{SO}_4^{=}$ [Campos et al., 1994a, b]. Between September 1988 and January 1991, the nutrient concentrations of NO_3^- range between $0.36 \mu\text{mol L}^{-1}$ and $2.0 \mu\text{mol L}^{-1}$ and those of PO_4 between $0.06 \mu\text{mol L}^{-1}$ and $0.66 \mu\text{mol L}^{-1}$. The N:P ratio by weight for these dissolved inorganic nutrients is usually below 5, as are the TN:TP molar ratios. In contrast, the N:P ratios in precipitation for those samples in which both elements are measured is 12, with a range of 3-37. These ratios indicate a potential nitrogen limitation for phytoplankton growth in Lago Toro [Soto et al., 1994].

Like many high-latitude terrestrial ecosystems in the southern hemisphere [McGuire et al., 1992], terrestrial ecosystems in TdP are nutrient poor and some are N limited [Soto et al., 1994]. These systems receive nitrogen from several sources, including atmospheric deposition, nitrogen fixation, mineralization, and migrating animals. Net primary production (NPP) by terrestrial ecosystems at the latitude of TdP requires $360\text{-}2,600 \text{ mol ha}^{-1} \text{ yr}^{-1}$ of nitrogen ($0.5\text{-}3.7 \text{ g N m}^{-2} \text{ yr}^{-1}$ [Melillo et al., 1993]). Since the last glaciation about 10,000 years ago, these ecosystems have

Table 3. Chemical Species in Precipitation at Remote Marine and Continental Sites

	Torres del Paine, Chile	Amsterdam Island, Indian Ocean	Katherine, Australia	Barbados, West Indies	Lijiang, China
<i>Volume-weighted average (VWA) concentration, $\mu\text{eq L}^{-1}$</i>					
H ⁺ , total	10.9	8.0	17.1	6.2	9.6
H ⁺ , mineral	5.5	4.5	5.4	2.3	5.9
pH, mineral	5.26	5.35	5.27	5.64	5.23
K ⁺	0.2 ^a	0.4 ^a	0.8 ^b	0.3 ^a	0.3 ^b
Mg ⁺⁺	0.2 ^a	1.9 ^a	1.0 ^b	2.3 ^a	0.4 ^b
Ca ⁺⁺	0.5 ^a	1.3 ^a	1.5 ^b	4.5 ^a	2.0 ^b
NH ₄ ⁺	0.6	2.4	2.8	2.8	4.0
NO ₃ ⁻	0.5	1.0	3.6	2.9	1.5
Cl ⁻	1.6 ^a	7.3 ^a	6.1 ^b	5.4 ^a	1.9 ^b
SO ₄ ⁼	1.2 ^a	3.2 ^a	3.0 ^b	4.0 ^a	5.7 ^b
CH ₃ SO ₃ ⁻	0.19	0.13	---	0.06	---
HCOO ⁻	4.9	3.0	9.6	2.7	2.9
CH ₃ COO ⁻	0.5	0.5	2.1	1.2	0.8
<i>Volume-weighted-average (VWA) concentration, $\mu\text{mol L}^{-1}$</i>					
HCOO _t	5.5	3.2	10.5	2.8	3.1
CH ₃ COO _t	1.0	0.8	4.2	1.8	1.4

Concentrations of K⁺, Mg⁺⁺, SO₄⁼, Cl⁻, and Ca⁺⁺ for Torres del Paine are from this study; for Amsterdam Island, Indian Ocean, from GPCP unpublished data (J. N. Galloway and W. C. Keene, University of Virginia, 1995); for Katherine, Australia, from *Likens et al.* [1987]; for Barbados, from J. N. Galloway and W. C. Keene (University of Virginia, unpublished data, 1995); and for Lijiang, China from *Keene et al.* [1995b].

^aNon-sea-salt concentrations.

^bTotal concentrations.

received most nitrogen from external sources either by (1) fixation of N₂, (2) atmospheric deposition of nitrogen fixed by lightning or by other ecosystems (terrestrial and marine) and then transported to TdP via the atmosphere, or (3) migrating organisms. Over the centuries so much external N has accumulated in the TdP ecosystems that internal cycling (N mineralization) has become the primary source. For example N mineralization in high-latitude boreal forests and grasslands supplies from 640 to 1900 mol ha⁻¹ yr⁻¹ (9–27 kg N ha⁻¹ yr⁻¹ [*McGuire et al.*, 1992]), which is in the same range as required for NPP. Current rates of N deposition (Table 1) are relatively minor nutrient sources for biota when compared to the N supplied by mineralization.

