Introduction. Elevated emissions of atmospheric reactive nitrogen (Nr) have lead to concerns that Nr deposition may result in long-term negative impacts on natural ecosystems e.g., acidification, eutrophication. Atmospheric ammonia (NH₃), the dominant Nr species emitted in agricultural regions, is highly variable (spatially and temporally) owing to its high deposition velocity; moreover, recent studies have shown significant emissions in urban centres (vehicle exhaust). Continuous observations of NH₃ are limited, within Ontario there is only one station with continuous NH₃ monitoring: Centre for Atmospheric Research Experiments (CARE), Egbert, operated by Environment Canada. Passive samplers have been widely used to capture spatial variability as they provide a low cost method and can be deployed across many sites. Willems badge passive samplers have been used across southern Ontario since August 2007 (exposed in triplicate at two week intervals) at 38 sites (continuous at 2: CARE and Dorset; Figure 1). Ammonia concentrations were first measured under the Trent Regional Ammonia Monitoring using Passive Samplers (TRAMPS) network (September 2007–September 2008) followed by the RAIN’N network (September 2008–April 2009). In the current study (March 2010–March 2011), NH₃ concentrations are being monitored in a region of intensive agricultural activity (Brussels) and in an urban centre (Toronto).

Spatial variability: intensive agriculture (January–September 2010, 17 sample periods). Site average NH₃ concentrations ranged from 2.48–8.36 µg m⁻³ (orange circles) with a minimum of 0.31 µg m⁻³ and a maximum of 16.41 µg m⁻³ (Figure 3). Future work will use land use regression to evaluate the relationship between concentrations and land use practices surrounding individual sampling sites in an effort to explain the spatial variation in observed concentrations (Figure 4).

Urban (March–September 2010, 11 sample periods). Urban average NH₃ concentrations were in the mid to low range of those in the intensive agricultural region and were less variable. Average concentrations ranged from 1.13–4.44 µg m⁻³ (purple circles) with a minimum of 0.72 µg m⁻³ and a maximum of 5.47 µg m⁻³ (Figure 3). Nonetheless, summertime concentrations (July 6–20, 2010: spatial survey) were generally higher than the intensive agricultural region (Figure 4).

Temporal variability. There was a strong seasonal pattern in observed NH₃ concentrations; lowest were during the winter (January / February), and peaked during late spring (May) associated with increased agricultural activity (e.g., fertilizer, slurry spreading).

A similar temporal pattern was observed across Ontario in background, rural, urban and intensive agricultural regions (Figure 5). This suggests that agricultural emissions influence background concentrations across Ontario throughout the year.

Isotopic analysis of N-NH₃ (collected on filters) is planned for each region to determine if regional NH₃ isotopic signatures are influenced by intensive agricultural regions.

Sampler validation. The Willems badge has been evaluated against a modified Thermo 42C trace level chemiluminescence based analyzer (R² = 0.86) at CARE, and against a denuder system at CARE and Riverside, California (R² = 0.96, Figure 2). The sampler has also been evaluated against other passive samplers (Gradko (R² = 0.97), Figure 2), Radiello® and Ogawa.

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Figure 1. Map of NH₃ sampling sites in Ontario. Insets show intensive agriculture region (Brussels) with 38 sampling sites (orange circles) within a 15 km x 15 km grid (red square); and Urban (Toronto) with 9 Willems (purple circles) and Gradko sites (yellow circles, July 6–20, 2010 only). Coloured circles correspond to land use classification in spatial and temporal sequences (Figures 3, 4 and 5).

Figure 2. Comparison of NH₃ concentrations (µg m⁻³) measured with the Willems badge sampler compared to an active denuder system (left) and Gradko tubes (right).

Figure 3. Range in NH₃ concentrations (µg m⁻³) measured at Brussels (n = 18), Toronto (n = 9), CARE and Dorset. Sample period corresponds with temporal sequence (Agriculture and Urban, see Figure 5).

Figure 4. Maps showing NH₃ spatial variability in intensive agriculture region (red square, Figure 1) and urban region (Toronto, Figure 1) during July 6–20, 2010. Ammonia concentrations range from 1.64–8.76 µg m⁻³ (intensive agriculture) and 1.11–10.02 µg m⁻³ (urban; yellow circles using Gradko samplers normalised to Willems, Figure 2).

Figure 5. Temporal sequence of NH₃ concentrations (August 2007–September 2010). The sequence is divided by study (with corresponding legend); sites are grouped by land use (background, rural / agricultural, intensive agriculture, etc.). For each land use, average NH₃ concentration are presented (coloured circles). Dorset and CARE concentrations are shown as a line graph. Range (box plot) and average (orange circles) NH₃ concentrations are shown for Brussels (intensive agriculture, n = 18).