

Wet and dry deposition of nitrogen compounds in the southeast Pacific coast: Montemar, central Chile

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Abstract. Atmospheric concentration in the marine boundary layer and direct deposition measurements of total nitrate and ammonium for an eastern South Pacific coastal site near Valparaíso, Chile, were carried out during the period January 1992 through March 1993. Concentrations in air for both nitrogen forms exhibit a seasonal pattern with low values in summer and a pronounced increase in winter, having a mean annual concentration of 32.6 nmol m^{-3} for total nitrate and of 44.8 nmol m^{-3} for total ammonium. Wet deposition is characterized by annual precipitation weighted concentrations of 6.0 and $8.1 \text{ } \mu\text{mol dm}^{-3}$ for nitrate and ammonium, respectively. The main factor regulating wet deposition for both nitrate and ammonium is rainfall amount, so that changes in precipitation amount alone originated by climatological factors can produce changes in their relative deposition levels. Existing climatological pattern determines an overall dominance of dry over wet deposition, with totals of 12.9 and 7.34 mmol m^{-2} per year, the reduced forms of nitrogen being generally more abundant.

Introduction

Air to sea flux of nitrogen compounds plays an important role in the biogeochemical cycling of that element. Growing interest in understanding the processes involved in the transfer to the sea of both oxidized and reduced forms of nitrogen led to a number of publications addressing the questions of their atmospheric concentrations and deposition over the past decade [e.g., Ayers and Gras, 1980, 1983; Galloway *et al.*, 1983; Galloway and Gaudry, 1984; Galloway, 1985; Knap *et al.*, 1986; Galloway and Welpdale, 1987; Hastie *et al.*, 1988; Prospero and Savoie, 1989; Prado-Fiedler, 1990a]. Since the works of Brimblecombe and Stedman [1982] giving evidence of a remarkable long-term increase of nitrate concentrations in rain and of Paerl [1985] showing the possibility of significant enrichment of coastal primary production derived from nitrate enriched rainwater, the impact of atmospheric deposition on new production has been considered very important and has been taken into account in new reviews on the matter [Legendre and Gosselin, 1989; Sharp, 1991].

Global estimates of the impact of atmospheric input on open ocean productivity were first given by Duce [1986]. More recent flux estimates on a global scale have been given by Duce *et al.* [1991]. This last work illustrates the important fraction of total oxidized nitrogen entering the ocean by wet deposition and the marked northern/southern hemisphere contrast in fluxes. The growing significance of atmospheric nitrogen deposition in determining alterations of primary productivity, nutrient fluxes, and trophic changes leading to coastal eutrophication on a regional scale has been recently revised by Paerl [1993]. Depending on the source strengths and the receiving environment, from 10% to more than 50% of coastal nitrogen loading can stem from wet and dry deposition alone [Prado-Fiedler, 1990a; Loye-Pilot *et al.*, 1990; Duce, 1991; Fisher

and Oppenheimer, 1991]. Because of research being concentrated in the northern hemisphere, especially in the North Atlantic, there is a lack of actual deposition data for all southern oceans. Their necessity was regarded as critical by Duce *et al.* [1991]. Moreover, a substantial increase of the emission rates of NO_x in the next 25 years should be expected for the southern hemisphere, as a result of the combination of the rates of industrial development with population growth [Galloway, 1989]. Published data of measured deposition fluxes of nitrate and ammonium in marine and coastal locations of the South Pacific Ocean are restricted to its west part [Pszenny *et al.*, 1982; Savoie *et al.*, 1994]. This hampers the comparison of computed fluxes with direct deposition measurements. Here the results of the first annual study of atmospheric inputs of both species for an eastern South Pacific location are given.

Methods

Sampling was carried out facing the sea on the roof of the approximately 15 m high building of the Oceanographic Institute Montemar, Universidad de Valparaíso, located at Viña del Mar, Chile ($33^{\circ}02'S$, $71^{\circ}34'W$). The sampling site is directly on the shore of the Valparaíso Bay, looking with an unobstructed view toward the Pacific Ocean. Prevailing winds come with few exceptions from the sea landward all the year round, blowing from the southwest during good weather conditions and from the northwest during frontal passage or storm events. The climate corresponds to a Mediterranean type, with a longer dry season and rain concentrated between May and August (wintertime). Relative humidity has a mean of 77% in summer and 86% in winter.

Atmospheric total nitrate and ammonium were sampled with filter packs containing a polytetrafluoroethylene (PTFE)-Nylon-W41 filter combination. The methodology described by Church *et al.* [1991] was applied, including the indications of Anlauf *et al.* [1985] relative to the extraction procedures. The filtration system had a characteristic air flux of $14 \text{ dm}^3 \text{ min}^{-1}$. Filter packs were changed weekly during the dry season and after each rain event during wet periods. Depending on this operation time, air sampled by each

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pack ranged from 21 to 155 m³. Sampling began on January 1992 and ended in March 1993. A total of 71 filter pack samples were collected during the sampling period.