Galloway et al. [1994] estimate that in 2020 NO_y deposition in this region will increase to about 40 mol ha⁻¹ yr⁻¹ compared to the ~15 mol ha⁻¹ yr⁻¹ that currently exists. Assuming fertilizer use and other agricultural activities in upwind regions results in an equivalent increase in NH_x deposition, total N deposition in the next few decades will be on the order of 100 Tg N yr⁻¹. Given their N-limited status, future increases in N deposition will probably first result in additional productivity of freshwater ecosystems. For terrestrial ecosystems, our projection of 2020 N deposition is well below the estimated mineralization supply rate of 640–1900 mol ha⁻¹ yr⁻¹. However, increased rates of N deposition may indirectly enhance projected increases in NPP from rising CO₂ and perhaps temperature. *Melillo et al.* [1993] suggest that the response of NPP in high-latitude ecosystems to such increases will be dampened because of N limitation. If this limitation is modified by increased atmospheric deposition, then NPP may increase, which, in turn, could affect earth's albedo, water balance, etc. In addition, as N deposition to old-growth forests increases from less than 70 mol ha⁻¹ yr⁻¹ to levels greater than 300 mol ha⁻¹ yr⁻¹, nitrogen losses from watersheds may

begin to increase because of enhanced nitrate formation and discharge [*Hedin et al.*, 1995]. Hence, as the terrestrial ecosystems at TdP receive additional N, mobilization of N to the downstream aquatic ecosystems may increase.

Precipitation Composition at TdP Versus Other Regions

Precipitation composition in remote regions provides information about the likely composition of precipitation in the northern hemisphere before the industrial revolution. Consequently, it can be used as a baseline against which precipitation composition in more populated areas can be assessed [*Galloway et al.*, 1982; 1984; 1987]. The concentrations of nss SO₄⁼, NO₃⁻, and NH₄⁺ in precipitation at TdP were within the ranges of those at other high-latitude sites in the southern hemisphere (Table 2) but were substantially lower than those at marine (Barbados, Atlantic Ocean, and Amsterdam Island, Indian Ocean) and continental (Lijiang, China, and Katherine, Australia) locations at lower latitudes (Table 3). *Galloway et al.* [1984, 1987] compare precipitation composition in remote regions to that in populated regions of the developed and developing world. In all cases, concentrations and depositions of nss SO₄⁼ and NO₃⁻ are significantly greater in the populated regions. The TdP data are consistent with these relationships.

In contrast to the situation for strong mineral acids, concentrations and per-event depositions of carboxylic acids fell within the ranges of values at other remote and impacted locations [e.g., *Keene and Galloway*, 1988]. Such relationships support the hypothesis that carboxylic species primarily originate from biogenic processes that involve either direct emissions or emissions of precursor hydrocarbons. Anthropogenic processes appear to be relatively unimportant

sources for HCOOH and CH₃COOH in the global troposphere.

Any comparison of precipitation acidity in different regions is complicated because pH is not conservative; carboxylic acids and, to a minor extent, the bicarbonate system provide finite buffering capacity. Thus the addition of pollutant mineral acids to precipitation does not correspond to a proportionate change in H⁺ concentrations [Keene *et al.*, 1983]. In addition, many programs do not adequately preserve precipitation samples against microbial degradation after collection. Thus biologically important constituents (e.g., carboxylic acids and NH₄⁺) are often metabolized and lost from untreated samples before analysis, which causes systematic changes (typically increases) in the original pH [e.g., Keene and Galloway, 1984]. Because of these complications, care must be exercised when comparing pH measured in different regions by different programs.

Likens *et al.* [1987] infer a background pH from mineral acids of approximately 5.08 based on the analysis of unpreserved aliquots of precipitation from Katherine, Australia. This approach may slightly overestimate the actual contribution of mineral acids to free acidity for two reasons: (1) residual concentrations of carboxylic acids are occasionally present in such samples [e.g., Galloway *et al.*, 1982], and (2) NH₄⁺ is consumed [e.g., Keene *et al.*, 1983] possibly contributing to free acidity. Because untreated aliquots of sample from TdP were not routinely analyzed and to eliminate the potential for the above problems, we adopted a different approach for estimating the background pH corresponding to mineral acids.

