Available online at www.sciencedirect.com
ScienceDirect
Atmospheric Environment 41 (2007) 4227–4241
ATMOSPHERIC ENVIRONMENT
www.elsevier.com/locate/atmosenv

Nitric acid and the origin and size segregation of aerosol nitrate aloft during BRACE 2002

J.R. Arnold[a,*,1], Winston T. Luke[b]

[a]*Atmospheric Sciences Modeling Division, National Oceanic and Atmospheric Administration, Air Resources Laboratory, 1200 6th Avenue/9th FL/OEA-095, Seattle, WA 98101-1128, USA*
[b]*Air Resources Laboratory, National Oceanic and Atmospheric Administration, Silver Spring, MD, USA*

Received 9 February 2006; received in revised form 19 July 2006; accepted 21 July 2006

Abstract

As part of the BRACE 2002 May field intensive, the NOAA Twin Otter flew 21 missions over terrestrial, marine, and mixed terrestrial and marine sites in the greater Tampa, Florida, airshed including over Tampa Bay and the Gulf of Mexico. Aerosols were collected with filter packs and their inorganic fractions analyzed post hoc with ion chromatography. Anion mass dominated both the fine- (particle diameters $\leqslant 2.5\,\mu$m) and coarse-mode (particle diameters 10.0–2.5 μm) inorganic fractions: SO_4^{2-}in the fine fraction, 3.7 $\mu g\,m^{-3}$ on average and Cl^- and NO_3^- in the coarse fraction, 0.6 $\mu g\,m^{-3}$ on average and 1.4 $\mu g\,m^{-3}$ on average, respectively. Ammonium ion dominated the inorganic fine-mode cation mass, averaging 1.2 $\mu g\,m^{-3}$, presumably in association with SO_4^2. Coarse-mode cation mass was dominated by Na^+, but the concentrations of Ca^{2+} and K^+ together often equaled or exceeded the Na^+ mass which was, on average, 0.6 $\mu g\,m^{-3}$. Nitrate appeared predominantly in the coarse rather than the fine fraction, as expected, and the fine fraction never contributed >15% of the total NO_3 concentration. Nitric acid dominated the NO_3^- contribution from both aerosol size fractions, and constituted at least 45% of the total NO_3 in all samples. Coarse-mode Cl^- depletion, and hence NO_3^- replacement, reached 100% within the first 4 h of plume travel from the urban core in some samples, although it was most often less than 100% and slightly below the expected 1:1 ratio with coarse-mode NO_3^- concentration: the slope of the regression line of NO_3^- concentration to Cl^- depletion was 0.9 in the coarse fraction. In addition, terrestrial samples were markedly lower in Cl^- depletion, and thus in substituted NO_3^-, than were marine and mixed samples: 15–25% depletion in terrestrial samples vs. 50–65% in marine samples with the same air mass age. Thus, we conclude that NO_3^- and its progenitor compound HNO_3 were present in the Tampa airshed in insufficient amounts to titrate fully the slightly alkaline coarse-mode particles there, and to replace completely the Cl^- from the coarse-mode NaCl.
Published by Elsevier Ltd.

Keywords: Sea salt; Chloride depletion; Nitrate limitation; Aerosol constituents; Coastal ecosystems

---

1. Introduction

1.1. Atmospheric production of reactive nitrogen

Human output of reactive nitrogen (N) from production of energy and food now exceeds the

---

*Corresponding author. Tel.: +206 553 8579; fax: +206 553 8210.
E-mail address: arnold.jeff@epa.gov (J.R. Arnold).

[1] In partnership with the National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency.

