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Elucidating multipollutant exposure across a complex metropolitan area by systematic deployment of a mobile laboratory

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Abstract

In urban areas, air quality is the outcome of multiple emission sources, each emitting a different combination of air pollutants. The result is a complex mixture of pollutants with a different spatiotemporal variability for each constituent. Studies exploring average spatial patterns across urban areas typically rely on air quality monitoring networks of a few sites, short multi-site saturation monitoring campaigns measuring a limited number of pollutants and/or air quality models. Each of these options has limitations.

This study elucidates the main complexities of urban air quality with respect to small scale spatial differences for multiple pollutants so as to gain a better understanding of the variability in exposure estimates in urban areas. Mobile measurements of 23 air pollutants were taken at high resolution in Montreal, Quebec, Canada, and examined with respect to space, time and their interrelationships. The same route was systematically followed on 34 measurement days spread over different seasons and measurements were compared to adjacent air quality monitoring network stations. This approach allowed linkage of the mobile measurements to the network observations and to generate average maps that provide reliable information on the typical, annual average spatial pattern. Sharp differences in the spatial distribution were found to exist between different pollutants on the sub-urban scale, i.e. the neighbourhood to street scales, even for pollutants usually associated with the same specific sources. Nearby microenvironments may have a wide range in average pollution levels varying by up to 300 %, which may cause large misclassification errors in estimating chronic exposures in epidemiological studies. For example, NO_2 measurements next to a main road microenvironment are shown to be 210–265 % higher than levels measured at a nearby urban background monitoring site, while black carbon is higher by 180–200 % and ultrafine particles are 300 % higher.

For some pollutants (e.g. SO_2 and benzene), there is good correspondence on a large scale due to similar emission sources, but differences on a small scale in proximity to these sources. Moreover. hotspots of different pollutants were identified and

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quantified. These results demonstrate the ability of an independent heavily instrumented mobile laboratory survey to quantify the representativeness of the monitoring sites to unmonitored locations, reveal the complex relationships between pollutants and understand chronic multi-pollutant exposure patterns associated with outdoor concentrations in an urban environment.

1 Introduction

The air pollutant mix we breathe as urban dwellers is the result of multiple emission sources (traffic, industry, residential, commercial and biogenic activities), each of which is emitting a different distribution of constituents. These primary pollutants react among themselves to produce secondary pollutants such as ozone and fine particles. The quantity formed depends on ambient conditions (e.g. photochemistry, moisture, temperature) and primary pollutant concentrations. Given these non-linear processes, the spatial variability in pollution sources and sinks over short distances and the heterogeneity in the pollutant mix emitted, the urban environment is challenging with respect to accurate characterization of air pollutant patterns and subsequent estimates of individual exposures.

Current methods for estimating long term or chronic human exposure levels in urban areas include direct use of point measurements at air quality (AQ) monitoring sites; advanced techniques for interpolation of monitoring site measurements; dispersion models and/or other physically-based numerical models; and empirical approaches such as Land Use Regression (LUR) models which typically use short term saturation measurement campaigns for model development (e.g. Cyrys et al., 2005; Isakov et al., 2007a; Marshall et al., 2008; Szpiro et al., 2010). While AQ monitoring networks represent long term conditions, they cannot account for the spatial variability existing in the urban environment (Wheeler et al., 2008). Spatial interpolation techniques (e.g. ordinary kriging, inverse distance weighting) do not take into consideration urban features like road networks or buildings. Multipollutant numerical models are limited by

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the grid cell size of a few square kilometers at best and therefore cannot resolve sub-grid (i.e. neighbourhood scale) variability. Finally, saturation campaigns deploying on the order of 10–100 passive monitors in a city over short time periods of a few weeks, which typical serves as the source of the dependent variable in empirical model development (e.g. Kanaroglou et al., 2005) are not necessarily representative of long term conditions given the temporal variability in meteorology and emissions which can lead to a selected two week period being unrepresentative of typical conditions. Another weakness with most of these approaches is the small number of air pollutants they consider, which limits detailed studies of multipollutant effects.

In order to examine the intra-urban variability of air pollutants and hence potential exposure patterns some studies have used measurements taken with mobile platforms. These are typically used to obtain highly resolved measurements both in time and space during relatively short time periods (Bukowiecki et al., 2003; Durant et al., 2010; Fujita et al., 2011; Hagler et al., 2010; Isakov et al., 2007b; Weimer et al., 2009; Westerdahl et al., 2005; Zwack et al., 2011). While some of the past mobile studies focused on the spatial variability of several pollutants, others examined the temporal variability and most only considered a limited number of pollutants. However, in order to fully characterize the multipollutant mix in a complex urban environment a systematic approach is needed. This approach should involve multiple measurements at the same locations over different days and different seasons with high spatiotemporal resolution and with a large suite of measuring devices examining both gaseous and particulate pollutants simultaneously.

In this study, high resolution mobile measurements of multiple air pollutants were taken in the city of Montreal, Quebec, Canada, over multiple days with a focus on multipollutant spatial contrasts. A number of hypotheses can be explored given these mobile data, including: measurements taken by a monitoring network are not representative of all areas within a city and underestimate maximum exposures; predictions from numerical air quality models at fine grid resolution cannot account for the variability in pollution levels existing within a neighbourhood scale; hotspots of different pollutants exist

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that are relevant to neighbourhood scale exposure patterns and are difficult to identify and account for using traditional monitoring, passive sampling campaigns, emissions inventories or fine grid air quality models; NO_2, often used as a marker for traffic pollution, can indicate different pollutants in different locations and during different seasons; $PM_{2.5}$ within large urban areas exhibits more variability than currently appreciated.

The objective of this paper is to describe the mobile measurement platform and the strategy developed for its deployment in a large city and to present results from the analysis of the resulting mobile measurements to test some of the above mentioned hypotheses. Here we focus on an evaluation of the representativeness of mobile measurements in relation to existing monitoring sites and longer term conditions. We also focus on the application of such measurements for qualitative and quantitative assessments of the spatial variability in human exposure to multiple outdoor air pollutants. Related papers build from this work exploring correlation among pollutants and near road gradients (Levy et al., 2012a,b).

2 Methods

Air quality and meteorological measurements were taken by Environment Canada's mobile lab: Canadian Regional and Urban Investigation System for Environmental Research (CRUISER). CRUISER is a diesel engine vehicle (GMC C7500 medium duty truck) equipped with a power generator and climate control systems that maintain stable conditions inside the customized vehicle body, housing research-grade measurement instruments. To maximize data collection, during deployments CRUISER measurements are typically taken on a 24 h basis for the entire time period it is present in a study location. Much of the data are obtained when the vehicle is parked and plugged in at its "home base" location and depending upon the study objectives there are typically multiple periods of mobile measurements when CRUISER drives and measures, occasionally stopping to obtain fixed point data, meteorological measurements and to cross-reference with existing AQ monitoring sites.

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2.1 Study area

The study was conducted on the Island of Montreal, which has 1.8 million inhabitants (Statistics Canada, 2011), but a larger population in the city of Montreal and the surrounding area of 3.8 million, being the second largest city in Canada (Statistics Canada, 2011). As with most large cities, air pollution in Montreal is spatially variable (Crouse et al., 2009; Gilbert et al., 2005). Pollution sources on the island besides traffic include a variety of industrial activities, oil and gas refining, storage and distribution facilities, petrochemicals, metal refining, light manufacturing, multiple port areas, as well as heating (in the winter) (Environment Canada, 2006). Figure 1 shows a map of the city providing information on the different land uses, main roads and major point sources.

2.2 Measurements

The Montreal measurement campaign was conducted during 2009 in three seasons (winter, summer and autumn), with the combined analysis of the entire period referred to as the "annual" season. There was a three week deployment in each season and this paper focuses on the mobile portion of these measurements, i.e. excluding times CRUISER was parked overnight and other non-driving days.

