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Estimation of the particle and gas scavenging contributions to wet deposition of organic nitrogen

Silvia M. Calderón[a,*], Noreen D. Poor[b], Scott W. Campbell[c]

[a]*Universidad de Los Andes, Escuela de Ingeniería Química, Núcleo La Hechicera, Edificio B Oficina 2N93, Mérida 5101, Venezuela*
[b]*University of South Florida, College of Public Health, 13201 Bruce B. Downs Boulevard, Tampa, FL 33612, USA*
[c]*University of South Florida, Department of Chemical Engineering, 4202 E. Fowler Avenue, Tampa, FL 33620, USA*

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Abstract

We estimated the wet deposition flux of dissolved organic nitrogen (DON) to Tampa Bay, Florida, using 24-h integrated aerosol and rainwater samples collected simultaneously on days with rainfall between July and September 2005. In rainwater, dissolved inorganic nitrogen (DIN) and DON average concentrations were 54.7 ± 44.0 and $4.7 \pm 2.7\,\mu$M-N, respectively, and DON represented $8.9 \pm 5.8\%$ of the total dissolved nitrogen (TDN = DIN + DON). Our estimates of wet deposition fluxes for NH_4^+, NO_3^- and DON were 1.40, 3.18 and 0.34 kg-N $ha^{-1}\,yr^{-1}$, respectively. In aerosols (PM_{10}), DIN and DON concentrations were 78.5 ± 56.2 and 6.3 ± 2.6 nmol m^{-3}, respectively, and DON represented $10.3 \pm 7.3\%$ of TDN. Particle scavenging rates were calculated assuming a lognormal size distribution for particles and lognormal, gamma and Marshall–Palmer size distributions for raindrops. For the range of precipitation rates and measured aerosol concentrations, below-cloud scavenging of aerosol-phase DON contributed only $1 \pm 0.7\%$ to rainwater N concentrations. Dimethylamine (DMA) was observed in aqueous extracts of fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) aerosol samples, but could be quantitatively measured only in fine particles with an average concentration of 688 ± 615 pmol-N m^{-3}, representing an average contribution of $12.8 \pm 6.7\%$ of the total DON concentration measured in the same particle fraction. AIM 2 vapor–liquid equilibrium modeling predicted an average gas-phase DMA concentration of 107.4 ± 176.9 pmol-N m^{-3}. Although DMA concentrations were below our analytical detection limit on all rainwater samples, the average modeled gas and particle DMA contribution to DON concentration in rainwater was $0.4 \pm 0.7\%$.

Keywords: Aliphatic amines; Ammonia; Nitric acid; Dimethylamine; Size distribution

1. Introduction

During 1970s and early 1980s, Florida's Tampa Bay estuary showed signs of eutrophication. Poor water quality and a decline in seagrass meadows were caused by a decrease in light penetration in the presence of high phytoplankton concentrations. Water quality models have positively correlated phytoplankton concentrations to total nitrogen levels in water and have predicted a strong response of phytoplankton concentrations in Tampa Bay to changing nitrogen inputs (Tomasko et al., 2005; Wang et al., 1999). Direct atmospheric deposition of inorganic nitrogen contributed ~20% of the 3500

*Corresponding author. Tel.: +58 274 2402141; fax: +58 274 2402958.
E-mail address: silvimar@ula.ve (S.M. Calderón).

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metric tons of annual nitrogen loading to Tampa Bay between 1996–1999; of this, ~60% was from wet deposition (Poor et al., 2001). This earlier estimate did not include wet and dry deposition of organic nitrogen.

Calderón et al. (2006) measured dissolved organic nitrogen (DON) in particulate matter ($PM_{2.5}+PM_{10-2.5}=PM_{10}$) and found that DON contributed $10.1\pm5.7\%$ of the total dissolved nitrogen (TDN). DON recovered from fine particles represented an average of $79.1\pm18.2\%$ of the total organic nitrogen found. Although the chemical composition of DON is still unknown, the ratios of nitrogen species generated after UV-photooxidation of DON suggested the presence of aliphatic amines. Gas-to-particle conversion processes were also suggested as source for DON in particles (Calderón et al., 2006).