The onset of precipitation in 1992 was March, and events ceased by the end of November. All the precipitation events that occurred in that period were collected. Precipitation samples were collected on an event basis using an automatic wet-only sampler having a PTFE funnel of 11.68 cm internal diameter fitted with 1000 cm³ bottles of fluorinated ethylene propylene (FEP). All parts in contact with the sample were cleaned using a 2% solution of EXTRAN® MA 03 followed by thorough rinsing in high-purity deionized water. A blank was carried out before each sample bottle installation to ascertain background levels on the sampler as well as any analyte introduced by our handling and sampling procedures, making a total of 30 blanks. Full procedural blanks performed on the rain sampling equipment gave concentrations for nitrate and ammonium which were always less than 3% of the sample concentrations, making negligible contribution to the volume weighted mean. These blanks are therefore ignored. To prevent biological activity in the precipitation samples between the rain event and the laboratory analysis, the sampling bottle was placed in darkness by covering it with a foil during collection. Laboratory tests showed no significant loss within a day with this procedure. Rain samples were analyzed immediately after retrieval (with a delay of minutes after event stop during the day or a few hours in case of event stop at evening, having a maximum delay of 11 hours overnight).

The collection efficiency of the rainfall sampler was assured by comparing it to a standard meteorological gauge having an analogic recorder and staying 2 m apart. With the exception of two copious events, the rainfall collected by the sampler was somewhat less than that of the standard gauge. Differences for rainfall amounts greater than 1 mm were 6.3% on average, with only one case reaching up to 26% (last event of the year in November). For rainfall amounts less than 1 mm (six cases), the average negative differences of the sampler were 28%, climbing 2 times up to 50%. This reduced sampling efficiency for short events of light rain appears to be due to the slightly heated rain sensor adjusted to avoid the opening of the sampler lid in the case of fog.

Taking into account that there are almost always at least 2 months with no precipitation in the study area and recognizing that there is no simple device capable of measuring accurately the dry deposition flux directly, PTFE surrogate surfaces were used to obtain a semiquantitative picture on dry deposition temporal trends. This information was complemented with the measurements of atmospheric concentrations, using the filter packs so far described. The utilized surfaces were PTFE disks of 11.7 cm diameter, having no rims and placed beside the rain sampler. The disk was covered automatically with a lid to protect the sample in the case of rain. The deposited material was rinsed weekly with deionized water and aliquots of the extract were analyzed for nitrate and ammonium.

Nitrate was determined by reduction with copperized cadmium followed by the sulfanilamide/N-(1-naphthyl)-ethylenediamine colorimetric method [Grasshoff, 1983] and ammonium using indophenol colorimetric method [Koroleff, 1983] (with small dilution modifications for the samples). Analytical detection limits of the techniques (3 s.d. on replicate determinations of the blank) were 0.1 and 0.2 $\mu\text{mol dm}^{-3}$, respectively. The variation of tenfold repeated measurements of rainwater samples for nitrate was $\pm 2.1\%$ and for ammonium was $\pm 3.2\%$. The recovery rate of added nitrate and ammonium in rainwater was 98.6% and 97.4%, respectively. Calibration was done with fresh working standards prepared daily from 10.0 mmol dm⁻³ stock NO₃⁻ and NH₄⁺ standards.

Wet deposition was computed for each sample as the product of the measured precipitation height multiplied by the concentration of

interest. The overall uncertainty in wet deposition was derived mainly from collection efficiency and is 15% for nitrate and 11% for ammonium.

Results and Discussion

Filter pack Sampling

No significant correlation was found between total nitrate or ammonium and air volume sampled. That was also the case for the particulate phases but not for the gas forms for which a significant positive correlation at an $\alpha=0.05$ resulted. This correlation was more evident for HNO_{3(g)}. Therefore no attempt was made to analyze the data set for the sampled particulate or gaseous forms separately.

The uncertainties already described for the filter pack technique regarding the quantitative estimation of the gas components HNO₃ and NH₃ make this method in that sense limited. As pointed out elsewhere, filter samples are subject to more volatilization losses than others [Zhang and McMurry, 1992]. This volatilization may determine an overestimation of approximately 10-15% of the gaseous species in coastal regions [Schwikowski et al., 1988]. Recent intercomparison with diffusion techniques revealed that the discrimination between nitric acid and nitrate by means of teflon-nylon filter packs is not properly obtained, particularly in the presence of high ammonium nitrate concentrations [Febo et al., 1993]. Differences in the measurement of particulate nitrates, giving some lower values especially at night, have been also reported [Anlauf et al., 1985]. Negative artifacts in particulate nitrate measurements are reactions among particles, reactions between collected particles and flowing air stream, and reactions between collected particles and sample substrates. Volatilization of NH₄NO₃ from the teflon filter within the filter pack could render enhanced levels of HNO₃ on the nylon filter and NH₃ on the W41 filter. NH₃ may also be neutralized by acids collected upon the nylon filter. Lack of knowledge of the concentration levels of NH₄NO₃ and NH₄Cl in the coastal regions of Chile makes this a source of uncertainty. Reactions between nitrate deposits and particulate and gaseous strong acids were found to be important mechanisms for nitrate losses for samples collected in Los Angeles [Appel and Tokiwa, 1981]. NO₃⁻ production on NaCl as a surface product has not been observed in the NO₂ or N₂O₅ system even with relative humidities of up to 80%, but a significant contribution to the budget of HNO₂ appears in coastal areas with high NaCl content in the aerosol and high pollution levels [Junkermann and Ibusuki, 1992]. These limitations and the fact that it yields only integrated concentrations allow this technique to provide only a general idea of the relative variability of the gas plus aerosol nitrogenous species, rendering it incapable of quantifying them separately. Therefore the choice of the filter pack method rests mainly on its simplicity and low cost. Nevertheless, at least for the sum of the gas and aerosol, nitrate artifacts should not be a major problem, since gas-phase HNO₃ accounts for less than about 10% of the total nitrate in the marine boundary layer [Savoie and Prospero, 1982; Church et al., 1991] and the particulate nitrate in the same layer exists predominantly in the supramicrometer sea-salt particles [Gravenhorst et al., 1979; Savoie and Prospero, 1982; Saltzman et al., 1986] which are efficiently retained by the filters used in this study.