Measurements of 23 different species were taken simultaneously from the CRUISER platform throughout the campaign at time resolutions ranging from 0.5 s to 2 min. Geolocation was recorded with a Garmin 176C GPS system every second and CRUISER's speed was determined from the GPS data. A list of the parameters measured, instruments used, their temporal resolution and detection limit is given in Table 1. The inlets for the air quality instruments were located at the roof of the vehicle, 3.6 m a.g.l. oriented near the front left side. The GRIMM Dust monitor, used for particle mass measurements (i.e. PM_{10}, $PM_{2.5}$), had a separate inlet to enable the capture of coarse particles, but due it is slow flow rate and the impact of horizontal speed on the capture efficiency of larger particles a small correction based upon CRUISER's speed was

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applied. A description of the inlets, data management and speed correction done to the GRIMM particle measurements is given in the Appendix.

Data were flagged for invalid periods, below detection limit and missing values for each instrument. The data were then combined to one dataset with the time increment set to one second, and instruments with greater time intervals were given repeating values to reflect the more-integrated sampling. An additional flag was used to indicate the likely impact of CRUISER's own plume when it was at stop sites (Fig. 1), so as to exclude such measurements in the analysis. Data from multiple studies indicate that this impact was most likely occurring when the vehicle speed was $< 10\,\mathrm{km\,h^{-1}}$, brief peak concentrations are observed with NO levels ≥ 20 ppbv and particle counts > 3000 #/cc. This resulted in 4 % of the mobile measurements being flagged, of which those occurring at stop sites were excluded.

2.3 Mobile measurement strategy

The strategy for CRUISER's mobile measurements was to travel along pre-defined routes, passing along or near highways, main roads and local streets, as well as residential, commercial and industrial areas (Fig. 1c). Two routes were determined and systematically followed: (1) East Montreal; (2) Central and West Montreal. The east route was used most often due to greater impact of industrial emissions and because of an asthma study being conducted in that part of the city (Dobbi et al., 2011). For both routes, the starting point of travel along the route was changed randomly each day so as to avoid sampling the same location at the same time of day. On any given mobile measurement day, which was typically between 09:00–20:00 local time (LT) (i.e. nighttime conditions were not part of the mobile campaign), the entire route was completed, while on a few days the route was covered twice or 1.5 times with the reminder completed the next day. This allowed for multiple samplings of the same locations on different days, times and seasons. The goal was to have sufficient measurements spread over days and seasons so as to increase confidence that the summary statistics derived for any given part of the route were representative of typical conditions.

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The median travel speeds calculated from the GPS were 20, 28 and 30 $km\,h^{-1}$ for winter, summer and autumn, respectively. Due to these slow traveling speeds, CRUISER was rarely on highways when in such areas and instead tended to drive on service roads parallel to the highways at some distance from the busiest lanes, sometimes with a dividing wall (2–5 m high) separating the express lanes from the service road. Figure 1c shows that a large majority of the sampling was conducted in residential areas and other areas where the population spends most of its time.

The mobile routine also involved measurements at 17 pre-defined parking locations (stop sites), such as government AQ monitoring sites. These systematic stationary sites were visited for 10–30 min each time to create a selection of "point samples". Meteorological measurements were only possible during these stationary periods due to the 10 m height of the telescoping tower. When stopping near a site was not possible (e.g. wind was too stagnant to allow orientation of CRUISER to avoid its own plume), the vehicle drove at slow speeds near the location, with such measurements referred to as "pseudo-stops". CRUISER's measurements were flagged to note times when it was stationary, pseudo-stationary or mobile.

There were 11, 17 and 6 mobile measurement days in the winter, summer and autumn, respectively, with 2–13 h on each day (median of 9 h). Figure 1c shows the number of measurements per km of road for the entire campaign; indicating more than 2000 one second measuring points km^{-1} along the pre-defined route. The greater the number of visits to an area the more representative the available data will be of the long term. Xu et al. (2007) used Canadian monitoring data from multiple cities to show that the number of random visits needed to estimate the long term average with a desired percent error (e.g. 20 %) depends upon pollutant. Fewer visits are required for NO_2, while more are needed for NO or CO. About 20 one hour visits per season are needed to have a 95 % chance of estimating the annual average NO_2 with 10 % error.

The eastern route was completed 26 times, of which 11 were in the winter, 14 in the summer and 1 in the autumn. Based upon Xu et al. (2007) this translates, approximately, into 95 % confidence that the estimate in annual average NO_2 is within 15 %

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of the actual value for the summer and winter. While long term representativeness is important and is discussed below, the spatial patterns and pollutant interrelationships presented in this paper are expected to be a reliable representation of the conditions in Montreal given that all locations were visited on the same days and all pollutant measurements were obtained simultaneously. In fact, the spatial patterns shown in this paper are believed to represent a significant improvement over most, if not all, other mobile studies of spatial patterns and near roadway gradients (e.g. Beckerman et al., 2008; Hagler et al., 2010) given the large number of measurements for multiple pollutants obtained in a systematic nature in a large, complex city.

2.4 Spatial analysis

Since CRUISER's measurements were taken along roads and because of the sharp gradient in concentrations of some pollutants with distance away from the road (e.g. Karner et al., 2010), analysis of the measurements was done by grouping them according to road segment, using ESRI's ArcGIS 9.3 (ESRI, Redland, CA). First, the road network of Montreal was used to extract only the roads CRUISER had visited, so as to avoid attributing measurements to the crossing roads. Then, each of CRUISER's measurement points were assigned to the nearest road segment within a distance of 20 m. Samples were averaged per road segment first by day and then averaged for all days, so as to give an equal weight for every day and avoid bias towards days with more measurements (e.g. greater measurements on a segment due to slower driving speed).

To assure proper representativeness of the measurements at each road segment, only segments that meet the following criteria were used in the analysis: more than 100 valid one second measurements of the examined pollutant, more than 100 valid measurements per km of the examined pollutant and that the measurements were spread over 3 or more different days. Most road segments included in the analysis were sampled on 17 different days or more. Statistical analysis was done with the open-source statistical language R (RDCT, 2009).

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Since CRUISER is inherently limited to taking measurements while traveling on roads, an argument can be made that these measurements are limited in that they only represent road emissions and traffic related pollution and not exposure levels at a home address, which are often used in health studies, for example. However, for 38 % of the time CRUISER took measurements on local roads in residential areas, where it met few other vehicles and therefore measured ambient residential pollution levels. Similarly, even on busier roads, there were many periods when cross-winds blew the air and pollutants from over the areas adjacent to the road to CRUISER's inlet. This implies that the dominant impact on the mean road segment concentrations was not solely the result of very local emissions associated with nearby traffic, but instead tended to be representative of a realistic mix of the local emissions and general "neighbourhood" conditions over that part of the driving route.

3 Results

In this section, we first compare the measurements obtained by CRUISER to routine measurements taken by the air quality monitoring network in the study area. We then qualitatively examine the spatial variability of several pollutants at the sub-urban scale with respect to their emission sources. Last, we quantitatively examine the representativeness of air quality monitoring sites to various microenvironments in their vicinity.

3.1 Representativeness of the mobile measurements

Regular stops as close as possible to seven different AQ sites (Fig. 1a) were used for comparison between the mobile and routine measurements (i.e. government monitoring network sites). In addition to providing some measure of quality control and direct comparability, this was done to provide insight into the fine scale spatial representativeness of the AQ network site locations and of the long term representativeness of the CRUISER measurement periods. Although routine monitoring typically reports hourly

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data, the local government agency (Ville de Montreal; "VdM") provided one minute readings (CO, NO, NO_x, SO_2, O_3) for the periods corresponding to the CRUISER mobile campaign.

For the direct comparison, the concurrent CRUISER and VdM one minute measurements during each 10–30 min stop were averaged. Before averaging over the whole time period of each stop CRUISER's one second measurements were first averaged to one minute values. Only minutes with more than 45 one second measurements available (i.e. after excluding 1 s measurements due to probable impacts from CRUISER's own emissions) for both CRUISER and VdM were used to compute the stop period averages. This data completeness criteria helped insure the most appropriate matching of the two sets of measurements for comparison. There were six AQ sites with such paired measurements, although a full suite of pollutants were not monitored by VdM at each site. Also, due to the proximity of safe or accessible parking locations relative to the sites the actual distance between CRUISER and each site varied (~ 10–100 m; typically 20 m). In addition, for one site (AQ4) there was a large difference in sampling height since the VdM measurements were from a rooftop of a few stories.