The VWA concentration of H⁺ contributed by carboxylic and mineral acids in precipitation at TdP was 10.9 μeq L⁻¹ (pH = 4.96). To compare this with unpreserved samples of precipitation from polluted regions (and ignoring minor influences of the carbonate system), we subtracted the contributions of dissociated HCOOH and CH₃COOH to free acidity; the residual fraction of H⁺ contributed by mineral acids was 5.5 μeq L⁻¹ (pH = 5.26). Similar calculations for data from other remote sites in both marine and continental regions yielded a tight pH range of 5.23 to 5.64 for the VWA contributions of mineral acids to free acidity (Table 3). This estimated range reflects upper limits for the influence of mineral acids from natural sources since anthropogenic acids undoubtedly contribute minor fractions of free acidity at all these sites [e.g., Moody *et al.*, 1991]. We infer from these data that, on a volume-weighted basis, strong mineral acidity in precipitation of eastern North America [e.g., Galloway *et al.*, 1984] has increased by factors of about 10 to 15 as a result of anthropogenic influences.

Conclusions

Precipitation at TdP was slightly acidic (pH 4.96) with a dilute seawater component. The long fetch across the Pacific Ocean and the strong seasonality in the concentrations and deposition rates of many species (i.e., HCOO_i, CH₃COO_i, nss SO₄⁼, CH₃SO₃⁻, and NH₄⁺) indicated that natural processes were the primary controls. HCOO_i and CH₃COO_i probably originated from a combination of direct biogenic emissions from terrestrial ecosystems and the oxidation of hydrocarbons emitted by marine and terrestrial biota. Nss Cl⁻ was produced by reactions involving sea-salt

aerosol and other atmospheric constituents. Nss SO₄⁼ and CH₃SO₃⁻ primarily originated from the oxidation of (CH₃)₂S from marine biogenic sources. NO₃⁻ probably came from several sources, including local biogenic emissions, lightning, transport of emissions from biomass or fossil-fuel combustion in lower latitudes, and transport from the stratosphere. The concentrations of nss SO₄⁼, NO₃⁻, and NH₄⁺ in precipitation at TdP were within the range of those at other high-latitude sites in the southern hemisphere but were substantially lower than those at marine (Barbados, Atlantic Ocean, and Amsterdam Island, Indian Ocean) and continental (Lijiang, China, and Katherine, Australia) locations at lower latitudes.

In the next few decades, precipitation composition at TdP will most likely change because of internal and external factors, including population growth, and energy and food production. Increased N deposition has the potential to increase the productivity of N-limited aquatic ecosystems.

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References

- Andreae, M. O., Soot carbon and excess fine potassium: Long-range transport of combustion-derived aerosol, *Science*, **220**, 1148-1151, 1983.
- Aristarain, A. J., and R. J. Delmas, Firn core study from the southern Patagonia ice cap, South America, *J. Glaciol.*, **39**, 249-254, 1993.
- Ayers, G. P., J. P. Ivey, and R. W. Gillett, Coherence between seasonal cycles of dimethyl sulphide, methanesulphonate and sulphate in marine air, *Nature*, **349**, 404-406, 1991.
- Bardwell, C. A., J. R. Maben, J. A. Hurt, W. C. Keene, J. N. Galloway, J. F. Boatman, and D. Wellman, A technique using high-flow, dichotomous filter packs for measuring major atmospheric chemical constituents, *Global Biogeochem. Cycles*, **4**, 151-163, 1990.
- Bates, T. S., B. K. Lamb, A. Guenther, J. Dignon, and R. E. Stoiber, Sulfur emissions to the atmosphere from natural sources, *J. Atmos. Chem.*, **14**, 315-337, 1992.
- Berresheim, H., Biogenic sulfur emissions from the sub-Antarctic and Antarctic Oceans, *J. Geophys. Res.*, **92**, 13,245-13,262, 1987.
- Brimblecombe, P., and S. L. Clegg, The solubility and behaviour of acid gases in the marine aerosol, *J. Atmos. Chem.*, **7**, 1-18, 1988.