Concentrations in Air

A time series plot of the original data of total nitrate and ammonium in air can be seen in Figure 1. An outstanding feature is

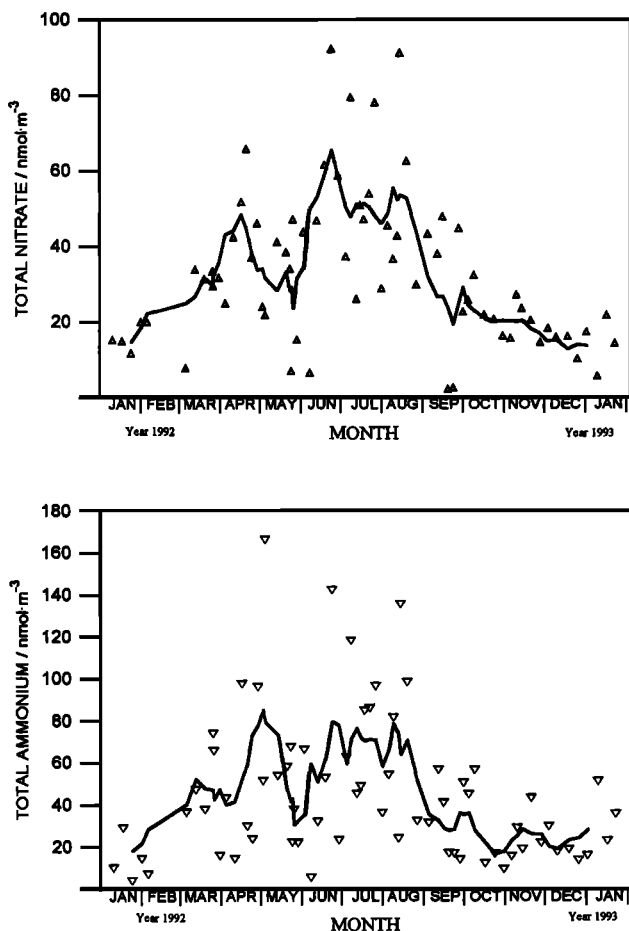


Figure 1. Time series plots of total nitrate (nitric acid plus particulate nitrate) and total ammonium (ammonium plus ammonia) in air for January 1992 through January 1993. Triangles represent actual samples. The lines connect five term moving averages calculated from samples to show time trends.

the higher variability shown by the data between March and September; ammonium is usually more abundant and variable than nitrate. Most of the variability is distributed within the range 10-60 nmol · m⁻³, that comprises 80% of the observations for nitrate and 70% for ammonium. Moving averages of concentrations provided to indicate trends as a function of time allow recognition of a more or less common seasonal pattern characterized by low concentrations in summer (December to February) and high concentrations during part of autumn and in winter. This pattern can be due to prevailing winds from the south in summer, while in the cold season north

winds occur frequently. Autumn-winter/spring-summer ratios for nitrate and ammonium are 2.3 and 2.5, respectively. Concentrations begin to rise by February. This rise is more intense in the case of ammonium which reaches its maximum by the end of April. The highest concentrations for total nitrate are found in June. A rapid drop of both nitrate and ammonium levels in the air begins in August, decreasing to less than 30 nmol m⁻³ on average by the end of September. Annual mean concentrations (± standard error) were 32.6 ± 2.4 nmol m⁻³ for nitrate and 44.8 ± 4.1 nmol m⁻³ for ammonium.

There is very little information, if any, on the concentrations of all nitrogen species both gaseous and aerosol for the southeast Pacific. That is especially the case for the reduced species. Data for the coastal southeast Pacific are almost nonexistent. No HNO₃ data is available for that region. There is also a lack of information regarding NH₄⁺ or NH₃ for the southeast Pacific Ocean. Table 1 compares the mean concentrations in the air of total nitrate and ammonium measured in the present study site of the coastal region of central Chile with other available studies in the South Pacific.

The higher values for Montemar indicate that the data obtained here cannot be considered representative of southern hemisphere background. If the concentrations measured in the central South Pacific are considered representative of its oceanic background, then roughly 99% of the total nitrate and 97% of the total ammonium measured in air of the Valparaiso Bay is derived from continental sources. Comparable results with a range of 21 to 164 nmol · m⁻³ have been reported for ammonium stemming from Australian continental origin at Cape Grim, Tasmania [Ayers and Gras, 1983]. Part of the continental-derived nitrate at Montemar could be a local effect overlapping the total nitrate stemming from long distance transport, since the sampling site is close northerly to Valparaiso-Viña del Mar and is therefore susceptible to being sometimes affected by the emissions of the city, driven by local wind conditions. The predominant winds for the area blow from the southwest sector, with a frequency of 49% during the year and a mean speed of 7.7 m s⁻¹ in summer and 4.6 m s⁻¹ in winter. These SW winds are able to transport the nitrogenous species emitted in Valparaiso to the sampling point. There are no emission inventories available for this region. An approximate picture of emitted oxidized nitrogen can be formed from the data of the number of vehicles in the city and the national statistics of fuel consumption. This shows a rather smooth trend throughout the year with a small 10% increase in emissions in January-February that contrasts with the lower concentrations of total nitrate measured in the air (Figure 1). The presence of a copper refinery and a thermal power station at Ventanas de Quintero, some 20 km north of the sampling site, both with massive emissions, may also affect nitrate concentrations during north wind periods. Such winds have a frequency of 15-17% of the year, being concentrated in winter (up to 24% of the time