Although important for mobile surveys to undertake, direct comparison is complicated by the fact that there can be considerable differences in the measurement methods used. Table 1 lists the methods on CRUISER. Similar to CRUISER, VdM used Thermo Scientific instruments (Waltham, MA). However, for the routine VdM monitoring, trace level instruments were not used and calibrations were done over a larger range with less focus on low concentrations. Also, there were fewer zero readings compared to CRUISER (critical for low CO) and one minute VdM readings for $PM_{2.5}$ were not possible (VdM used a Thermo Scientific Tapered Element Oscillating Microbalance with the Filter Dynamic Measurement System option to improve measurement of semivolatile material; FDMS-TEOM). In addition, one instrument was used by VdM for NO and NO_x with switching between measurement modes every 30 s, which can lead to incorrect NO_2 in areas impacted by frequent NO plumes. Furthermore, the

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converter used in the VdM instruments did not provide a specific measure of NO_2 (Lee et al., 2011) as was the case for CRUISER.

Given the differences in the instruments, how they were operated, the short time for each comparison (typically ≤ 15 min of paired readings per point) and the distance between inlets, reasonable agreement was found for the available pollutants. Figure 2 shows scatter plots of CRUISER vs. VdM measurements during times when CRUISER was parked near the AQ sites. For NO, NO_2, NO_x, CO, O_3, $PM_{2.5}$ and SO_2 the R^2 values are 0.83, 0.62, 0.85, 037, 0.81, 0.60 and 0.16, respectively, and the slopes (CRUISER/AQ) are 0.94, 0.72, 0.78, 0.93, 0.88, 0.66 and 0.77, respectively. For SO_2 (Fig. 2d), we have excluded one high point associated with a local plume (SO_2 = 34 ppbv) that occurred during a stop because it was highly influential on the regression results and obscured the relationship at the more typical lower concentrations. When this point is included the R^2 is large (0.96) and the slope increases to 1.07 thus indicating better agreement over the larger range of concentrations possible. For CO there are a limited number of points for comparison due to few VdM sites with data. There were also considerable differences in the operation of the instruments and thus, a low correlation is not surprising. The fact that considerably more of the VdM CO values in Fig. 2a are less than typical regional background levels suggests that for the low concentrations occurring in Montreal the CRUISER method was producing more accurate results. Similarly for $PM_{2.5}$ (Fig. 2c), the measurement methods were significantly different and VdM only reported hourly values. There are good correlations for NO, NO_2 and NO_x. For NO_2 and NO_x VdM concentrations tended to be higher than CRUISER at the higher concentrations with a larger discrepancy for NO_2, which is likely due to the non-specific measure of NO_2 utilized by VdM.

When short term surveys are used to infer urban gradients in concentrations for the purpose of informing the magnitude of chronic exposures and the differences among the population and for most other studies on urban air quality it is important to consider the longer term representativeness of short term data. Overall, data in this study were limited for close examination of how well average concentrations based upon

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CRUISER's 2009 visits were able to represent the actual annual average concentrations. This was the case even when combining CRUISER observations during stops and pseudo-stops to utilize as much of the information for an area as possible. The main reasons were that for East Montreal, which was the focus of the study and so experienced a greater number of unique visits to VdM AQ monitoring sites (≥ 18), there are only three such sites and not all pollutants were measured at each of these sites. Note that three sites covering an area the size of East Montreal is not atypical with respect to density of monitoring in many cities, Canada or elsewhere. In addition, despite developing criteria to identify and exclude such 1 s measurements there remains some uncertainty regarding when CRUISER's generator plume was influencing the measurements. Nonetheless, for all seven sites within CRUISER's route (east, central and west) we compared CRUISER and VdM averages to assess representativeness.

Two different 2009 annual metrics were calculated to represent the long term; the daily average (i.e. all 24 h) and the daytime average (i.e. between 09:00–20:00 LT), which better corresponds to the times of day CRUISER was driving. These two long term metrics are compared to two different short-term averages; (1) the VdM daily averaged values on the days CRUISER took mobile measurements during the nine separate weeks it spent in Montreal and (2) the average of all CRUISER stops and pseudo stops after eliminating minutes suspected of being impacted by the mobile lab plume. These CRUISER data were first averaged according to visit and then for all visits at an AQ site so that each visit received equal weight. These comparisons are shown for NO_x in Fig. 3 and the ratio of the different metrics is given in Table 2. This one pollutant (NO_x) is selected because, due to the methodological differences discussed above for each pollutant, the most confident comparison of CRUISER's estimate of the annual average (i.e. chronic exposure) in each area to the actual AQ network values is expected to be based upon NO_x.

The VdM average among all the driving days was calculated to determine if, collectively, the days in each season selected for mobile measurements were atypical (i.e. did we choose typical days for the measurement campaign?). Table 2 shows that on

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the selected driving days NO_x tended to be higher on average by 18 %, compared to the 2009 daily averages. However, the overall ranking among the sites during these days was similar to the annual pattern (Fig. 3). For example, AQ5, which is near two major highways, is seen to be the site with the highest levels – consistent with the annual average. AQ1 is the "cleanest" site in both measures although according to the 2009 averages there is limited difference in NO_x among the four other AQ sites. These small differences, indicating homogeneity in NO_x as seen in urban background areas throughout the city, presents an additional challenge to using the AQ network to test if CRUISER's limited number of visits can realistically quantify annual average NO_x patterns from background to peak concentration areas.

Comparisons of CRUISER vs. the VdM 2009 averages for the other pollutants are shown in Fig. A1 in the supplemental material. The average difference between the study period VdM observations and the annual average among the sites with measurements were 9 %, 16 %, −1 %, −23 %, 28 % and 12 % for CO, $PM_{2.5}$, SO_2, O_3, NO and NO_2, respectively (Table 2). For all pollutants except O_3 and SO_2 the study period had higher concentrations than the annual average at all AQ sites. Ozone was the opposite, being biased low during the study at all AQ sites. SO_2 was higher than average (10 %) at two sites and was biased low at the third site by 23 % (Table 2). The facts that this comparison is between VdM data (i.e. there are no methodological differences in the measurements) implies that the measurement days when CRUISER was driving in Montreal were somewhat representative of the long term averages. They tended to be biased high, except O_3, which was biased low. However, in terms of combustion pollutant levels (NO_x), the average high bias was 18 % for the period, while for NO_2, which is often of most interest as an exposure indicator, the bias was relatively small, at 12 %. These differences indicate that collectively the days selected for driving were reasonably representative of what Montreal typically experiences.

CRUISER's limited, but relatively random collection of daytime measurements at and around each VdM site also tended to yield reasonably representative values for NO_x. Table 2 shows that at the two sites with the greatest number of visits CRUISER

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estimates of average NO_x were higher than the 2009 daily average by 23 % (AQ1) and 5 % (AQ2). At the three other sites, where there were only 8 visits, CRUISER average NO_x estimates were biased low, from 3–24 %. This is reasonable given the small number of visits. It is also important to note that despite limited measurements CRUISER observations correctly identified the high NO_x site (AQ5). CRUISER was biased low here (29.2 vs. 37.7 ppbv) because there was a greater tendency for easterly winds (i.e. away from the highway) during the 8 visits.

Consistent with the 2009 average pattern CRUISER also showed that the variability among the all sites except AQ5 was relatively small. However, due to the limited number of observations, CRUISER observed a greater variability than tended to exist. Thus, there is some uncertainty in CRUISER's annual average estimates. However, where there was > 18 visits, which corresponds to the survey in East Montreal (i.e. the focus of the rest of this paper), the range between the two VdM sites was 16.1–16.6 ppbv (2009 daily average), while CRUISER reported a 17.4–19.8 ppbv range.

As indicated above, information on the differences between CRUISER short term estimates of the average and the actual 2009 average for the other pollutants is shown in Fig. A1. These comparisons should be interpreted with some caution, however, given the measurement method differences and the overarching issue of limited data at most sites except 2–3 in the east. This figure shows, for example, that for NO_2 CRUISER was within 20 %, on average. However, for the sites only visited 5 times the CRUISER longer term average NO_2 estimate was biased low by up to 35 % compared to the true annual average.