- Campos, H., D. Soto, W. Steffen, G. Aguero, O. Parra, and L. Zuniga, Limnological studies of Lake del Toro, (Chile): Morphometry, physics, chemistry and plankton, *Arch. Hydrobiol. Suppl.*, *99* (1/2), 199-215, 1994a.
- Campos, H. D. Soto, W. Steffen, O. Parra, G. Aguero, and L. Zuniga, Limnological studies of Lake Sarmiento (Chile): A subsaline lake from Chilean Patagonia, *Arch. Hydrobiol. Suppl.*, *99* (1/2), 217-234, 1994b.
- Chameides, W. L., and D. D. Davis, Aqueous phase source of formic acid in clouds, *Nature*, *304*, 427-429, 1983.
- Charlson, R. J., S. E. Schwartz, J. M. Hales, R. D. Cess, J. A. Coakley, Jr., J. E. Hansen, and D. J. Hoffman, Climate forcing by anthropogenic aerosols, *Science*, *255*, 423-430, 1992.
- Crutzen, P. J., The role of the NO and NO₂ in the chemistry of the troposphere and stratosphere, *Annu. Rev. Earth Planet. Sci.*, *7*, 443-472, 1979.
- Delmas, R., The acidity of polar precipitation, Chapter 10 in *Acid Deposition Assessment Report*, edited by D. M. Welpdale and M. S. Kaiser, in press, WMO/UNEP, Geneva, 1996.
- Dentener, F. J., and P. J. Crutzen, A three-dimensional model of the global ammonia cycle, *J. Atmos. Chem.*, *19*, 331-369, 1994.
- Duce, R. A., et al., Organic material in the global troposphere, *Rev. Geophys.*, *21*, 921-952, 1983.
- Facchini, M. C., et al., Phase-partitioning and chemical reactions of low molecular weight organic compounds in fog, *Tellus*, *44B*, 533-544, 1992.
- Finlayson-Pitts, B. J., Chlorine atoms as a potential tropospheric oxidant in the marine boundary layer, *Res. Chem. Intermed.*, *19*, 235-249, 1993.
- Fishman, J., K. Fakhruzzaman, B. Cros, and D. Nganga, Identification of widespread pollution in the southern hemisphere deduced from satellite analyses, *Science*, *252*, 1693-1696, 1991.
- Galloway, J. N., The deposition of sulfur and nitrogen from the remote atmosphere, background paper, in *Biogeochemical Cycling of Sulfur and Nitrogen in the Remote Atmosphere*, edited by J. N. Galloway, R. J. Charlson, M. O. Andreae, and H. Rodhe, pp. 143-175, D. Reidel, Norwell, Mass., 1985.
- Galloway, J. N., and A. Gaudry, The composition of precipitation on Amsterdam Island, Indian Ocean, *Atmos. Environ.*, *18*, 2649-2656, 1984.
- Galloway, J. N., G. E. Likens, W. C. Keene, and J. M. Miller, The composition of precipitation in remote areas of the world, *J. Geophys. Res.*, *87*, 8771-8786, 1982.
- Galloway, J. N., G. E. Likens, and M. E. Hawley, Acid precipitation: Natural versus anthropogenic components, *Science*, *226*, 829-830, 1984.
- Galloway, J. N., D. Zhao, J. Xiong, and G. E. Likens, Acid rain: China, United States, and a remote area, *Science*, *236*, 1559-1562, 1987.
- Galloway, J. N., W. C. Keene, R. S. Artz, J. M. Miller, T. M. Church, and A. H. Knap, Processes controlling the concentrations of SO₄⁻, NO₃⁻, NH₄⁺, H⁺, HCOO^T, and CH₃COO^T in precipitation on Bermuda, *Tellus*, *41B*, 427-443, 1989.
- Galloway, J. N., D. L. Savoie, W. C. Keene, and J. M. Prospero, The temporal and spatial variability of scavenging ratios for nss sulfate, nitrate, methanesulfonate, and sodium in the atmosphere over the North Atlantic Ocean, *Atmos. Environ.*, *27A*, 235-250, 1993.
- Galloway, J. N., H. Levy II, and P. S. Kasibhatla, Year 2020: Consequences of population growth and development on deposition of oxidized nitrogen, *Ambio*, *23*, 120-123, 1994.
- Galloway, J. N., W. H. Schlesinger, H. Levy II, A. Michaels, and J. L. Schnoor, Nitrogen fixation: Anthropogenic enhancement-environmental response, *Global Biogeochem. Cycles*, *9*, 235-252, 1995.
- Gorham, E., Factors influencing supply of major ions to inland waters with special reference to the atmosphere, *Geol. Soc. Am. Bull.*, *72*, 795-840, 1961.
- Graedel, T. E., and T. Eisner, Atmospheric formic acid from formicine ants: A preliminary assessment, *Tellus*, *40B*, 335-339, 1988.
- Graedel, T. E., and W. C. Keene, The tropospheric budget of reactive chlorine, *Global Biogeochem. Cycles*, *9*, 47-77, 1995.
