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Atmospheric organic and inorganic nitrogen inputs to coastal urban and montane Atlantic Forest sites in southeastern Brazil

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ABSTRACT

Tropical regions are currently experiencing changes in the quantity and form of nitrogen (N) deposition as a result of urban and industrial emissions. We quantified atmospheric N inputs to two coastal urban and two montane (400 m and 1000 m) Atlantic Forest sites downwind of the Metropolitan Region of Rio de Janeiro (MRRJ), Brazil, from August 2008 to August 2009. Concentrations of total dissolved nitrogen (TDN), dissolved inorganic nitrogen (DIN) and urea were measured in bulk precipitation at all sites, as well as in canopy throughfall in the lower montane forest. Dissolved organic nitrogen (DON) was calculated as the difference between TDN and DIN ($NH_4^+ + NO_3^- + NO_2^-$). Annual volume-weighted mean bulk concentrations of all N species were higher at the coastal urban than montane forest sites, with DON accounting for 32–56% and 26–32%, respectively, of the TDN concentration in bulk precipitation. Bulk deposition of TDN ranged 12.1–17.2 kg N ha^{-1} yr^{-1} and tended to decrease with increasing distance from the coastal urban region. In the lower montane forest, throughfall TDN flux, 34.3 kg N ha^{-1} yr^{-1}, was over 2-fold higher than bulk TDN deposition, and DON comprised 57% of the total N deposited by throughfall to the forest soil. Urea comprised 27% of DON in throughfall compared to up to 100% in bulk precipitation. Our findings show that DON is an important, yet understudied, component of TDN deposition in tropical forest regions, comprising one-third to greater than one-half of the N deposited in rainfall and throughfall. Further, in this lower montane Atlantic Forest site, throughfall DIN flux was 1.5–3 fold higher than the suggested empirical critical load for humid tropical forests, highlighting the potential for increasing N pollution emitted from the MRRJ to impact N cycling in adjacent ecosystems.

1. Introduction

In the coming decades, nitrogen (N) emissions and deposition are projected to increase in tropical regions as a result of urbanization and industrialization (Galloway et al., 2008; Matson et al., 1999). In Latin America, some major metropolitan areas, including Rio de Janeiro, São Paulo, Mexico City, Guayaquil (Ecuador) and San Jose (Costa Rica) already experience significant atmospheric N pollution from vehicular and industrial sources (Baldasano and Jiménez, 2003; CETESB, 2013; Clean Air Institute, 2013; Herrera et al., 2009; INEA, 2009; Molina and Molina, 2004; Murilo and Marín, 2010). In these regions, studies have shown that forest ecosystems downwind from urban source areas receive elevated deposition of inorganic N (5–20 kg N ha^{-1} yr^{-1}) via rainwater and throughfall (water that passes through forest canopies) (Eklund et al., 1997; Fenn et al., 1999; Forti et al., 2007; Goller et al., 2006; Hofhansl et al., 2011; Perry, 2007; Rodrigues et al., 2007; Schwendenmann and Veldkamp, 2005; Wilcke et al., 2001), but the contribution of organic N to total N (inorganic and organic) input is seldom quantified.

Previous research indicates that dissolved organic nitrogen (DON) often comprises an important fraction of the total dissolved nitrogen (TDN) in wet-only (rainwater), dry (particles and gases) and occult (fog) deposition, and in marine aerosol (Cape et al., 2010, 2011, 2012; Cornell, 2011; Cornell et al., 2001; Jickells et al., 2013; Matsumoto et al., 2014; Neff et al., 2002; Violaki and Mihalopoulos, 2010, 2011; Violaki et al., 2014; Weathers et al., 2000a). Even though the specific chemistry contributing to DON is still poorly characterized in tropical regions, some individual N-containing organic compounds have been identified in rainwater and atmospheric particles: dissolved free amino acids and urea (Gioda et al., 2011; Mace et al., 2003a; Rocha-Silva, 2009).

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Studies conducted in marine, coastal and continental environments around the world indicate that DON is a ubiquitous component of rainwater and that concentrations are highly variable (Cape et al., 2011; Cornell et al., 1995; Cornell, 2011; Hofhansl et al., 2011; Jiang et al., 2013; Jickells et al., 2013; Li et al., 2012; Neff et al., 2002; Pacheco et al., 2004; Zhang et al., 2012). These studies show that DON comprises 7 to 92% of the TDN in wet-only and bulk precipitation. In Brazil, reported concentrations of DON in rainwater range from 1.5 to 30 μmol L^{-1}, comprising 22 to 86% of TDN (Araújo, 2011; Cornell et al., 1995; Filoso et al., 1999; Parron et al., 2011; Rocha-Silva, 2009; Williams et al., 1997), highlighting its potential importance to N cycling in tropical ecosystems.

Previous measurements of wet and bulk deposition conducted in Rio de Janeiro state (de Mello, 2001; de Mello and Almeida, 2004; de Souza et al., 2006; Perry, 2007; Rodrigues et al., 2007) reveal that the Serra dos Órgãos mountain range receives relatively high atmospheric inorganic N ($NH_4^+ + NO_3^-$) inputs (7–12 kg N ha^{-1} yr^{-1}) compared to coastal, urban and other mountain sites (4.6–5.4 kg N ha^{-1} yr^{-1}). These findings suggest that Serra dos Órgãos is vulnerable to atmospheric deposition of pollutants resulting from anthropogenic emissions in the Metropolitan Region of Rio de Janeiro (MRRJ) that are subsequently transported by the prevailing southerly winds, which blow landward from the ocean. In none of these sites, however, has the atmospheric deposition of organic N been investigated. Therefore, the purpose of our study was to investigate the spatial variation of organic and inorganic N concentrations and depositions via bulk precipitation between coastal urban and montane Atlantic Forest sites, as well as changes in the quantity and quality of N species in throughfall upon passage through a lower montane Atlantic Forest canopy near the northern limit of the MRRJ.

