Application of Passive Sampling Devices in Characterizing Near-Road Spatial Gradients of Nitrogen Dioxide

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Background
Nitrogen dioxide (NO₂) is a critical pollutant formed from the oxidation of atmospheric nitrogen and nitrogen oxides released from combustion of fossil fuels. According to many epidemiological studies, NO₂ is associated with adverse effects on respiratory and cardiovascular health. NO₂ is also a source of nitric oxides, contributing to climate change such as smog formation [1]. Road traffic is a major atmospheric source of NO₂, therefore human exposure near high road traffic is a concern.

A characterization of near-road traffic air pollution spatial variability is essential for the development of air pollution control strategies. Past literature indicates decrease in NO₂ conc. within large distances from freeways [2][3][4]. More investigation is needed for small-scale variations and also for vertical NO₂ spatial variations. Both continuous and passive monitoring techniques have been used in literature. Passive monitoring is a practical alternative to continuous monitoring in terms of cost effectiveness and ease of deployment. However, the accuracy and reliability of passive measurements is highly dependent on sample handling during deployment, storage, and extraction stages of passive samplers.

Objectives
The main objectives for this study were to:
1. Use passive sampling devices (PSDs) in characterizing nitrogen dioxide (NO₂) spatial variability with increasing distance and elevation from road traffic
2. Validate the passive sampling technique for small area spatial variation studies

Methodology
Passive Sampling Devices
Opgawa bag type PSDs used in this study are two sided diffusion tubes that use a chemical Absorbent to collect NO₂ in air as nitrite. Sample analysis were conducted under Opgawa sampler protocol [4].

Deployment description:
40 Opgawa bag type PSDs were deployed
• 6 blanks (3 trip and 3 field blanks) were included
• Each PSD contained duplicate NO₂/NOx filters coated with triethanolamine (TEA)
• Each PSD was sheltered from direct sunlight and precipitation
• Three 2-week exposure periods (June 21-July 22, 2011)

Filter Analysis – Ion Chromatography (IC):
• NO₂ extracted as nitrite in 310.Lm de-ionized water
• Dionex IC 2100 and 2000 systems used for IC separation by conductivity detection

Continuous Monitoring Instruments
Four continuous NOx (NOx/NO₂) monitoring instruments (Fig. 5) were sampling air on College St. at sites 1 and 3 for validating PSD results. Side-by-side comparison with PSD and comparison of sites along College St. were conducted. Fig. 6 indicates that NO₂ concentrations are lower at upward compared to downstream locations of College St. – this is consistent with PSD results as well as literature [5].

Sampling Design
A total of 4 collocated sampling sites situated in proximity to College St. In Toronto. College St. is a four lane road with traffic flow of about 10,000 vehicles/day. NO₂ concentration spatial variations analyzed in this study are with respect to College St. Each sampling site was designed for at least one of three experimental analysis: horizontal gradient, vertical gradient, and comparison to continuous monitoring instruments. Other traffic emission sources contributed from surrounding roads were considered, namely Kings College Rd, Queens Park Crescent, Hokin Ave, Spadina Ave, and St. George St. Other minor anthropogenic NO₂ sources were not significant in this study.

For horizontal gradient:
• Site 2 and 4 covers 0-900m in horizontal distance from primary emission source in this study (urban background located at 900m)

Vertical gradient:
• Sites 1, 3, and 4 covers 0-3m in height from street level (urban background located at 3m)

Comparison to CM:
• Sites 1, 3, and 4 are laboratories where CMFs are sampling air from the primary emission source of this study

Data Interpretation
Duplicates correlated well with R²=0.8966 and slope 1.09. One outlier due to contamination during deployment was removed. Ion concentrations from IC analysis were field trip blank-corrected and then converted to concentration in ambient air using Eq. (1). The following conversion of concentration is a function of vapour pressure, temperature, and relative humidity (4). The influence of these factors were evident in this study.