- Hedin, L. O., J. J. Armesto, and A. H. Johnson, Patterns of nutrient loss from unpolluted, old-growth temperate forests: Evaluation of biogeochemical theory, *Ecology*, *76*, 493-509, 1995.
- Hirsch, R. M., and E. J. Gilroy, Methods of fitting a straight line to data: Examples in water resources, *Water Resour. Bull.*, *20*, 705-711, 1984.
- Hynes, A. J., P. H. Wine, and D. H. Semmes, Kinetics and mechanism of OH reactions with organic sulfides, *J. Phys. Chem.*, *90*, 4148-4156, 1986.
- Jacob, D. J., Chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate, *J. Geophys. Res.*, *91*, 9807-9826, 1986.
- Jacob, D. J., and S. C. Wofsy, Photochemical production of carboxylic acids in a remote continental atmosphere, in *Acid Deposition at High Elevation Sites*, edited by M. H. Unsworth and D. Fowler, Kluwer Acad., Norwell, Mass., 1988.
- Keene, W. C., and J. N. Galloway, Organic acidity in precipitation of North America, *Atmos. Environ.*, *18*, 2491-2497, 1984.
- Keene, W. C., and J. N. Galloway, Considerations regarding sources for formic and acetic acids in the troposphere, *J. Geophys. Res.*, *91*, 14,466-14,474, 1986.
- Keene, W. C., and J. N. Galloway, The biogeochemical cycling of formic and acetic acids through the troposphere: An overview of current understanding, *Tellus*, *40B*, 322-334, 1988.
- Keene, W. C., J. N. Galloway, and J. D. Holden Jr., Measurement of weak organic acidity in precipitation from remote areas of the world, *J. Geophys. Res.*, *88*, 5122-5130, 1983.
- Keene, W. C., A. A. P. Pszenny, J. N. Galloway, and M. E. Hawley, Sea-salt corrections and interpretation of constituent ratios in marine precipitation, *J. Geophys. Res.*, *91*, 6647-6658, 1986.
- Keene, W. C., A. A. P. Pszenny, D. J. Jacob, R. A. Duce, J. N. Galloway, J. J. Schultz-Tokos, H. Sievering, and J. F. Boatman, The geochemical cycling of reactive chlorine through the marine troposphere, *Global Biogeochem. Cycles*, *4*, 407-430, 1990.
- Keene, W. C., B. W. Mosher, D. J. Jacob, J. W. Munger, R. W. Talbot, R. S. Artz, J. R. Maben, B. R. Daube, and J. N. Galloway, Carboxylic acids in clouds at a high elevation forested site in central Virginia, USA, *J. Geophys. Res.*, *100*, 9345-9357, 1995a.
- Keene, W. C., Liu Jiaqui, R. S. Artz, J. N. Galloway, J. M. Harris, J. L. Moody, and B. J. B. Stunder, Processes controlling variability in the chemical composition of precipitation at a remote, temperate site in south-central China, poster presented at Fourth Scientific Advisory Council, International Geosphere-Biosphere Programme, Meeting, Beijing, October, 1995b.
- Keene, W. C., D. J. Jacob, and S.-M. Fan, Reactive chlorine: A potential sink for dimethylsulfide and hydrocarbons in the marine boundary layer, *Atmos. Environ.*, in press, 1996.
- Langford, A. O., F. C. Fehsenfeld, J. Zachariassen, and A. S. Schimel, Gaseous ammonia fluxes and background concentrations in terrestrial ecosystems of the United States, *Global Biogeochem. Cycles*, *6*, 459-483, 1992.
- Legrand, M. R., and C. Feniet-Saigne, Methanesulfonic acid in South Polar snow layers: A record of strong El Nino?, *Geophys. Res. Lett.*, *18*, 1991.
- Legrand, M. R., and S. Kirchner, Origins and variations of nitrate in South Pole precipitation, *J. Geophys. Res.*, *95*, 3493-3507, 1990.
- Legrand, M., and C. Saigne, Formate, acetate and methanesulfonate measurements in Antarctic ice: Some geochemical implications, *Atmos. Environ.*, *22*, 1011-1017, 1988.
- Legrand, M. R., C. Feniet-Saigne, E. S. Saltzman, and C. Germain, Spatial and temporal variations of methanesulfonic acid and non-sea-sulfate in Antarctic ice, *J. Atmos. Chem.*, *14*, 245-260, 1992.
- Likens, G. E., F. H. Borman, R. S. Pierce, J. S. Eaton, and N. M. Johnson, *Biogeochemistry of a Forested Ecosystem*, 146 pp., Springer-Verlag, New York, 1977.
- Likens, G. E., W. C. Keene, J. M. Miller, and J. N. Galloway, Chemistry of precipitation from a remote, terrestrial site in Australia, *J. Geophys. Res.*, *92*, 13,299-13,314, 1987.

- Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McElroy, Atmospheric chemistry: A global perspective, *J. Geophys. Res.*, **81**, 7210-7254, 1981.
- Madronich, S., and J. G. Calvert, Permutation reactions of organic peroxy radicals in the troposphere, *J. Geophys. Res.*, **95**, 5697-5715, 1990.
- Martens, C. S., J. J. Wesolowski, R. C. Harriss, and R. Kaifer, Chlorine loss from Puerto Rican and San Francisco Bay area marine aerosols, *J. Geophys. Res.*, **78**, 8778-8792, 1973.
- Maupetit, F., and R. J. Delmas, Chemical composition of falling snow at Dumont D'Urville, Antarctica, *J. Atmos. Chem.*, **14**, 31-42, 1992.
- Mayewski, P. A., and M. R. Legrand, Recent increase in nitrate concentration of Antarctic snow, *Nature*, **346**, 258-260, 1990.
- McGuire, A. D., J. M. Melillo, L. A. Joyce, D. W. Kicklighter, A. L. Grace, B. Moore III, and C. J. Vorosmarty, Interactions between carbon and nitrogen dynamics in estimating net primary productivity for potential vegetation in North America, *Global Biogeochem. Cycles*, **6**, 101-124, 1992.
- Melillo, J. M., A. D. McGuire, D. W. Kicklighter, B. Moore III, C. J. Vorosmarty, and A. L. Schloss, Global climate change and terrestrial net primary production, *Nature*, **363**, 234-240, 1993.
- Miller, J. M., J. L. Moody, J. M. Harris, and A. Gaudry, A 10-year trajectory flow climatology for Amsterdam Island, 1980-1989, *Atmos. Environ.*, **27A**, 1909-1916, 1993.
- Moody, J. L., A. A. P. Pszenny, A. Gaudry, W. C. Keene, J. N. Galloway, and G. Polian, Precipitation composition and its variability in the southern Indian Ocean: Amsterdam Island, 1980-1987, *J. Geophys. Res.*, **96**, 20, 769-20,786, 1991.
- Mulvaney, R., E. C. Pasteur, D. A. Peel, E. S. Saltzman, and P. Y. Whung, The ratio of MSA to non-sea-salt sulphate in Antarctica Peninsula ice cores, *Tellus*, **44**, 295-303, 1992.
- Munger, J. W., D. J. Jacob, B. C. Daube, L. W. Horowitz, W. C. Keene, and B. G. Heikes, Formaldehyde, glyoxal, and methylglyoxal in air and cloudwater at a rural mountain site in central Virginia, *J. Geophys. Res.*, **100**, 9325-9333, 1995.
- Murphy, J., and J. P. Riley, A modified single solution method for the determination of phosphate in natural waters, *Anal. Chim. Acta*, **27**, 30, 1962.
- Nguyen, B. C., N. Mihalopoulos, J. P. Putaud, A. Gaudry, L. Gallet, W. C. Keene, and J. N. Galloway, Covariations in oceanic dimethyl sulfide, its oxidation products and rain acidity at Amsterdam Island in the southern Indian Ocean, *J. Atmos. Chem.*, **15**, 39-53, 1992.
- Pszenny, A. A. P., Particle size distributions of methanesulfonate in the tropical Pacific marine boundary layer, *J. Atmos. Chem.*, **14**, 273-284, 1992.
- Pszenny, A. A. P., A. J. Castelle, J. N. Galloway, and R. A. Duce, A study of the sulfur cycle in the Antarctic marine boundary layer, *J. Geophys. Res.*, **94**, 9818-9830, 1989.
- Quinn, P. K., R. J. Charlson, and T. S. Bates, Simultaneous observations of ammonia in the atmosphere and ocean, *Nature*, **335**, 336-338, 1988.