Estimating the current contribution of atmospheric deposition of N species to montane Atlantic Forest canopies and soils is important to improve our understanding of regional N cycling under the influence of emissions from adjacent large urban and industrial centers. This knowledge is essential given that increasing N deposition to forest ecosystems can contribute to biodiversity loss, change in carbon storage, soil and stream acidification, nutrient loss and alterations in the emissions of nitrogen oxides (NO and N_2O) from forest soils (Bobbink et al., 2010; Brookshire et al., 2012; Lu et al., 2010; Butterbach-Bahl et al., 2013; Jickells et al., 2013; Matson et al., 1999; Pilegaard, 2013; Vitousek et al., 1997).

2. Material and methods

This study was conducted in the eastern part of the MRRJ, an area little influenced by local industrial emissions, and in a downwind Atlantic Forest reserve (Serra dos Órgãos National Park) located in the Serra dos Órgãos coastal mountain range (the portion of Serra do Mar forming the northern border of Guanabara Bay basin), southeastern Brazil (Fig. 1). The MRRJ has a population of 12 million inhabitants and is the second largest urban and industrial center in the country (IBGE, 2012; IPP, 2012)

Annual NO_x emissions in the MRRJ are ca. 28 Gg N, of which ~2/3 are attributed to mobile sources (cars, buses, and trucks) and ~1/3 to power plants and petrochemical industries (INEA, 2009; Loureiro, 2005). The international airport in MRRJ contributes less than 1% of total NO_x emissions (Maia, 2005). Ammonia (NH_3) emissions from Guanabara Bay are ca. 1.3 Gg N yr^{-1} and result mainly from discharge of raw and undertreated sewage into the bay's inner western tributaries (Guimarães and de Mello, 2006; Kjerfve et al., 1997). Other potential local sources of NH_3 in the MRRJ, whose emission rates have not been quantified, are: a) petrochemical industries, municipal landfills and polluted estuaries in the western portion of the MRRJ; b) cattle pastures in the northeastern lowlands of the MRRJ; c) vehicles, and d) dry season biomass fires.

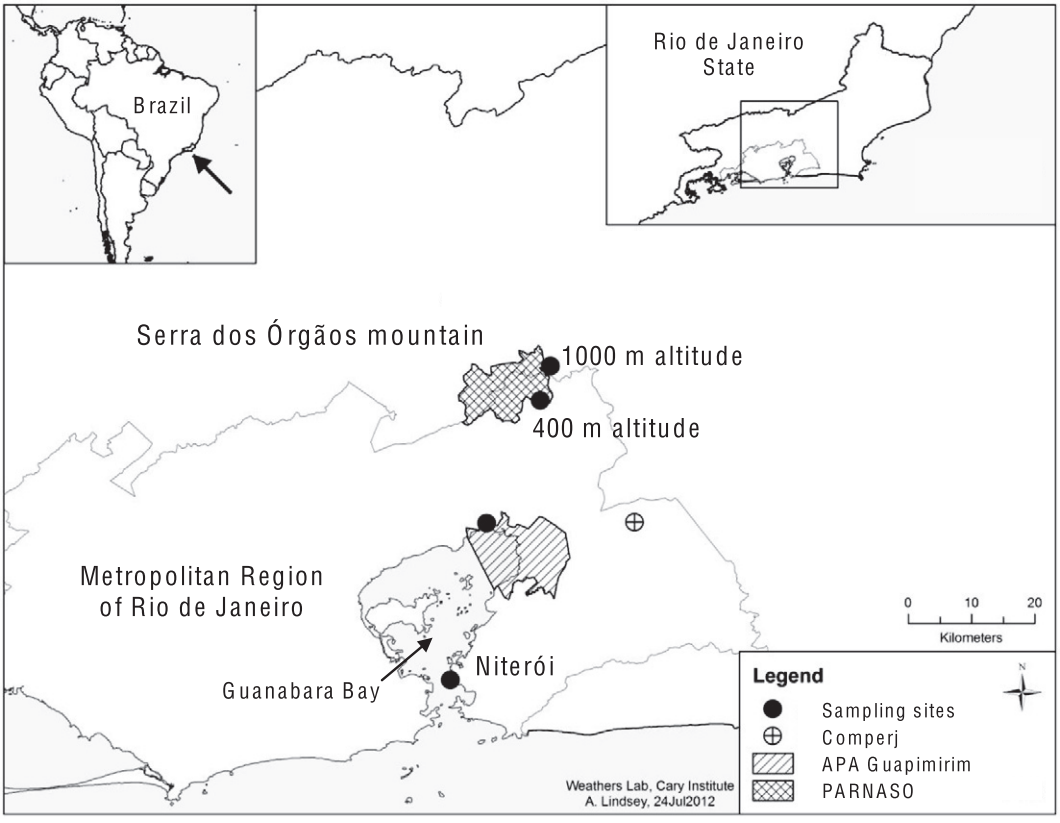

Fig. 1. Location of the study area and sampling sites (black dots): Niterói (coastal urban site near sea level), APA Guapimirim (coastal peri-urban site near sea level), and lower montane forest (400 m asl) and montane forest (1000 m asl) in Serra dos Órgãos National Park (PARNASO), southeastern Brazil. Comperj: Complexo Petroquímico do estado do Rio de Janeiro.