3.2 Intra-urban variability observed by CRUISER

The heterogeneity in emission sources in Montreal (Fig. 1) resulted in large spatial variations in concentrations, as expected. The multiple pollutant measurements on CRUISER allowed for focus on differences in spatial patterns among pollutants. Such differences are exemplified for four pollutants (NO_2, UFP, SO_2 and benzene) in the East Montreal maps shown in Fig. 4. Traffic related pollutants, such as NO_2 and UFP, show

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highest concentrations near the highways (e.g. NO_2 mixing ratios of up to 80 ppbv and UFP counts of up to 215 000 #/cc near Highways 40 and 25 shown in Fig. 4a, b). Lower concentrations were measured on major roads (12–28 ppbv NO_2 and 30 000–55 000 #/cc UFP) and the lowest in residential areas (< 12 ppbv NO_2 and < 30 000 #/cc UFP). These differences are consistent with the reported emissions for Quebec in 2007, that the transportation sector accounted for 74 % of NO_x emissions, compared to 15 % from industrial sources, including 2 % from oil refineries (Busque et al., 2009).

Other pollutants that have a significant contribution from industrial emission sources, such as SO_2 and benzene, show a different intra-urban spatial pattern, with high concentrations around the industrialized eastern part of the city between highways 40 and 138 (Fig. 4c, d, respectively; roads identified in Fig. 1b). Although the AQ sites also indicate some of the areas of high and low NO_2 and SO_2 across Montreal, only broad scale patterns can be detected and not nearly the level of detail provided by the mobile survey. For SO_2, Busque et al. (2009) report that, provincially, transportation accounted for only 11 %, compared to 7 % from the oil refineries, with the aluminum smelters contributing 30 % and other industrial sources contributing 24 %. With no aluminum smelters on the Island of Montreal and transportation being spread over the entire road network, oil refineries and other industrial point sources have a dominant contribution to SO_2 as is seen in Fig. 4c. Benzene emissions are not reported independently in Busque et al. (2009), however for volatile organic compounds (VOC's) transportation accounted for 37 %, gasoline and diesel marketing for 5 % and other industries for 27 %.

Sulphur dioxide and VOCs such as benzene are of interest in East Montreal given their link to the refining and petrochemical industries. The mobile measurements indicate that even though broad similarities for these two pollutants are evident over the urban scale shown in Fig. 4, there are differences in their behaviour on smaller scales. For example, the peak area with SO_2 concentrations (marked A in Fig. 4c) is located further north-east than the benzene peak area (marked B in Fig. 4d).

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Considerable differences in multipollutant behaviour are also observed in residential areas. For example, while SO_2 has high concentrations just northeast of Luis-H. Lafontaine Hospital (marked C in Fig. 4c), benzene shows only a small increase. In contrast, benzene shows increased levels north of the Marie Claire Daveluy park (marked D in Fig. 4d), but SO_2 shows low concentrations in that location. Differences in the variation in SO_2 and benzene concentrations also exist on an even smaller scale. For example, a comparison of measurements along a road crossing Highway 40 and passing next to the Petro-Canada oil refinery to the north and the Ultramar oil distribution terminal to the south (Avenue Marien, location shown by arrow in Fig. 4a) shows that some peaks in concentration occur together while others do not (Fig. A2). Furthermore, ratios of toluene to benzene in the peaks and between peaks also vary.

3.3 Microenvironments and sub-neighbourhood scale variability

In order to characterize the extent that chronic exposure levels vary among a range of typical settings in an urban environment, ten small East Montreal areas that were systematically visited by CRUISER were selected and compared (Fig. 5). The "annual" distributions among these different settings are also compared to measurements taken by CRUISER when at the nearest AQ site during stops and pseudo-stops. These latter sites are included in Fig. 5 to provide insight into the representativeness of the monitoring sites and hence the possible error or bias resulting from deriving exposure estimates from a central site.

The ten areas were selected so that they represent a range of urban microenvironments while also being relatively close in proximity to one another, thus reflecting the activity space over which individuals might typically travel, especially children and the elderly. Their locations within the city are shown in Fig. 1b, labeled as A–E, and in greater detail in Fig. 5. The areas selected include: the intersection of two main roads – Rue Sherbrooke E and Blv. St-Jean-Baptiste (A1); an active commercial area on Rue Sherbrooke E (A2) near A1; a residential street (Rue Forsyth) ~80 m east and parallel to A2 (A3). These are located on the east side of the island in proximity to the oil

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refineries and are compared to the nearest monitoring site (AQ1, within 1.2 km of all these areas).

In the middle of Fig. 5 another grouping of sites is shown in comparison to their local monitoring site (AQ2), at distances of 0.7–1 km. The settings for these five areas are: a moderately busy road in a residential area (Anjou) next to houses (B1); a section of the same road next to an active commercial area (B2); a local road in a residential area next to a service road and a busy highway (HW-15), but with a noise blocking wall separating the highway and the service road from the local road (C1); near an exit ramp of the local major highway (HW-15) bordering the residential area without a noise blocking wall (C2); a street corner in a residential area with a small car repair shop (D) in Anjou. The pair B1 and B2 is located east of the busy interchange of Highways 40 and 25.

The last grouping of microenvironments, shown on the right side of Fig. 5, corresponds to monitoring site AQ3 at a distance of 2 km or less. These two areas are located west of the other areas and are generally upwind from the major stationary emission sources and traffic corridors and include a residential street (E1) and an intersection of two local roads (E2) some 500 m from E1.

Each area in Fig. 5, as well as the AQ sites, were visited an equal number of times, mostly on the same days and in all seasons. The distributions in Fig. 5 show all of CRUISER's measurements for these periods, first averaged by day and then presented in box plots for all days for different pollutants. Visually, differences in the levels among the areas are evident. Significant differences between the areas were assessed for each pollutant separately by the non-parametric Kruskal–Wallis test followed by the Wilcoxon Rank Sum test for pairwise group comparisons. Areas with a similar letter are significantly different (p-value < 0.05). Based only upon the distributions of the values averaged by day for each location the differences were only significant for NO_2 and BC. However, due to the small sample size for these tests (< 20 days) the analysis was repeated with the actual 1 s data. As shown in Fig. A3 many more significant differences are detectable for all pollutants examined using the higher resolution data.

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The mean NO_2 mixing ratios (red squares in Fig. 5) at the traffic affected areas A1 and A2 are double the 10 ppbv measured next to the nearest monitoring site, AQ1, while the residential area A3 has mixing ratios similar to AQ1. This indicates that the monitoring site under-estimates the exposure levels for A1 and A2 while providing a representative estimate for A3. AQ1 also under-represents $PM_{2.5}$, BC and UFP for A1 when examining both median (A1 is higher by 49 %, 21 % and 60 %, respectively) and mean (A1 is higher by 78 %, 68 % and 128 %, respectively). Comparing the busy intersection A1 with the active commercial area A2 and the residential street A3, concentrations of NO_2 are higher for A1 than A2 and for A2 than A3 (Fig. 5a), as can be expected given the characteristics of those areas. The same differences in the distributions are also seen for UFP for these three areas (Fig. 5e).

NO_2 measurements next to the main road microenvironment at C1 and C2 are considerably higher than the monitoring site AQ2 with the median (mean) higher by 10 and 14 ppbv, respectively (20 and 16 ppbv, respectively), an increase of 210–265 %. Ozone at C1 and C2 is showing a corresponding decrease of 32 % from AQ2 levels. BC and UFP also have higher concentrations at C1 and C2 compared to AQ2 of more than 180 % for the median and 200 % for the mean of BC and 300 % for both mean and median of UFP. The mean $PM_{2.5}$ next to C2 is also higher than AQ2 by about 20 %, providing evidence of its spatial variability. The resemblance between C1 and C2 for these pollutants, however, implies that on average the noise blocking wall in C1 has little effect on air pollution. Comparing areas E1 and E2, higher values of NO_2 (13.6 vs. 9.4 ppbv), BC (3.1 vs. 2.0 $\mu g\,m^{-3}$), UFP (27,950 vs. 21,575 #/cc) and toluene (0.63 vs. 0.48 ppbv) and lower O_3 (18.1 vs. 19.3 ppbv) are measured at the intersection area of E2 compared to the residential area E1 near it. Clearly, any time spent at such an urban microenvironment enhances exposure and leads to greater misclassification if exposure is assigned according to the nearest AQ site.