\[
\frac{([NO₂]_w)}{[NO₂]_a} = \frac{m_{NO₂ \text{ filter}}}{m_{NO₂ \text{ filter}}} \times \frac{\alpha_{NO₂}}{\alpha_{NO₂}} = \frac{\alpha_{NO₂}}{\alpha_{NO₂}}
\]

\[
\alpha_{NO₂} = \text{concentration ion conversion coefficient} \times \frac{\text{weight} ([NO₂]_w)}{\text{weight} ([NO₂]_a)}
\]

Temperature and humidity:

\[
\text{P} = \text{vapour pressure}
\]

\[
\text{RH} = \% \text{relative humidity}
\]

According to raw IC results, high NO₂ correspond to lower NO₂ concentrations and vice versa. NO₂ measurements for period 1 (June 21-July 5) were lower and period 2 (June 28-July 12) were higher (Fig. 5), this was evident uniformity across all sampling sites.

Horizontal Gradient Analysis – Interpolation
Mean NO₂ concentrations in horizontally located sites ranged from 11.7-18.8ppb. From Fig. 10 and 11 statistical analysis shows a decrease in NO₂ concentration with increasing distances from College St. An interpolation of results from sites 2 and 4, shows that NO₂ concentrations drop most significantly at a distance between 100m and 150m from College St. The chosen urban background was theoretically justified when 25m is the characteristic distance for both sites. At 50m and 111m were calculated from regression models for sites 4 and 2 respectively.

Validation
Side-by-side Comparison of PSD with NOx Analyzer and Airpintar yielded results similar to the continuous measurement with standard deviation ranging from 0.33 to 2.2ppb throughout the three sampling periods (Fig. 14).

Conclusions
Spatial gradient analysis of NO₂ concentrations shows:
• decrease with increasing distance from a major road. There is a significant drop in conc. at horizontal distances of 170m-1530m from the road (P<0.05).
• decrease with increasing elevation from street level with varying traffic densities overall. Analysis suggests a significant drop in conc. at about 20m above street level (P<0.05). Observations show a slight fluctuation around 6-8m in height, indicating a possibility of NO₂ decay and/or effects on vegetation.

For the validation of the PSD application, NO₂ PSD measurements:
• were lower at upward locations than at downward locations from this road. This is consistent with CMF results and past literature [3].
• meteorological effects on NO₂ trends were consistent
• were agreeable with CMF results with standard deviation of at most 2.25ppb; PSD and NOx analyzers differ within 5%.

Although the accuracy of passive measurements are highly sensitive to precision of sample handling and are unable to provide real-time measurements, with proper deployment PSDs are valid and practical alternatives to continuous monitoring instruments. PSDs is less expensive and provides better measurement coverage spatially. This study suggests that PSDs can be appropriately applied to small-scale spatial variation analysis.

Next steps in this study include: an analysis of micro-scale (0-15m) spatial gradients using CMD, validate spatial gradients with gradients derived from mathematical dispersion models, and explore spatial

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Figure 1: PSD deployment setup at Bahen Centre, College St. and Wellesley Building respectively from left to right

Figure 2: Opgawa bag type PSD (H)

Figure 3: PSD deployment setup at Bahen Centre, College St. and Wellesley Building respectively from left to right

Figure 4: Filter extraction protocol

Figure 5: TECO 42i NOx Analyzer (courtesy of Thomas Scientific) and Airpirntan used in this study

Figure 6: Upward (at Gap) and Downward (at Well) comparison with continuous monitors

Figure 7: Location of study where 4 main PSD sampling sites were collocated indicated by horizontal red markers. Map courtesy of University of Toronto.

Figure 8: Window diagram indicating consistent south-west winds with wind speed ranging from 0.6 m/s. All sites except for site 1 are downwind. Meteorological data collected at site 1.

Figure 9: Temp. and RH (%) daily averages throughout sampling periods (Uncert: site A results for example)

Figure 10: NO₂ horizon gradient measurement and comparison to PSD data at College St. 1

Figure 11: Statistical parameters from regression modeling derived from mean of PSD replicate data

Figure 12 and 13: NO₂ concentration at increasing heights (m) with urban background at 30m and statistical parameters of regression models derived from mean of PSD replicate data.

Figure 14: Side-by-side comparison of PSD (at Airpintar) and NOx Analyzer NO₂ in College St. (ppb) per periods 1 to 3