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Ambient concentrations of atmospheric ammonia, nitrogen dioxide and nitric acid in an intensive agricultural region

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HIGHLIGHTS

- Ambient NH_3 concentrations and deposition were more variable than NO_2 and HNO_3.
- NH_3 was responsible for ~70% of gaseous reactive nitrogen dry deposition.
- Spatial variation in NO_2 concentrations was associated with agricultural traffic.
- Future policy designed to reduce N deposition should focus on reducing NH_3 emissions.

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ABSTRACT

The spatial and temporal distribution of ambient atmospheric gaseous reactive nitrogen (Nr) species concentrations (ammonia [NH_3], nitrogen dioxide [NO_2] and nitric acid [HNO_3]) were measured at the field scale in an intensive agricultural region in southern Ontario, Canada. Atmospheric concentrations were measured with the Willems badge diffusive passive sampler (18 sites for NH_3, 9 sites for NO_2 and HNO_3) for one year (April 2010–March 2011; under a two week measurement frequency) within a 15 km × 15 km area. Dry deposition was calculated using the inferential method and estimated across the entire study area. The spatial distribution of emission sources associated with agricultural activity resulted in high spatial variability in annual average ambient NH_3 concentrations (<3–>8 μg m^{-3} within a 2 km distance, coefficient of variation ~50%) and estimated dry deposition (4–13 kg N ha^{-1} yr^{-1}) between sample sites. In contrast, ambient concentrations and deposition of both NO_2 (~5.2–>6.5 μg m^{-3}; 1.0–1.5 kg N ha^{-1} yr^{-1}) and HNO_3 (0.6–0.7 μg m^{-3}; 0.5–1 kg N ha^{-1} yr^{-1}) had low variability (coefficient of variation <10%). The observed NH_3 concentrations accounted for ~70% of gaseous Nr dry deposition. High NH_3 concentrations suggest that reduced nitrogen species (NH_x) will continue to make up an increasing fraction of Nr deposition within intensive agricultural regions in southern Ontario under legislated nitrogen oxide emission reductions. Further, estimated total inorganic Nr deposition (15–28 kg N ha^{-1} yr^{-1}) may lead to potential changes in soil processes, nutrient imbalance and altered composition of mycorrhiza and ground vegetation within adjacent semi-natural ecosystems (estimated at ~10% of the study area).

1. Introduction

During the last two centuries anthropogenic production of reactive nitrogen (Nr, primarily from intensive agricultural activity, fertilizer production [Haber–Bosch process] and combustion of fossil fuels) has surpassed natural production as the global demand for food and energy has increased (Galloway et al., 2003). Widespread accurate estimates of Nr atmospheric concentrations are limited owing to the many different Nr species (both oxidized [NO_y] and reduced [NH_x] forms), which have different chemical and physical properties impacting atmospheric transport and ability to be absorbed or captured by a surface. Oxidized nitrogen (N) species are primarily produced from fossil fuel combustion, biomass burning and soil microbial production (Lee et al., 1997), and are emitted to the atmosphere as nitrogen oxides ([NO_x], primarily nitrogen oxide [NO] and a small portion of nitrogen dioxide [NO_2]). The majority of NO_2 is produced as a secondary pollutant from oxidation of NO. Gaseous NO_2 contributes to acidic deposition and is a precursor to the formation of photochemical oxidants like nitric acid (HNO_3), a major component of photochemical smog, which at high concentrations may cause direct human health impacts (Kraft et al., 2005; Latza et al., 2009). Reduced N species include gaseous ammonia (NH_3) primarily associated with emissions from

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agriculture, and particulate ammonium (pNH_4^+) formed from the reaction of NH_3 with HNO_3, sulphuric acid or hydrochloric acid and associated with long-range transport (Erisman et al., 1998).

The global increase in Nr emissions has lead to concerns that chronic elevated atmospheric concentrations and deposition of NO_y and NH_x may result in long-term negative effects on natural ecosystems (Davison and Cape, 2003; Matson et al., 2002; Krupa, 2003; Kurvits and Marta, 1998) and exceedances of critical levels and critical loads for N. A critical level is defined as "*the concentration in the atmosphere above which direct adverse effects on receptors, such as plants, ecosystems or materials, may occur according to present knowledge*" and a critical load is defined as "*a quantitative estimate of deposition of one or more pollutants below which significant harmful effects on specified elements of the environment do not occur according to present knowledge*" (Posthumus, 1988). Air monitoring networks have been established across Canada (e.g., Canadian Air and Precipitation Monitoring Network (CAPMoN) operated by Environment Canada (EC)) and Ontario (e.g., Air Quality Index (AQI) operated by the Ontario Ministry of the Environment (MOE)) to assess the potential impacts to ecosystem and human health, support policy, determine spatial patterns, establish temporal trends, evaluate atmospheric models and issue human health air pollution warnings.