TABLE 1. Concentrations of Nitrate and Ammonium in the Air of Different South Pacific Regions

Type	Nitrate	Ammonium	Location	Reference
Remote oceanic regions	0.32-0.40		South Pacific	Savoie et al. [1989a] Duce et al. [1991]
Coastal regions		2	central South Pacific	Parungo et al. [1986]
	3.1	4.3	Cape Grim, Tasmania	Ayers and Gras [1983]
	1.84		New Zealand	Savoie et al. [1989a, b]
	1.1		American Samoa	Savoie et al. [1994]
	32.6	44.8	southeast Pacific border	Duce et al. [1991]
			Montemar, Valparaiso/Chile	present work

Concentration units are in nmol m⁻³.

with a mean speed of 4.2 m s^{-1}] and almost absent in summer. Peak concentrations of nitrate were coincident with north winds preceding storm events in winter. The higher content of total nitrate in the air during winter shown by Figure 1 may be therefore attributed to a near-source effect.

Dry Deposition

Estimates of the annual deposition of nitrate and ammonium computed from the measurements carried out during the whole year 1992 are given in Table 2. Dry deposition measurement is difficult to carry out, and no single method can be regarded as better suited for that purpose [Hicks *et al.*, 1993; Erisman *et al.*, 1994]. With few exceptions, use of indirect methods for dry deposition measurement has been discouraged on the grounds that these methods are insufficiently accurate for routine monitoring use [Hicks *et al.*, 1980]. In the same document, Davidson and Lindberg [1980] argued that surrogate surfaces complemented with measurements of atmospheric concentrations may be able to provide useful semiquantitative information. So far, different solid surfaces have been preferentially used for that purpose [Dasch, 1985], recognizing that deposition appears to be strongly influenced by the affinity of the surface for gases and the retention characteristics of the surface for particles. The gaseous collection of HNO_3 by such surfaces is of negligible importance until wet [Dasch, 1985]. The evident lack of capacity of surrogate surfaces to simulate the characteristics of the receiving natural surface results in serious criticism of the reliability of dry deposition estimates obtained by using them. Nevertheless, a relatively good agreement (within a factor of 3) has been found for dry deposition between results from model calculations and direct measurements using surrogate surfaces [Arimoto *et al.*, 1985]. Surrogate surfaces may thus provide a simple means of obtaining some indication on temporal trends in dry deposition. Within this context, an estimate of the dry deposition of nitrate and ammonium was set out here, obtained by using a PTFE surface and by determining their concentrations in air. The approach based on atmospheric concentrations relies on the estimate of the dry deposition velocity. Average deposition velocities can be obtained by means of the so-called granulometric approach of the mass distribution [Arimoto and Duce, 1986] or directly from cascade impactor data [Dulac *et al.*, 1989]. Since the necessary equipment to do that was not available for this study, the estimate of 0.25 cm s^{-1} given by Savoie *et al.* [1987] for nitrate and that of 0.21 cm s^{-1} for ammonium given by Rendell *et al.* [1993] were adopted here. Dry deposition at Montemar can be approximated by a minimum of about $0.5 \mu\text{mol m}^{-2} \text{ d}^{-1}$

and a maximum of almost $20 \mu\text{mol m}^{-2} \text{ d}^{-1}$ for nitrate (up to $30 \mu\text{mol m}^{-2} \text{ d}^{-1}$ for ammonium, with a similar minimum). Estimates from surrogate surface for each month are given in Table 2. Dry deposition appears to dominate total deposition. The long dry period in this region with no less than 2 months with total absence of rain seems to determine the greater contribution of the dry deposition.

Wet Deposition Processes

Nitrate as well as ammonium concentrations in rain do not show any recognizable time trend. Their highest values irrespective of the season are found for events recording less than 1 mm rainfall. For precipitation amounts greater than 1 mm, ammonium only once reached more than $100 \mu\text{mol dm}^{-3}$ and nitrate always remained below that concentration. Annual precipitation weighted average concentrations were $6.0 \mu\text{mol dm}^{-3}$ for nitrate and $8.1 \mu\text{mol dm}^{-3}$ for ammonium. An analysis of the rain amounts, the aqueous concentrations, and the resulting wet deposition showed that the variability of the latter is mainly explained by rainfall amount differences. Deposition on an event basis showed a significant positive correlation with rainfall amount at an $\alpha=0.01$ for both nitrate ($r=0.570$) and ammonium ($r=0.619$). There is no correlation to concentration. The highest figures for event deposition were found coinciding with higher rainfall amounts. Therefore a change in precipitation amount alone can produce changes in the relative deposition levels of nitrate and ammonium. The fact of a dominance of the precipitation amount on the control of wet deposition processes for nitrate and ammonium has been established previously [Prado-Fiedler, 1990b]. A similar power law relationship holds for the deposition data of the present work.