Last, area D shows similar values to what is measured next to the monitoring site AQ2 for most pollutants, with the exception of toluene. The presence of a small paint and body shop in that area caused the high values of this organic compound with

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a mean of 1.14 ppbv. Toluene levels in this localized microenvironment were 2–3 times higher than at the nearby monitoring site AQ2 (0.37 ppbv), and versus the nearby areas B1, B2, C1, C2 (0.40, 0.45, 0.53 and 0.45 ppbv, respectively). The levels were even somewhat higher than the mean measured at areas A1–A3 (0.76, 0.78 and 0.69 ppbv, respectively) and the monitoring site AQ1 (0.98 ppbv), which are in closer proximity to the petroleum industry. The difference between area D and the others for toluene is much higher in the summer season (not shown), probably due to greater evaporation of this compound in higher temperatures and the fact that the shop more often operated with open doors in the summer.

4 Discussion

Short term measurement campaigns are common in atmospheric chemistry and air quality studies (e.g. Daum et al., 2003; Lee et al., 2011; Pennington et al., 2012). For exploring chemical and physical processes this is not a limitation if a reasonable number of cases are captured and the conditions can be shown to be typical. However, for describing spatial and temporal behaviour, such as intra-urban variability for informing and developing empirical population exposure models (e.g. Dijkema et al., 2011) or the nature and frequency of certain events of interest (e.g. exceedence of guidelines) it is important to consider the representativeness of the short term study period. Yet this is rarely examined quantitatively, though it can be relevant for framing the conclusions in the proper context. If available, AQ monitoring network data can be used to assess representativeness of the short term study period and to compare with and complement the more intensive, but short term measurements collected in such campaigns.

As discussed above, Xu et al. (2007) examined this issue for multiple pollutants and several Canadian cities and this provided a starting point for the CRUISER deployment. For VOCs Miller et al. (2012) showed that measurements in the transition seasons tend to be more representative. Consistent with this, Henderson et al. (2007) carried out their two week Vancouver, BC, monitoring campaigns in the late winter and late

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summer based upon the greatest likelihood of representativeness. However, they did not subsequently assess how representative their measurements were based upon the actual period monitored. In terms of chronic exposure rankings Wheeler et al. (2008) compared the variation observed across 54 sites in Windsor, Ontario, among seasons. They found Spearman correlations between an individual season and the average pattern among seasons of 0.84 (summer) to 0.97 (spring) for NO_2. This range decreased to 0.75–0.93 for SO_2, but overall the ranking of locations captured by a discrete two week periods appeared to be quite stable. Wheeler et al. (2008) obtained similar results for benzene and toluene.

In this study, short term measurements taken with the mobile lab were compared both to the concurrent measurements at AQ monitoring sites in Montreal and to the annual averages at the sites. This was possible because the mobile measurement strategy included repeated visits to points close to the AQ sites in the study area. The comparisons show that given the differences in measurement methods the "research grade" mobile survey observations were in reasonable agreement with the concurrent AQ monitoring site measurements. This lends confidence to the mobile data and to subsequent inferences made regarding differences between air quality at the long term monitoring sites and other unmonitored parts of the city.

Demonstrating how well the limited set of mobile lab measurements spread among three seasons captures the true long term pattern across Montreal is difficult. This is because it is necessary to rely on the existing monitoring sites to determine the long term value, yet there are only a limited number of monitoring sites, measurement methods are not the same between the network and the mobile lab and the mobile lab is not able to measure right next to the sample inlets at the sites. Despite these limitations we compared the averages of the short term (from CRUISER and from the corresponding day's 24 h data from VdM) and 2009 daily and daytime average values at a number of sites. Overall, the nine week study period was found to have experienced higher than average pollutant levels except for O_3, which was lower during the period. For example, NO_x, which is a good indicator of urban combustion pollution, was higher on average

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by 18 %, compared to the 2009 daily average. Averages derived from CRUISER's limited number of visits spread through three seasons were within ±24 % of the 2009 daily average. Not surprisingly both CRUISER's observations and the 9 weeks of VdM data correctly identified the location (AQ site) with the highest NO_x levels.

Identification of the AQ sites with notably higher vs. lower annual average concentrations was generally possible with the limited number of visits acquired by the mobile lab. However, there were discrepancies, particularly when the differences between the long term values at the sites were small. For example, the 2009 mean NO_x at four of the five sites visited only differed by a range of 1.3 ppb. Not surprisingly, the short term visits are not able to achieve the precision in their estimate of the annual average to similarly rank these sites within such a small overall concentration range. However, for characterizing spatial gradients and chronic exposure levels detecting such small differences are likely less important than capturing the larger exposure differences that exist among various areas. Thus, the tendency to place AQ sites in locations where they are more likely to observe urban or neighbourhood background levels means they generally do not document the full exposure gradients. This also means that they are of less use for assessing whether the exposure gradients captured by a short term mobile lab survey indicative of the true long term pattern. Conversely, due to this limitation in monitoring networks, conducting mobile surveys and short term saturation monitoring campaigns is necessary for better understanding chronic exposure and subsequent epidemiological studies. The limitations in the traditional monitoring site criteria is clearly one reason why in North America there is currently a large effort to implement near roadway monitoring locations (see http://www.epa.gov/ttnamti1/nearroad.html), as has been common in some European countries (Craig et al., 2008).

The capabilities of physically-based and empirical exposure models to determine urban spatial patterns have improved in recent years. For example, the ability of comprehensive, multipollutant air quality models to run for longer periods at grid resolutions of 1–5 km is increasing (e.g. Makar et al., 2010; Shrestha et al., 2009). Yet, as shown in this paper, there remains a large and complex variability even within the finest model

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grids (at best ~4 km^2 area) in use today. Only empirical models, such as land use regression (Johnson et al., 2010), have resolved this sub-grid scale and only for a limited number of pollutants and based upon short term saturation measurements. The only other approach to resolve this sub-grid scale is to use dispersion models (Isakov et al., 2007a; Nordling et al., 2008), however these require emissions and meteorological inputs, do not treat chemical or physical changes in the mix of pollutants and neither have been fully evaluated. Here we demonstrate, for example, that concentrations reduce from 20–80 ppbv for NO_2 and 55 000–215 000 #/cc for UFP to less than 12 ppbv and 30 000 #/cc, respectively, between a highway and a residential area over a distance of less than 1 km in the residential area of Anjou. While such gradients may be predicted by dispersion or LUR models, stationary monitoring networks clearly cannot account for them.

Measurements from the systematic deployment of a mobile lab presented in this paper indicate that changes in average air pollutants concentrations on small scales or even concentration hotspots can be the result of a small business operating in a residential area (e.g. dry cleaners, car repair shop or a restaurant), proximity to a commercial area or an intersection in a residential neighbourhood. Such small scale variations may result in large differences in exposures to air pollutants among the population, yet they are often not included in air quality models or other exposure models because of lack of detailed knowledge about the location and type of activity of small emitters or due to their small emission volumes compared to other major sources. Furthermore, our results show that local emitters may have an impact on a local scale that can be greater than that of major sources further away. This is exemplified here with the toluene hotspot in Anjou next to the paint and body shop in a residential area that is 2–3 times higher than other locations in its neighbourhood and somewhat higher than locations 2–4 km away in proximity to the petroleum industry sources. In this case toluene is likely an indicator of a suite of other unmeasured pollutants emitted by the same activity that may also have harmful effects.