Air monitoring networks in southern Ontario primarily operate in rural background regions (CAPMoN) or within urban areas (AQI), leaving large gaps in agricultural regions. Observation of gaseous NH_3, NO_2 and HNO_3 across a rural-urban-agricultural transect in southern Ontario (Zbieranowski and Aherne, 2012a) demonstrated that intensive agricultural regions have high atmospheric Nr concentrations and gaseous dry deposition, and that current monitoring and modelling approaches underestimate total Nr deposition across much of southern Ontario. Agricultural activities are a major emission source of Nr species to the atmosphere, specifically NH_3. The major emissions sources of NH_3 are volatilization from the collection, storage and spreading of liquid and solid manures (Davison and Cape, 2003; Krupa, 2003; Kurvits and Marta, 1998). At the local and field scale, NH_3 concentrations are highly spatially variable (Dragosits et al., 2002; Hellsten et al., 2008; Pitcairn et al., 2003; Thöni et al., 2004) owing to the high deposition velocity of NH_3 and large number of emission sources (Smith et al., 2000). Notably western Ontario (total area of farms: 16,280 km^2, 30% of Ontario total) accounts for approximately 50% of the total cattle and calves (1,982,651) and total pigs (3,950,592) in Ontario (OMAFRA, 2006). Reactive nitrogen emissions are also associated with vehicles used in agricultural practices, which are an important source of NO_x emissions contributing to the rural Nr budget (Davison and Cape, 2003; Kurvits and Marta, 1998), accounting for approximately 4% of NO_2 emissions in the United States (US; EPA, 2000). More importantly, emissions at the field scale in agricultural regions can result in high Nr deposition to surrounding semi-natural areas.

The objective of this study was to assess the spatial and temporal distribution of ambient gaseous Nr (NH_3, NO_2 and HNO_3) atmospheric concentrations and estimate dry deposition at the field scale in an intensive agricultural region of southern Ontario. Annual and seasonal average atmospheric concentrations and dry deposition for each species were calculated to assess their variability and individual contribution to total N deposition during the period April 2010–March 2011 using passive diffusive samplers.

2. Methods

2.1. Study area

Atmospheric concentrations of gaseous NH_3, NO_2 and HNO_3 were measured during the period March 30, 2010–March 29, 2011 (HNO_3 was not measured from July 20–November 23, 2010 owing to a supplier shortage) within a 15 km × 15 km area around the town of Brussels (BRS), Ontario, located approximately 150 km west of Toronto (Provincial capital; Fig. 1, Table 1). The study area was aligned with the 15 km × 15 km modelling domain of AURAMS (A Unified Regional Air-quality Modelling System), the principal

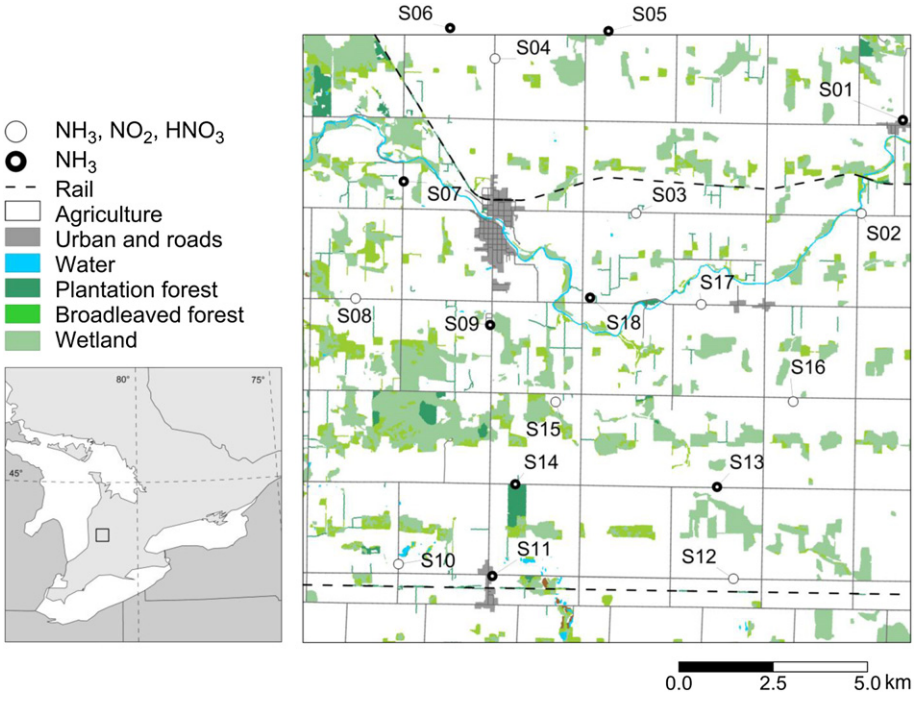

Fig. 1. Location of monitoring sites for measurement of ambient concentrations of ammonia [NH_3], nitrogen dioxide [NO_2] and nitric acid [HNO_3] within an intensive agricultural region in southern Ontario (study area: 15 km × 15 km). Land cover was defined using SOLRIS (Southern Ontario Land Resource Information System; rasterized to 100 m × 100 m resolution).