Scavenging ratios on a volume basis, defined as the ratio of concentration in rain to concentration in air in $\mu\text{mol dm}^{-3}$ units, could be estimated for 26 rain events. These ratios showed differences of up to 3-4 orders of magnitude, ranging from 4.2×10^4 to 7.88×10^6 for nitrate and from 2.37×10^4 to 1.57×10^7 for ammonium. The wide variability to be expected for scavenging ratios obtained from the paired data of aerosols and precipitation has been stressed in the work of Galloway *et al.* [1993]. Factors affecting the magnitude of scavenging ratios have been addressed by several authors cited therein. These factors are particle size distributions and solubilities, precipitation rates and amounts, droplet accretion processes, gas-phase scavenging, and air mass trajectories. For near continental marine areas, evidence of an apparent relationship between the scavenging ratio and the mass median diameter of trace elements particles has been given by Buat-Ménard [1986]. Such a

TABLE 2. Monthly Wet and Dry Deposition of Nitrate and Ammonium at the Coast of Montemar, Chile ($33^{\circ}02'S$, $71^{\circ}34'W$), During 1992

Month	NH_4^+ Wet, $\mu\text{mol m}^{-2}$	NH_4^+ Dry, $\mu\text{mol m}^{-2}$	NO_3^- Wet, $\mu\text{mol m}^{-2}$	NO_3^- Dry, $\mu\text{mol m}^{-2}$	Total, $\mu\text{mol m}^{-2}$
Jan.	0	749	0	908	1,657
Feb.	0	684	0	663	1,347
Mar.	237	66	209	283	795
April	557	1,606	466	156	2,785
May	1,827	1,133	548	100	3,608
June	681	16	822	13	1,532
July	96	19	95	16	226
Aug.	478	88	506	100	1,172
Sep.	241	715	369	778	2,103
Oct.	0	738	0	866	1,604
Nov.	111	719	95	837	1,762
Dec.	0	747	0	907	1,654
Year	4,228	7,280	3,110	5,627	20,245

relationship was not found for remote marine environments [Buat-Ménard and Duce, 1986]. The present data of continental coastal nature suggest the existence of a significant negative log-log relationship between individual paired scavenging ratios and precipitation amount at $\alpha=0.05$ (Figure 2). An explanation for this relationship could be a gradual reduction in the below-cloud scavenging contribution with increasing rainfall amount. Similar correlations for nitrate, sodium, and non-seasalt sulphate were reported by Savoie *et al.* [1987] for rainfall at Virginia Key and American Samoa. For the purpose of estimation of wet deposition fluxes, temporally averaged scavenging ratios should be used; those based on average aerosol and precipitation weighted means are the most appropriate [Galloway *et al.*, 1993]. Such annual mean scavenging ratios, obtained here on a volume basis from the annual precipitation weighted averages and annual mean concentrations in air indicated above, are 1.36×10^5 for nitrate and 1.37×10^5 for ammonium. Wet deposition estimates rendered by using them fell within 0.2% of actual values for nitrate and 0.4% for ammonium.

Regarding the proportion between oxidized and reduced forms of nitrogen in wet deposition, there is an overall dominance of the reduced forms, 57.6% of the nitrogen being deposited as ammonium during the year. Notwithstanding this fact, there is no clear-cut dominance of ammonium over nitrate all year round. A slight dominance of nitrate was observed in winter and spring events. Since each rain event has its own $\text{NH}_4^+:\text{NO}_3^-$ ratio and they occur at random, no tendency can be seen by looking at the indi-

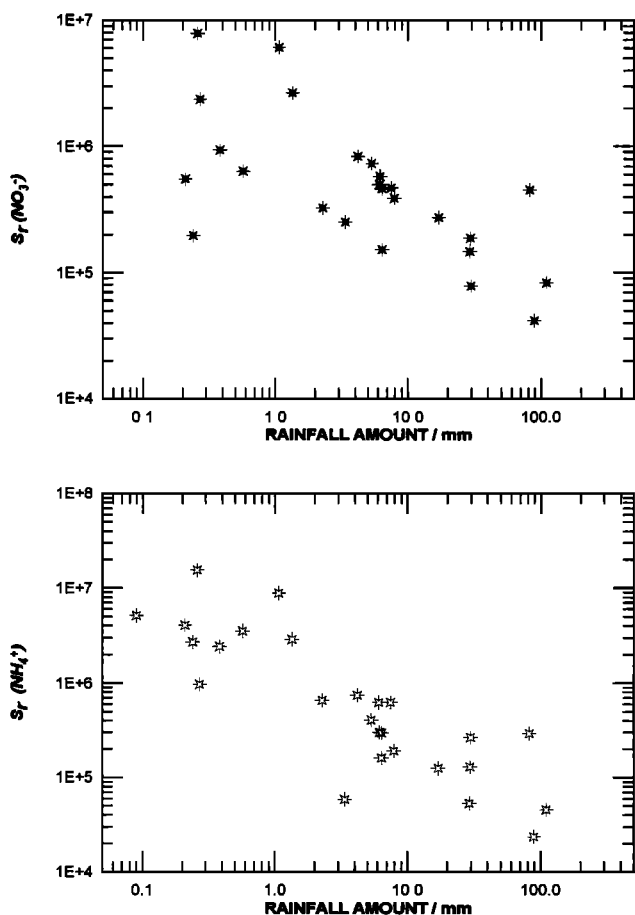


Figure 2. Variation of scavenging ratios S_r for nitrate and ammonium as a function of rainfall amount. Scavenging ratios are given on a volume basis, calculated from micromolar concentrations.