- Sanhueza, E., and M. O. Andreae, Emission of formic and acetic acids from tropical savanna soils, *Geophys. Res. Lett.*, **18**, 1707-1710, 1991.
- Sanhueza, E., M. Santana, and M. Hermoso, Gas- and aqueous-phase formic and acetic acids at a tropical cloud forest site, *Atmos. Environ.*, **26A**, 1421-1426, 1992.
- Santana, A., H. Fuenzalida, and P. Aceituno, El inestable clima de TdP hoy y un pronostico para el futuro, paper presented at A Patagonia Gem--The Ecology and Natural History of a World Biosphere Reserve: TdP National Park, Chile, Santiago, Chile, Jan. 10-12, 1992.
- Savoie, D. L., J. M. Prospero, R. J. Larsen, Huang F., M. A. Izaguirre, Huang T., T. H. Snowdon, L. Custals, and C. G. Sanderson, Nitrogen and sulfur species in Antarctica aerosols at Mawson, Palmer Station, and Marsh (King George Island), *J. Atmos. Chem.*, **17**, 95-122, 1993.
- Schlesinger, W. H., and A. E. Hartley, A global budget for atmospheric NH₃, *Biogeochemistry*, **15**, 191-211, 1992.
- Shepson, P. B., D. R. Hastie, H. I. Schiff, M. Polizzi, J. W. Bottenheim, K. Anlauf, G. E. Mackey, and D. R. Karecki, Atmospheric concentrations and temporal variations in C₁-C₃ in carbonyl compounds at two rural sites in central Ontario, *Atmos. Environ.*, **25**, 2001-2015, 1991.
- Singh, H. B., and P. L. Hanst, Peroxyacetyl nitrate (PAN) in the unpolluted atmosphere: An important reservoir for nitrogen oxides, *Geophys. Res. Lett.*, **8**, 941-944, 1981.
- Singh, H. B., et al., Relationship between peroxyacetyl nitrate and nitrogen oxides in the clean troposphere, *Nature*, **318**, 347-349, 1985.
- Soto, D., H. Campos, W. Steffan, O. Parra, and L. Zuniga, The Torres del Paine lake district (Chilean Patagonia): A case of potentially N-limited lakes and ponds. *Arch. Hydrobiol. Suppl.*, **99**, 181-197, 1994.
- Talbot, R. W., K. M. Beecher, R. C. Harriss, and W. R. Cofer III, Atmospheric geochemistry of formic and acetic acids at a midlatitude temperate site, *J. Geophys. Res.*, **93**, 1638-1652, 1988.
- Talbot, R. W., M. O. Andreae, H. Berresheim, D. J. Jacob, and K. M. Beecher, Sources and sinks for formic, acetic, and pyruvic acids over Central Amazonia, 2, Wet season, *J. Geophys. Res.*, **95**, 16,799-16,811, 1990.
- Talbot, R. W., B. W. Mosher, B. G. Heikes, D. J. Jacob, J. W. Munger, B. C. Daube, W. C. Keene, J. R. Maben, and R. S. Artz, Carboxylic acids in the rural continental atmosphere of the Eastern United States during SCAPE, *J. Geophys. Res.*, **100**, 9335-9343, 1995.
- Wilson, T. R. S., Salinity and the major elements of sea water, in *Chemical Oceanography*, edited by J. P. Riley and G. Skirrow, pp. 365-413, Academic, San Diego, Calif., 1975.
- Yin, F.-D., D. Grosjean, and J. H. Seinfeld, Photooxidation of dimethyl sulfide and dimethyl disulfide, I, Mechanism development, *J. Atmos. Chem.*, **11**, 309-364, 1990.

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