Atmospheric DON most likely comes from oceanic and agricultural sources, biomass burning, and dust re-suspension. Oceans are a source of organic nitrogen: for example, aerosolized sea spray contains amino acids (Neff et al., 2002); and metabolic processes of marine animals and bacteria release gas-phase amines (Yang et al., 1994). Agricultural sources of organic nitrogen include urea applied as fertilizer (Mace et al., 2003b; Cornell et al., 1998), and aliphatic amines from animal husbandry operations (Schade and Crutzen, 1995). Biomass burning releases amino acids (Mace et al., 2003a, b; Spitzy, 1990), as well as other substances such as humic acid-like compounds (e.g. fulvic acids) that can be photolyzed to release additional free-amino compounds (Matsumoto and Uematsu, 2005; Chan et al., 2005). L-glycine, L-serine, L-glutamine, L-alanine, L-threonine, L-arginine and L-asparagine were reported as the most common amino acids found during biomass burning emissions (Chan et al., 2005).

Among aliphatic amines the most commonly found are methylamine (MMA), dimethylamine (DMA), and trimethylamine (TMA), which are naturally produced by a variety of living organisms (Gronberg et al., 1992), such as phytoplankton and zooplankton. Seawater analyses of these amines showed concentration levels in the Arabian Sea from 0–66 nM with higher values for coastal waters, with MMA and DMA being the largest contributors (Gibb et al., 1999b). Estuarine waters from Flax Pond, NY, USA had concentrations of DMA ranging from 25 to 180 nM and increasing seasonally from winter to summer (Yang et al., 1994). Amines are also linked to domestic wastewater discharges because they are present in human and animal urine (Mitchell and Zhang, 2001), e.g. DMA is the most prevalent amine in human urine (Mitchell and Zhang, 2001; Teerlink et al., 1997). Real-time measurements using time-of-flight mass spectrometry have found strong amine signals when air is collected around busy freeways (Angelino et al., 2001), rural areas (Beddows et al., 2004) and large feedlots (Murphy et al. by Beddows et al., 2004). All of the above-mentioned DON sources are present within the Tampa Bay estuary watershed (Poor et al., 2006).

To improve estimates of wet deposition fluxes over Tampa Bay, DON and DIN concentrations were measured in $PM_{2.5}$, $PM_{10-2.5}$, and rainwater samples collected at a bayside monitoring site between July and September 2005. Samples collected during rain episodes were used to estimate particle and gas scavenging rates of nitrogen species. The simultaneous collection of samples aids in understanding the phase partitioning of species and in evaluating possible sources through the presence of similar species in both samples.

2. Theoretical basis

For particle and gas transport, rainfall scavenging rates depend on the number concentration/droplet size relation defined by the droplet size distribution (DSD). DSDs have been measured and fitted to several analytical functions in terms of the precipitation rate p_o (mm h^{-1}), which determines the total number of raindrops for a rain event. A DSD defines the number concentration or number of droplets $N(D_p)$ with a specific droplet diameter D_p (mm) suspended in a volume of air (m^3).

To quantify the DSD effect on scavenging rates and in the absence of better information about DSDs on our sampling site, we chose to work with three of the most common DSDs: the modified Marshall–Palmer (MP), the Gamma distribution (MM) by Massambani and Morales (1991) (Goncalves et al., 2000) and the lognormal distribution (L) (Mircea et al., 2000). Following the recommended values, lower and upper limits for droplet size were chosen to be 1.2 and 6 mm for the MP distribution (Eq. (1)), 0.3 and 6 mm for the MM distribution (Eq. (2)) and 0.127 and 6 mm for the L distribution (Eq. (3)).

To simplify the problem and in the absence of better information, we assumed that DSDs do not