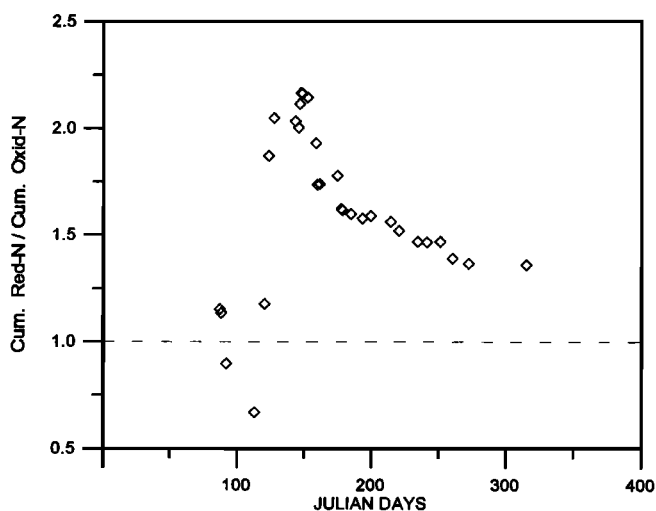


Figure 3. Time trend during 1992 of the ratio between cumulated wet deposition of reduced nitrogen (total ammonium) and cumulated wet deposition of oxidized nitrogen (total nitrate).

vidual events in a time plot. However, if the proportion of the cumulated wet deposition is plotted against time, a clear trend appears (Figure 3). The overall dominance of the reduced state is herewith obvious, with only a short time at the beginning of autumn characterized by ratios below 1. This is followed by a steep increase of the cumulated $\text{NH}_4^+:\text{NO}_3^-$ ratio that reaches its maximum by the end of May, declining almost continuously afterward because of changes in the deposition rates. This marked seasonality of the ammonium wet deposition is also reflected by a higher dry deposition in autumn, for which ammonium constitutes 74% of total deposited.

Regarding the meteorological conditions associated with the observed deposition, a classification of weather data was done by means of weather maps. Synoptic conditions for rain are mostly due to cold fronts reaching Valparaiso with their northern parts (13 cases out of 18). They can be associated with old depressions located in austral latitudes east of the Andes (Figure 4, left) or active depressions in the Pacific Ocean close to the Chilean coast (Figure 4, middle). The weather condition with which most of the events of high wet deposition of nitrogen species were associated was a situation of cold front tails with depressions localized closer to Antarctica at Weddel Sea, at Drake Passage, or at the Falkland Islands. An exceptional situation of high wet deposition was given by a stationary front occluding at the coast producing heavy rain during two days (Figure 4, right). Events with low deposition fluxes were associated with cold fronts and low pressure systems localized over the southeast Pacific at middle latitudes. Only one case of low deposition was associated with a warm front but with similar localization of the low pressure system.

Table 3 shows 18 rain episodes including Julian day, daily total rainfall in millimeters, and nitrate deposition in $\mu\text{mol m}^{-2}$. The fourth column from the left indicates the length of the previous dry period in days ignoring those days in which less than 1 mm was observed; this variable is considered to be bounded to 3 weeks at most. Cloud base, top, and thickness, expressed in hectopascals, were taken as the saturated layer in radiosonde diagrams for Quintero. Winds at 700 and 500 hPa levels (3000 and 5600 m height approximately) were also taken from these diagrams. Zonal and meridional wind components were evaluated. All velocities are expressed in knots. Synoptic patterns are classified in five types,

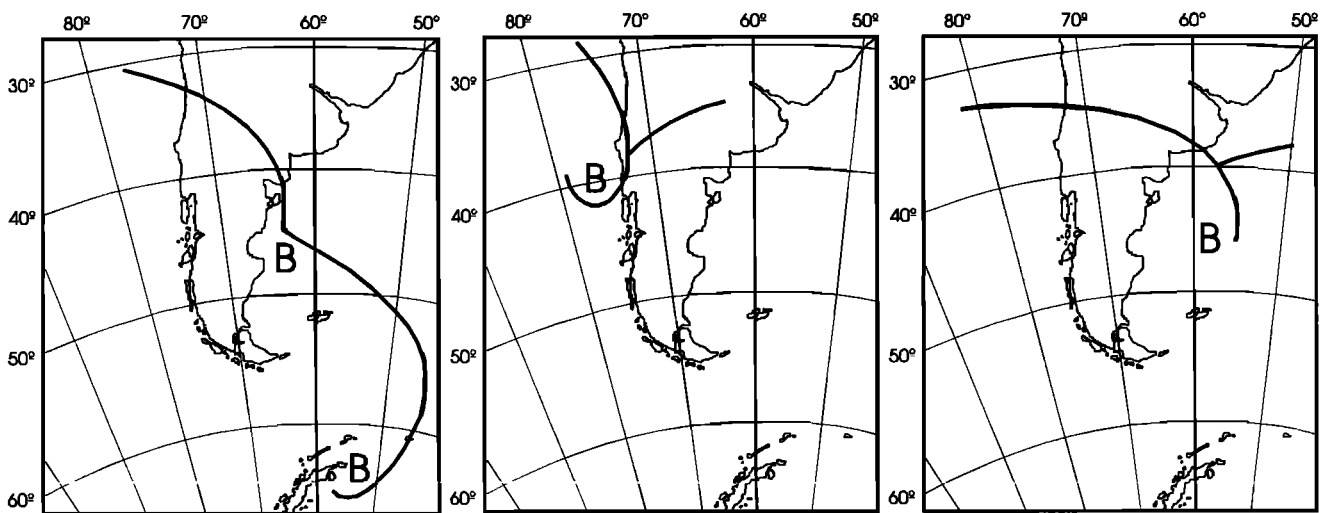


Figure 4. Weather types associated with high deposition of nitrogen species in front of central Chile. (left) Frontal pattern with old depression close to Antarctica, most characteristic weather type that renders high wet deposition. (middle) Frontal pattern with active depression facing central Chile, second most usual weather type giving high wet deposition. (right) Unusual weather situation with semistationary front, also rendering high wet deposition.

cold fronts being the most frequent. Finally, depositions evaluated by multiple regression (to 95% significance) are compared with observed values.