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The characterization of previously unknown local air pollution hot spots is impossible with traditional measuring techniques (i.e. stationary AQ monitors), given that measuring sites are selected to either measure ambient levels or examine previously known emission sources. The ability to identify small scale emission sources with mobile measurements has been previously demonstrated. For example, Dionisio et al. (2010) showed that measurements of $PM_{2.5}$ and PM_{10} at stop sites with multiple woodstoves were 30 $\mu g\,m^{-3}$ and 85 $\mu g\,m^{-3}$, respectively, higher than the neighbourhood average at the same times in a study in Accra, Ghana. Levy et al. (2001) also show some evidence of elevated $PM_{2.5}$ near diesel buses in a walking-mobile measurements study in Roxbury, Massachusetts, United States. Apart from the mobility aspect of these campaigns, which allows them to cover larger spatial domains, another advantage of mobile measurements that enables them to map fine spatial structures and identify hot spots is that they typically use shorter averaging times for the measurements of few seconds to few minutes (e.g. one second in this study and one minute by Levy et al., 2001).

Apart from showing the fine structure of air pollution concentrations in the urban environment, the results presented in this paper demonstrate the ability of mobile measurements, when taken in a systematic manner across days and seasons, to characterize a wider range of settings in a fashion that is relevant for chronic human exposure. Quantification of such patterns is difficult to achieve using modeling techniques or stationary measurements. Although a multipollutant mobile study such as the one described here is not feasible in many locations (mainly due to the high costs involved), the relatively recent emergence of portable technologies for measurements of environmental parameters (i.e. coupling portable digital devices and GPS with microsensors for air pollution, atmospheric parameters and biomonitoring in distributed stationary or mobile sensors networks) may fill the gap in our ability to estimate the spatio-temporal variability at the intra-urban scale, though likely with some cost to measurement accuracy or precision and only for certain pollutants.

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5 Conclusions

The complex emission sources in large metropolitan areas result in substantial spatial variations in air pollutant concentrations and hence in complex population exposure patterns. The characteristics of chronic exposure patterns across Montreal, Canada, from the neighbourhood down to the single street scale, were explored in this paper through a unique deployment of a comprehensive mobile air quality lab. The variability was observed to be different for each pollutant, even for those usually associated with a specific source such as traffic. This highlights the challenge facing epidemiological studies seeking to study the effects of exposure to multiple pollutants and differences between them. The patterns observed here for East Montreal appear reasonable given the known distribution of sources. Coupled with evidence that the mobile survey captured the larger spatial differences seen in the AQ monitoring network and given that the averages from the survey in East Montreal, where there were 18–21 visits to each AQ site across seasons, were in reasonable agreement with the 2009 averages, we conclude that the systematic approach to a mobile lab survey presented in this study provided representative estimates of the chronic exposure levels and gradients for the population in the eastern part of the city.

Existing methods for predicting exposure surfaces at intra-urban scales all have inherent limitations. While AQ monitoring networks are limited to a finite number of point measurements, dispersion models are challenged by the availability of input data for meteorology and emissions and empirical models are dependent upon the number of sites and the conditions they reflect during short term saturation monitoring campaigns, as well as on the ability of the predictors to capture the full variability that exists at the scales of interest. Furthermore, the predictions from these models, such as LUR, can only reflect the predictors used in the model. If the major contribution to the model is from traffic related predictors (e.g. road lengths inside a buffer), for example, then the model is only able to predict that portion of the ambient concentrations that results from traffic. The more complex and spatially variable the array of sources contributing

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to ambient concentrations, the lower the ability of the model to provide accurate predictions for a specific pollutant. The spatio-temporal complexity shown in this study helps to better characterize that part of the variability in ambient concentrations not currently captured by models.

In order to improve exposure estimates, future studies examining intra-urban variability of air pollutants will need better exposure predictions than currently available. Moreover, given the complex spatial behaviour of different pollutants shown in this study, characterizing multipollutant exposures is an even more difficult challenge to meet. One possible path to follow is by combining several modeling approaches (e.g. dispersion, air quality and LUR models) as well as different measurement techniques (e.g. satellites, remote sensing). Furthermore, with improvement in publicly available databases on small scale emitters, emerging technologies (e.g. distributed sensors networks) and statistical modeling approaches, progress on some of these challenges can be expected in coming years.

Appendix A

Instrumentation and speed correction

A1 Description of the instrumentation inlets to CRUISER:

The inlets for the air quality instruments are located at the roof of the vehicle, ~3.6 m above ground, oriented near the front left side. There were two particle and two gas inlets. The PTRMS had its own 1/4 inch Telfon inlet line with a Teflon filter outside at the entrance. The other gas analyzers utilized another separate Teflon line with splitting inside CRUISER as required for the different measurements. The main particle inlet draws air in at a 16.7 L min^{-1} through a cyclone to achieve a 2.5 µm size cut followed by a 3.18 cm OD stainless steel sampling tube of 1.88 m in length. Inside CRUISER this tube is surrounded by a 15.24 cm PVC pipe containing an external sheath air

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flow drawn from outside, which serves to keep the sample air containing particles at ambient temperature as long as possible to avoid condensation in summer and evaporation in winter. The AMS, CPC and PA are connected to the base of this 1.88 m tube drawing air, approximately isokinetically, to their individual inlets through stainless steel (1/8–1/4") and flexible conductive tubing. The GRIMM Dustmonitor has its own ~ 1.8 m stainless steel tube extending through the roof with the GRIMM multi-directional inlet drawing at 1.2 L min^{-1}. This separate inlet was needed to enable the capture of coarse particles (i.e. the main inlet has a cyclone), but due it is slow flow rate and the impact of horizontal speed on the capture efficiency of these large particles a small correction based upon CRUISER's speed was required.

HOA measurements were obtained from the AMS using the positive matrix factorization (PMF) method (Paatero and Tapper, 1993), which interprets the measurements using factor analysis methods. A recent review of multivariate factor analysis techniques applied to AMS is presented in Zhang et al. (2011). AMS measurements were run through PMF using the toolkit available from: http://tinyurl.com/PMF-guide

A2 Speed correction for particulate matter (PM) measurements:

Speed correction was applied to the particles measurements (PM_{10}, $PM_{2.5}$ and PM_1), to account for the effect of vehicle speed on airflow in the inlet to the GRIMM dust monitor. A factor was calculated for each particle size range by comparing PM values in the stop sites to the measurements during the approach to and leaving the stop site in a radius of 500 m around the site and within a timeframe of 30 min before and after the stopping period. The factors were then applied as:

Corrected PM = Original PM × (speed × CF + 1),

where the speed is measured in km h^{-1} and CF is the correction factor (13.40×10^3 for PM_{10}, 6.50×10^3 for $PM_{2.5}$ and 3.52×10^3 for PM_1). The larger correction factor for PM_{10} reflects the increased influence of air flow on the particles with larger mass.

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Table 1. List of pollutants measured by CRUISER and the methods employed.

Parameter	Avl.[a] (%)	Instrument model	Response time	Detection limit
NO	80	Thermo Scientific / TECO 42CTL	1 s	0.4 ppbv
NO_2	64	Thermo Scientific / TECO 42CTL with Photolytic converter	1 s	0.8 ppbv
NO_y	62	Thermo Scientific / TECO 42CTL with Photolytic converter and Mo converter	1 s	0.4 ppbv
NO_x	64	Calculated ($NO + NO_2$)	NA	NA
NO_z	46	Calculated ($NO_y - NO_x$)	NA	NA
SO_2	79	Thermo Scientific / TECO 43 TLE with a 5 µm pore size Teflon filter	10 s	1 ppbv
CO	78	Thermo Scientific / TECO 48 with a 5 µm pore size Teflon filter	10 s	100 ppbv
O_3	79	Thermo Scientific / TECO 49	20 s	1 ppbv
O_x	53	Calculated ($NO_2 + O_3$)	NA	NA
PM_{10}	88	GRIMM Dust Monitor 1.100	6 s	0.1 $\mu g\,m^{-3}$
$PM_{2.5}$	88	GRIMM Dust Monitor 1.100	6 s	0.1 $\mu g\,m^{-3}$
$PM_{1.0}$	88	GRIMM Dust Monitor 1.100	6 s	0.1 $\mu g\,m^{-3}$
UFP (Ultrafine particles)	87	GRIMM CPC 5.403	1 s	0.6 #/cc
BC (Black carbon)	49	Droplet Measurement Technologies / Photo Acoustic	1 s[b]	$< 3.3\,\mu g\,m^{-3}$

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Table 1. Continued.

