

P1.23 FIELD EVALUATION OF PASSIVE SAMPLERS AND DEPOSITION VELOCITY FOR NO₂

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1. INTRODUCTION

Gaseous nitrogen (N) forms are linked to various negative effects on ecosystems and human health, such as acid rain, eutrophication, ground-level ozone and loss of biodiversity (Kurvits and Marta, 1998). Most of these effects are due to increased input of N species to the earth's surface in precipitation (wet deposition) or in gaseous form due to turbulent diffusion (dry deposition).

Dry deposition has been estimated to contribute half of the total N loading. For gases, this specifically occurs in the forms of nitrogen dioxide (NO₂), ammonia (NH₃), and nitric acid (HNO₃) (Hanson and Lindberg, 1991).

Currently in Canada, there is no continuous monitoring network for the dry deposition of NO₂. Therefore the objectives of this study were to evaluate methods for quantifying ambient NO₂ concentrations and to calculate a deposition velocity (V_d) for NO₂.

2. MATERIALS AND METHODS

2.1 Site Description

Measurements were performed at the Elora Research Station (ERS) (48° 39' N, 80° 25' W), Ontario, Canada from May 17 to October 4, 2001. The site chosen was a grassy field surrounded from the north to the south-east by agricultural fields. To the north-east was the onsite weather station, to the east the research buildings, and south-west a small structure containing chemiluminescence analysers and other equipment associated with the flux measurements.

2.2 Concentration Measurements

Four types of passive samplers, Gradko Palmes Tube (PT), Maxxam Passive Air Sampling System (PASS), CSIRO Badge Sampler (BS), and Ogawa Sampler (OS) were exposed over 3 and/or 6-day periods. With the

exception of OS, each sampling period had three replicates where the samplers were exposed at a height of 0.5 m within less than 1 cm distance from each other. At the end of each sampling period, the individual samplers were capped, sealed in a plastic bag and stored at 4°C with their respective blanks until sent to the labs for analysis. Environmental conditions included the length of exposure, average air temperature, relative humidity and windspeed for the exposure periods.

In addition to the samplers, two chemiluminescence analysers were used to measure nitric oxide (NO) and nitrogen oxides (NO_x) concentrations for the purpose of NO₂ flux quantification and concentration.

2.3 Deposition Velocity

The deposition velocity (V_d) was calculated using:

$$V_d = \frac{F}{C}$$

where F is the measured flux of NO₂ and C is the measured concentration. The vertical gas flux was measured using the flux gradient method:

$$F = -K_z \frac{\partial C}{\partial z}$$

where F is the flux (ng m⁻² s⁻¹), $\partial C/\partial z$ (ng m⁻⁴) is the vertical concentration gradient of NO₂, and K_z (m²s⁻¹) is the eddy diffusivity coefficient for NO_x and NO at height z (m).

The concentration gradient was determined by measuring the concentration difference, ΔC (ng m⁻⁴) using two chemiluminescence analysers to measure NO and NO_x over a vertical distance, Δz (m). Due to the analysers lack of specificity for NO_x, the NO₂ calculated from the subtraction of NO from NO_x, represented NO₂ and some unknown amount of HNO₃. The NO₂ was thus symbolised as NO₂' and represented the upper limit of NO₂. Cup and sonic anemometers were set up in two plots in order to determine K and

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stability corrections necessary to calculate the fluxes.

The air was sampled at 30 s intervals from heights of 0.3 and 0.5 m. The data were filtered for the presence of intermittent sources and for the transition period between the two heights. The resulting data were then averaged over the hour and analysed.

3. RESULTS AND DISCUSSION

The PT compared well to the other samplers mirroring the data from the chemiluminescence the best. However, the PT data had numerous repetitive numbers due to the lack of sensitivity of the lab analysis. There were also difficulties with the low concentrations detected at ERS that were close to the blank value and thus increased the uncertainty of the PT data up to 50%. In addition, at the shorter sampling period, the PT frequently exceeded the data from the chemiluminescence, which were determined to represent the upper limit of the atmospheric concentration of NO_2 .

The PASS had much better precision than the PT and rarely exceeded the chemiluminescence data even at the shorter time periods. However, both the PASS and PT required longer exposure periods than 3 days for sites with atmospheric concentrations below 2 ppb of NO_2 although mean concentrations greater than 2 ppb were detectable for a 3 day exposure period.

The CBS was consistently the lowest value and never exceeded the chemiluminescence data. It compared well to the PASS and had a high level of precision.

Due to the limited data ($n=4$) collected for the OS, no conclusions were drawn.

Of the three samplers types, the PASS performed the best, followed by the CBS and the PT. For the PASS and PT, an exposure time of greater than 3 days is required for mean ambient concentrations below 2 ppb.

For the dry deposition study, the unfertilised grass field at ERS was a source of NO and a net sink for NO_2 . Wind direction played an important role in the concentration and flux of NO and NO_2 with the highest concentrations and greatest dry deposition of NO and NO_2 coming from the south-southeast direction.

Overall daily mean V_d for NO_2 for the summer experiment was $0.33 \pm 0.05 \text{ mm s}^{-1}$ with a range of mean hourly values of 14 to -23 mm s^{-1} . The diel pattern for the experiment, including the episodes of emission, showed V_d reaching a high of 1.5 mm s^{-1} at 0900 hr but quickly dropping.

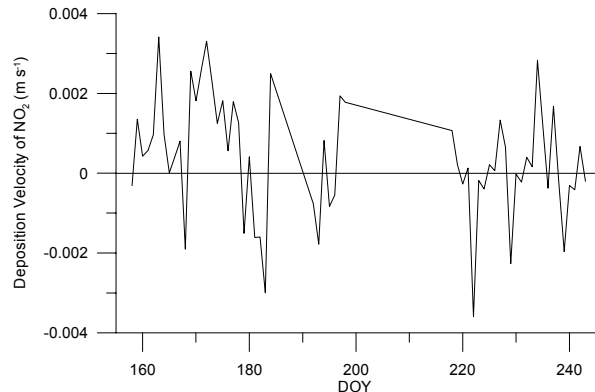


Figure 1 Mean daily deposition velocity of NO_2 at the Elora Research Station from May 17 to August 31, 2001.

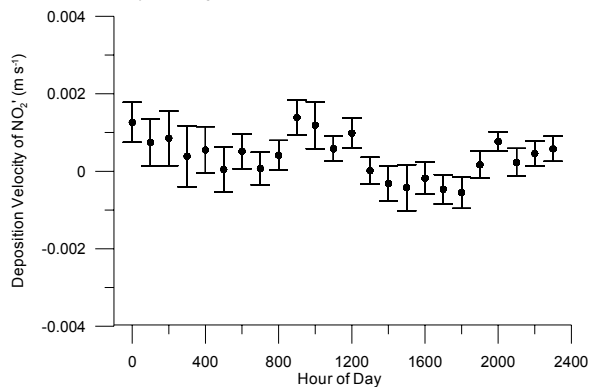


Figure 2 The diel pattern of the mean hourly deposition velocity of NO_2 at the Elora Research Station from May 17 to August 31, 2001.

By afternoon the V_d had dipped below zero reaching a low of -0.5 mm s^{-1} at 1800 hr. At night V_d increased almost reaching the daytime values by midnight but then slowly dropped off. This midnight peak coincides with the NO peak in emissions that occurs from midnight until 0400 hr, supporting the view that NO_2 uptake seemed to be directly related to NO emissions (Maggiotto et al., 2000).

4. REFERENCES

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