From Table 3, the importance of the previous dry period for large nitrate deposition episodes is apparent. All cases with values

larger than $100 \mu\text{mol m}^{-2}$ occur with dry periods larger than or equal to 1 week except one (day 146) which is the second day of a storm that started after 19 dry days. This indicates that an accumulation period is important. On the other hand, when it rains for more than 1 consecutive day (days 145-147 and 176-177) the last day recorded

TABLE 3. Comparison of Observed per Event Deposition of Nitrate Measured at Montemar and Multiple Regression-Computed Deposition Values for Rain Episodes

Day	Rain, mm	NO_3^- , $\mu\text{mol m}^{-2}$	No Rain, days	Cloud Base, hPa	Cloud Top, hPa	Cloud Thickness, hPa	W Sp 7, knots	W Dir 7, deg	U700, knots	V700, knots	Type	NO_3^- -reg, $\mu\text{mol m}^{-2}$
119	8.0	163	21	650	400	250	10	220	6.4	7.7	2	160
126	110	198	7	1020	500	520	45	330	22.5	-39.0	3	231
145	9.0	44	19	700	650	50	25	310	19.2	-16.1	3	66
146	32.0	110	1	850	400	450	30	330	15.0	-26.0	2	88
147	0.4	0	1	850	500	350	40	310	30.6	25.7	2	23
151	3.0	3	5	900	800	100	15	305	12.3	0.6	2	-39
173	0.6	22	21	600	500	100	20	330	10.0	-17.3	5	96
176	139	342	21	900	500	400	35	330	17.5	-30.3	4	327
177	20.0	0	1	820	480	340	40	340	13.7	-37.6	4	35
183	2.0	43	6	850	700	150	15	330	7.5	-13.0	4	-11
192	0.3	50	9	1000	720	280	25	330	12.5	-21.7	3	64
198	0.2	2	15	640	550	90	10	190	1.7	9.8	3	40
219	8.0	176	21	1020	870	150	40	330	20.0	-34.6	2	121
228	0.2	11	9	1020	850	170	30	340	10.3	-28.2	2	20
234	19.0	290	15	1020	600	420	40	330	20.0	-34.6	2	185
241	5.0	29	7	1020	700	320	40	350	6.9	-39.4	3	66
251	0.4	15	10	1020	930	90	20	340	6.8	-18.8	1	-2
258	28.0	264	19	1020	430	590	35	320	22.5	-26.8	5	293

Stepwise regression is to 95% significance. Table columns are as follows: Julian day number (Day); daily total rainfall (Rain); nitrate measured deposition (NO_3^-); length of the dry period previous to a precipitation event, considered bounded to 3 weeks at most (No Rain); saturated layer in radiosonde diagrams for Quintero, Chile (Cloud Base, Top, and Thickness); wind speed (W Sp 7) and direction (W Dir 7) at 700 hPa (ca. 3000 m) taken from the same diagrams; zonal (U700) and meridional (V700) speed components at 700 hPa; synoptic patterns (type): anticyclonic (1), cold front tail with austral depression (2), cold front with depression on Pacific coast (3), stationary front (4), and warm front (5); and nitrate deposition calculated by multiple regression (NO_3^- -reg).

little nitrate deposition in spite of the 20 mm rain for day 177, suggesting either that below cloud scavenging depleted the storage or that local emissions drift away from Montemar at the final stages of the storm.

Simple linear regressions of nitrate deposition with individual meteorological variables are marginal. In order of importance, they correlate with rainfall, cloud thickness, and number of dry days preceding the event. Dependence of nitrate concentration on precipitation amount has been demonstrated elsewhere [Prado-Fiedler, 1990b]. Nitrate deposition is best explained [82% of the variance] in a multiple regression by cloud thickness, number of previous dry days, and rainfall (at 95% level). Event-related winds do not explain the variations in nitrate concentration, because rain events occur with winds from the NW (13 out of 15 cases analyzed). However, dominant wind on rain events indicate that ascending warm air must have traveled from the north in the atmospheric boundary layer or close to it. In all cases but one with large nitrate deposition (6 cases), winds at 700 hPa are from the NW (330 degrees) during the 36 previous hours. The only case where this does not occur (April 26) the wind in lower levels is from the north during the rain episode.

Low nitrate deposition cases are mostly associated with a shallow saturated layer and/or an elevated cloud base producing little rain. Therefore, in concordance with the above evidence, it is possible to postulate that nitrate rich air comes both from the north and the sea after being accumulated for several days. Assuming that only continental sources can be responsible, only the cities of Valparaíso and Viña del Mar, located a short distance south of the sampling place, and Ventanas de Quintero, some 20 km north of it, can be regarded as important local sources. A thermal power station and a copper refinery, both with massive emissions, are located in Ventanas.