OM (Organic matter)	73	Aerodyne Aerosol Mass Spectrometer	2 min	0.15 $\mu g\,m^{-3}$
Sulfate	73	Aerodyne Aerosol Mass Spectrometer	2 min	0.04 $\mu g\,m^{-3}$
Nitrate	73	Aerodyne Aerosol Mass Spectrometer	2 min	0.02 $\mu g\,m^{-3}$
HOA (Hydrocarbon-like organic aerosols)	36	Aerodyne Aerosol Mass Spectrometer (PMF application[c])	2 min	0.15 $\mu g\,m^{-3}$
MZ57 (mass to charge ratio of 57)	36	Aerodyne Aerosol Mass Spectrometer	2 min	0.01 $\mu g\,m^{-3}$
benzene	73	IONICON High Sensitivity PTR-MS	10 s	20 pptv
C3 benzene	73	IONICON High Sensitivity PTR-MS	10 s	20 pptv
toluene	73	IONICON High Sensitivity PTR-MS	10 s	20 pptv
Xylenes	73	IONICON High Sensitivity PTR-MS	10 s	20 pptv

[a] Availability: percent of valid measurements from all 1 s measurements.
[b] Vibrations during mobile measurement result in a poor signal to noise ratio for 1 s resolution data of the Photo Acoustic's BC data. However, the analysis presented here aggregates multiple measurements and thus improves the detection limit. With a 30 min averaging time the detection limit improves to 0.71 $\mu g\,m^{-3}$ and road segment average values used in this paper generally represent averaging over at least 1700 s.
[c] For more information see Description of the instrumentation inlets to CRUISER

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Table 2. Ratios between different average pollution levels shown in Figs. 3 and A1.

	Ratio type[a]	AQ3	AQ1	AQ2	AQ4	AQ7	AQ5	AQ6	Average
NO_x	C/D		0.93	0.87	0.92		1.02	0.83	0.91
	B/D		1.17	1.20	1.20		1.09	1.22	1.18
	A/D		1.23	1.05	0.97		0.77	0.76	0.96
NO	C/D		1.01	0.89	0.94		1.06	0.81	0.94
	B/D		1.25	1.35	1.32		1.12	1.37	1.28
	A/D		2.04	1.80	1.76		1.64	2.69	1.99
NO_2	C/D		0.89	0.86	0.91		0.98	0.84	0.89
	B/D		1.14	1.13	1.15		1.05	1.15	1.12
	A/D		0.95	0.78	0.99		0.68	0.65	0.81
O_3	C/D	1.19	1.20		1.20		1.19	1.22	1.20
	B/D	0.79	0.81		0.76		0.73	0.78	0.77
	A/D	0.88	0.99		0.63		0.60	0.72	0.77
CO	C/D		0.94				1.08	0.90	0.98
	B/D		1.02				1.12	1.12	1.09
	A/D		0.99				1.61	1.47	1.36
$PM_{2.5}$	C/D	0.95	0.97	0.98	0.96	0.98	1.01	0.96	0.97
	B/D	1.16	1.12	1.36	1.13	1.10	1.14	1.08	1.16
	A/D	0.95	0.70	1.06	1.36	1.64	1.27	1.14	1.16
SO_2	C/D		1.02	0.98	0.98				1.00
	B/D		1.10	0.77	1.10				0.99
	A/D		1.37	1.56	0.99				1.31

[a] A: CRUISER's average during stops; B: VdM's average during CRUISER's measurement days; C: VdM 2009 daytime annual averages; D: VdM 2009 daily annual averages.

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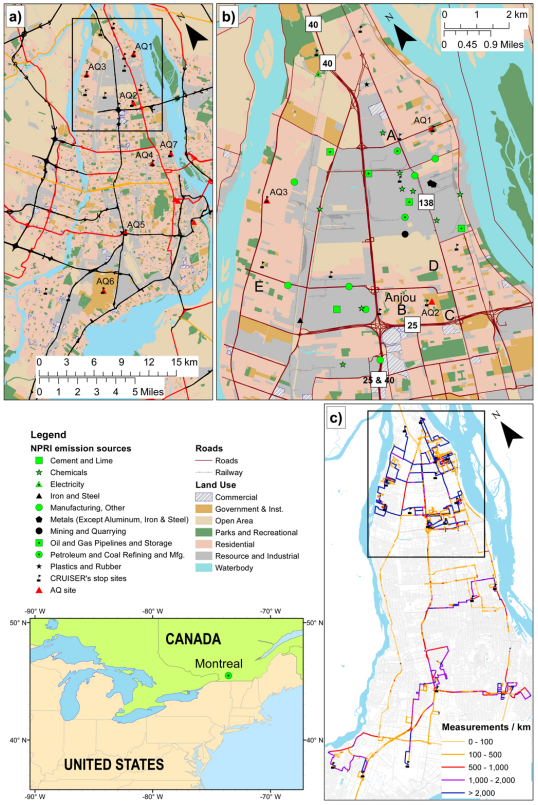

Fig. 1. Map of the study area **(a)** with a higher resolution on the east part **(b)**, showing major roads, land use types, major emission sources and CRUISER's stop sites, as well as measurement density per kilometer of road segment (measurements / km) for the annual period **(c)**. Letters A–E in **(b)** refer to areas discussed in Sect. 3.3 and Fig. 5.

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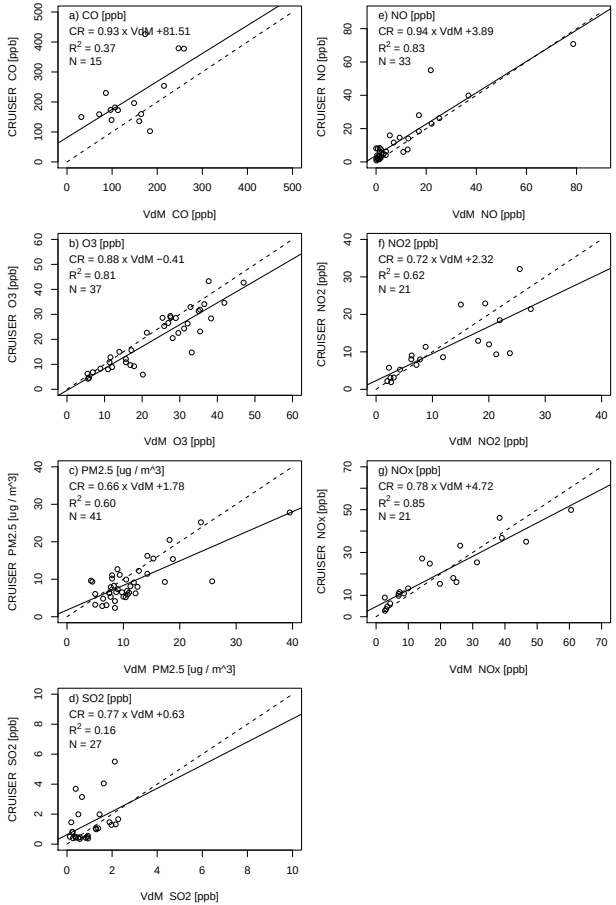

Fig. 2. Scatter plots of CRUISER's vs. VdM measurements during times CRUISER was parked in close proximity to AQ sites.

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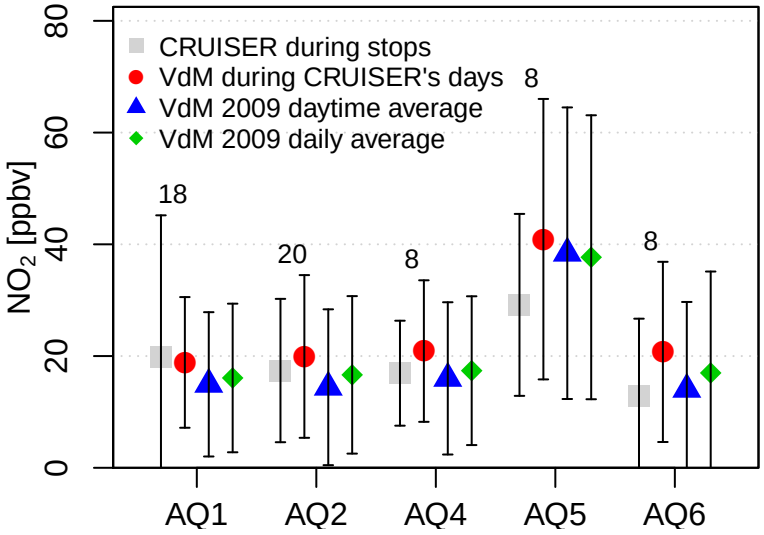

Fig. 3. Comparison of CRUISER's average pollution levels during time it was parked next to VdM's AQ monitoring sites (gray squares), VdM's average levels during CRUISER's measurement days (red circles), VdM 2009 daytime annual averages (blue triangles) and VdM 2009 daily annual averages (green diamonds) for seven relevant pollutants. Whiskers denote one standard deviation. Number above whiskers denotes number of visits to site.