1352-2310/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.atmosenv.2006.07.059

yields from lightning, bacterial fixation, and all other natural sources (Galloway et al., 2003), an increase that has overwhelmed the natural processes which remove it through denitrification to N_2. The accumulation of reactive N that results has complex negative consequences in the bio-, atmo-, and hydrosphere. On land, anthropogenic N acidifies soils, displacing other nutrients and changing species composition and biodiversity in forests and grasslands. In the atmosphere, nitrogen oxides ($NO_X = NO + NO_2$), chiefly from fossil fuel combustion, lead to production of ozone (O_3), aerosols, and acid rain in the troposphere, to the depletion of O_3 in the stratosphere, and contribute directly and indirectly to global warming and climate change. In the hydrosphere, reactive N from direct sources or deposited from the atmosphere can contaminate ground water, acidify freshwater lakes, streams, and rivers, and produce eutrophic conditions in estuaries and other coastal waters with concomitant loss of sheltering sea grasses and the higher biota supported there (UNEP, 2004; Howarth et al., 2000). Such changes in estuaries and shallow coastal waters may have significant global effects since roughly half of global oceanic primary production is estimated to come from these sites (Paerl, 1995).

An appreciable fraction of the reactive N loadings to critical ecosystems like estuaries comes from the atmospheric deposition of N pollutants, most derived from the NO_X released in fossil fuel combustion for power generation, transportation, and industrial processes. In the troposphere, NO participates in a complex chain of oxidizing chemical reactions driven by ultraviolet light and involving hydrocarbons. Intermediate and end products from this oxidizing chain include a series of odd oxygen (O_X) compounds, where O_X is the category label of all species that can act as reservoirs for atomic oxygen, primarily O_3, NO_2, nitric acid (HNO_3), and peroxyacetyl nitrate (PAN), with minor contributions from short-lived radical species like the nitrate ion (NO_3^-) and from higher organic nitrates ($RONO_2$).

The primary mechanism for odd oxygen production ($P(O_X)$) in the troposphere is the oxidation of NO to NO_2 by the hydroxy (OH) and peroxy (HO_2 and RO_2) radicals as in (R1) and (R2):

$$HO_2 + NO \rightarrow OH + NO_2, \tag{R1}$$

$$RO_2 + NO \rightarrow RO + NO_2. \tag{R2}$$

The NO_2 thus formed can then photolyze, returning the original NO as in (R3), or can undergo OH attack as in (R4):

$$NO_2 + h\nu \rightarrow NO + O(^3P), \tag{R3}$$

$$OH + NO_2 \rightarrow HNO_3. \tag{R4}$$

(R3) propagates $P(O_X)$ while (R5) terminates the reaction series by producing HNO_3, an end product that is largely stable in the troposphere on urban and regional time scales. Nitric acid adsorbs strongly to surfaces, is highly soluble in water and easily incorporated into aerosols, and can directly deposit to surfaces from the gas phase with a deposition velocity (V_d) at the limit of aerodynamic resistance, $1–5\,cm^2\,s^{-1}$. Thus, its lifetime in the troposphere is short, and HNO_3 constitutes the primary sink for NO released to the atmosphere.

1.2. Atmospheric reactive nitrogen in critical estuarine ecosystems

Acidic gas-phase species like HNO_3 in marine environments can be converted to solid or aqueous phase in reaction with solid or liquid sea salt aerosols. The presence of these particulate surfaces for heterogeneous reactions is significant both locally for marine ecosystems and more globally: sea salt's aggregate surface area over a given location represents from 1 to 10% on an annual average of the area of the underlying Earth's surface (Guelle et al., 2001), and 21% of the total column global aerosol surface area (Guelle et al., 2001). Gas- to solid-phase conversion of NO_3^- preferentially partitions HNO_3 in the marine environment onto these more prevalent coarse particles (particle diameters 10.0–2.5 μm), rather than into the fine-mode fraction (particle diameters $\leqslant 2.5\,\mu m$) typically encountered over terrestrial locations. The effect of this NO_3^- size segregation can be to increase the local N deposition, since coarse particles have much higher settling velocities than smaller ones, and to deplete the sea salt aerosol of Cl^-, since the HCl created by uptake of HNO_3 on the particle surface, as in (R5), volatilizes very efficiently (Mamane and Mehler, 1987; Clarke et al., 1999, Zhang et al., 1999):

$$HNO_{3(g)} + NaCl_{(p)} \leftrightarrow HCl_{(g)} + NaNO_{3(p)}. \tag{R5}$$

But NaCl is not the sole marine aerosol component, of course, and reactions analogous to (R5) occur with $CaCl_2$, KCl, and $MgCl_2$ as well. This set of N