Some local features regarding the accumulation region are worthy of consideration. Along the coast, normal conditions include a strong and persistent subsidence inversion at about 800 m above sea level, prevailing surface winds from the SW, and a sea breeze circulation system. The sea breeze can reach only up to 20 km in the inland direction because of the presence of the coastal range, but toward the sea, it can extend over a larger distance, so that the return flow above the inversion and the coastal cloud can reach quite a large distance into the sea (50 to 100 km). Therefore part of the emissions from both sources in the days preceding a precipitation event are trapped below the trade wind inversion, prevailing along the subtropical coast, and drifting northward while another part is diffused in the land-sea breeze system and transported above the inversion where ozone and solar radiation are responsible for their oxidation to water soluble compounds. When the storm arrives, the northern winds bring back the nitrate rich air, and it rises in the frontal cloud systems. The importance of cloud thickness and rainfall amount on the deposition of nitrogen suggests that in-cloud scavenging is the dominating process for the incorporation of nitrogen compounds into rain.

The relative importance of the two likely sources in the accumulation process is difficult to discriminate. The only fact that points to Valparaíso-Viña del Mar as the main source is the depletion of nitrate in the final stages of storms lasting more than 1 day since this should not occur with north winds coming from Ventanas. The difficulties in establishing a link between sources and concentrations in precipitation have been stressed elsewhere for other regions [e.g., Brook *et al.*, 1993]. This is even more complicated to do here with the limited data available.

There are no other deposition measurements for the whole west side of the South American continent with the exception of the data

of Galloway *et al.* [1996] reported as South Pacific by Duce *et al.* [1991, Table 13]. Galloway's data set, actually measured at the Chilean Torres del Paine National Park in the southernmost part of the continent, show extremely low deposition fluxes for both nitrate and ammonium of about 0.3 and 0.4 mmol m⁻² a⁻¹, respectively. These very low values measured by Galloway are due to several causes: (1) the extremely high rainfall all the year round characterized by several thousand millimetres of precipitation that occurs in the latitudinal belt of the sampling site; (2) the remote nature of the sampling place, rendering almost no anthropogenic contribution to the atmospheric nitrogen species pool in that region of the world; and (3) low annual rainfall in Torres del Paine, decreasing from 1000 mm in western summits to 400 mm on the east side because of its lee side condition of the Andes. Consequently, owing to high dilution and lack of near sources, the fluxes of nitrogen compounds measured by Galloway represent only a small fraction (about 10%) of those given herein for the coast of central Chile. The existing information regarding deposition for South America has been gathered by E. Sanhueza (Depositions in South and Central America, unpublished manuscript, 1993) and is very limited, restricted to that already mentioned plus a location in the Venezuelan savannah and a few other points with short-term measurements in Brazil. These deposition measurements having completely different climate (most tropical) and surrounding conditions (of continental nature) cannot be compared with those given in the present work.

Comparison with deposition fluxes based on global model calculations show that existing model data provide an underestimation of the annual deposition of total nitrate for the coastal area of central Chile. The information of the Global Chemical Transport Model (GCTM) of Geophysical Fluid Dynamics Laboratory / National Oceanic and Atmospheric Administration provide an estimate of the order of 5 mmol m⁻² for total annual NO_x deposition at 35°S 75°W in 1980 [Galloway *et al.*, 1994]. The model of the global universal tracer transport in the atmosphere (MOGUNTIA) of Stockholm University provides estimates of 1.3 mmol m⁻² for annual nitrate wet deposition and 4.4 mmol m⁻² for annual nitrate dry deposition at the same location (L. Gallardo, personal communication, 1994). This represents about 5.7 mmol m⁻² yr⁻¹ of total nitrate deposition. Both model values are consistently lower than the actual measurements. MOGUNTIA also give a higher proportion for dry/wet nitrate deposition, 3.4 against the ratio of 1.8 obtained from the measurements of this work. Moreover, monthly deposition values calculated by the actual version of MOGUNTIA give a bad representation of the seasonality for this latitude.

With the exception of the global estimates of Dentener and Crutzen [1994] model estimates for NH_x deposition were not available for this region. That is not surprising, taken into consideration the inadequate data bases existing for the southern oceans [Duce *et al.*, 1991], the uncertainty of which marine areas could be sources of NH₃ [Quinn *et al.*, 1987, 1988; Warneck, 1988] and the additional difficulties that such facts represent to modelers [Apsimon *et al.*, 1994]. The model of Dentener and Crutzen provide an estimate of the order of 7 mmol m⁻² for total annual NH_x deposition at 35°S 75°W, that is lower than our measurements but with less than 50 % deviation.

Conclusions

Coastal air near Valparaíso is characterized by a greater abundance of total ammonium over total nitrate during most of the year. The origin of both forms of nitrogen is fundamentally continental, especially in the case of nitrate in which an intense local effect overlapping the long distance transportation occurs. Concentrations

of total nitrate and ammonium in the atmospheric marine boundary layer of the studied area show a pronounced seasonal cycle, with their highest values in winter followed by a decrease by the onset of spring (end August).

The long dry period in this region determines a dominance of dry deposition on the atmospheric flux of nitrogen species. Rainfall amount is the main factor that regulates variability of the wet deposition processes. Event scavenging ratios are significantly correlated with precipitation amount in a log-log way. High wet deposition events of nitrate and ammonium associate mostly with cold fronts having depressions close to Antarctica. For nitrate, the duration of the dry period previous to a precipitation event has some importance to deposition. This relationship was not evident for ammonium.

Estimates of concentrations of nitrate and ammonium in air as well as those for their deposition fluxes in the coasts of central Chile can not be extrapolated from available global models. They would render a considerable underestimation because of the fact that part of the nitrogenous species are locally generated. These differences are of more than 1 order of magnitude for the concentration of nitrate in air and 4 times for that of ammonium. The results suggest that nitrate concentrations in rain and the corresponding input to surface coastal waters are partially influenced by emissions exported from coastal urban centers.

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