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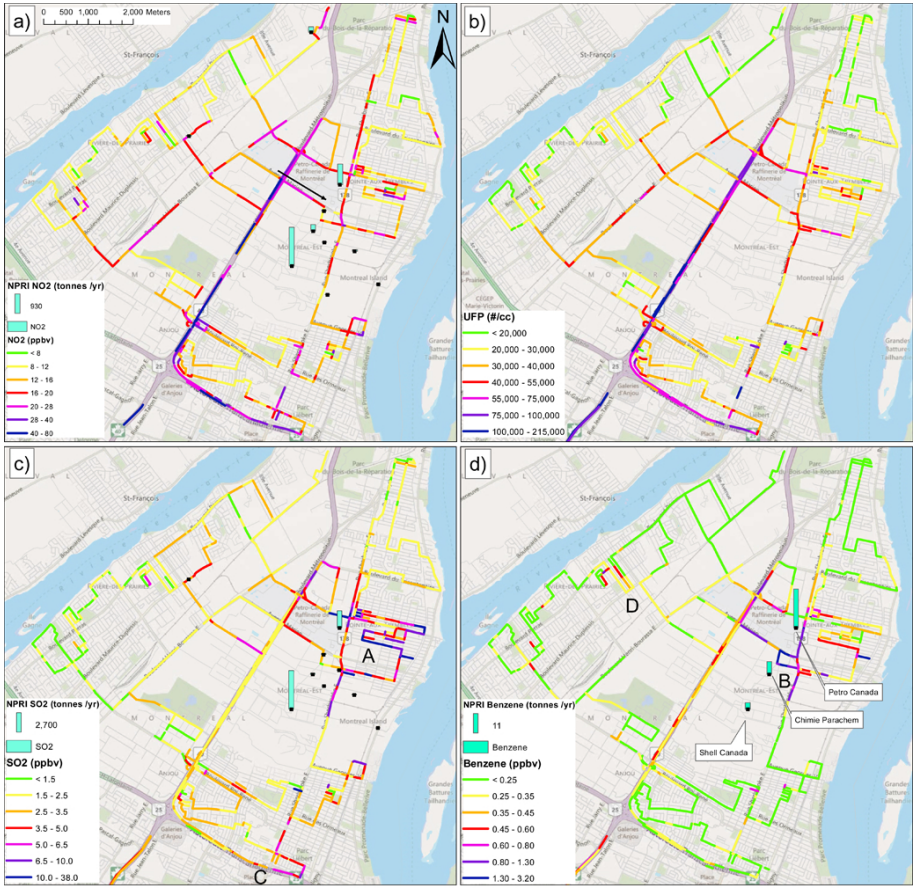

Fig. 4. "Annual" mean pollution levels at road segments for NO_2 **(a)**, UFP **(b)**, SO_2 **(c)** and benzene **(d)**, along with NPRI reported point emissions for the relevant pollutants. Roads were filtered as described in Sect. 2.4. NPRI emissions for NO_2 are nitrogen oxides expressed as NO_2. Arrow in **(a)** marks the location of the cross section discussed in Sect. 3.2 and Fig. A2.

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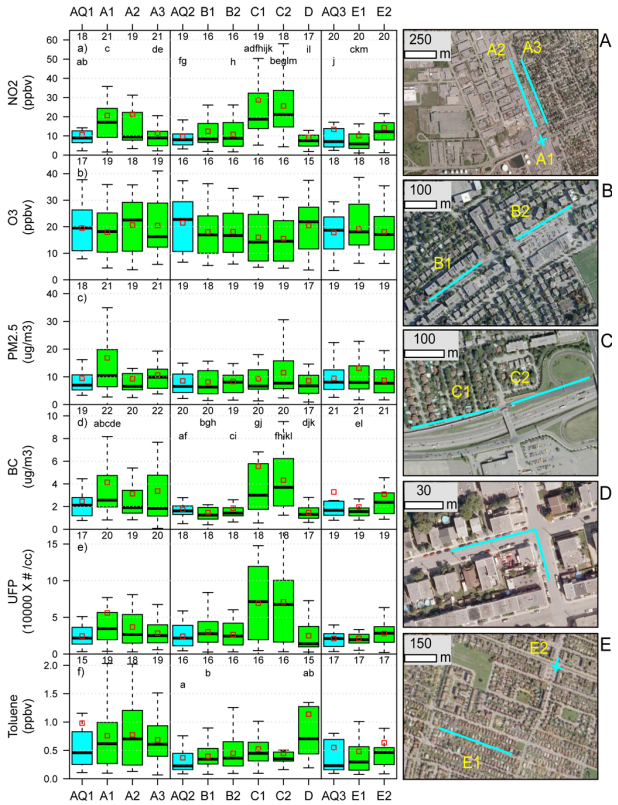

Fig. 5. Box plots showing pollutant levels (NO_2, O_3, $PM_{2.5}$, BC, UFP and toluene; **(a–f)**, respectively) at ten different areas (green) compared to measurements taken next to three air quality monitoring sites (blue). Red squares are the mean and numbers above each box mark the number of days included in the statistics. Right panel shows local settings of each area marked in blue (A–E). See Fig. 1b for locations within the city.

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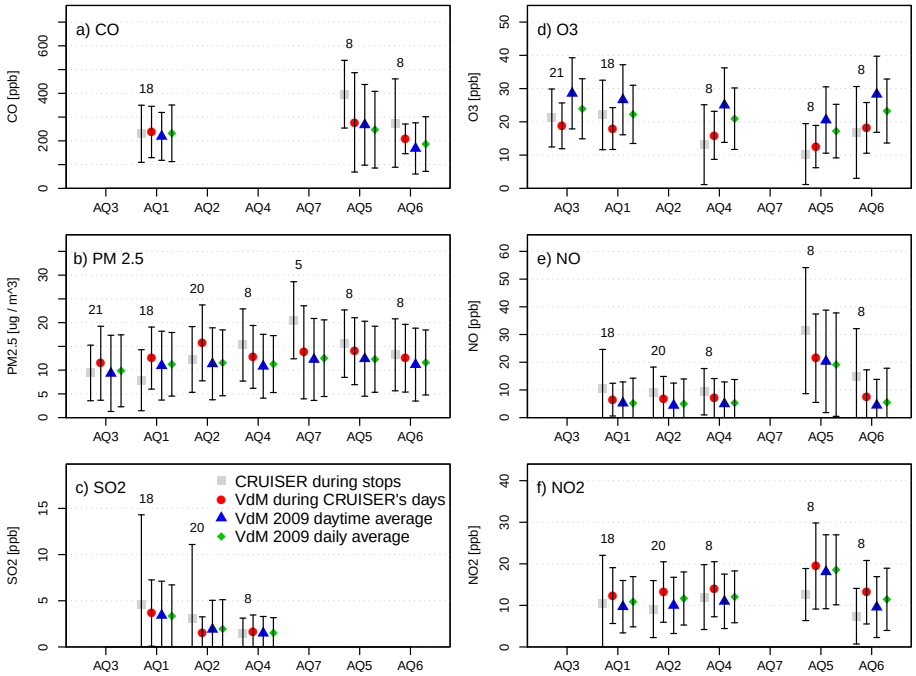

Fig. A1. Same as Fig. 3 for CO **(a)**, $PM_{2.5}$ **(b)**, SO_2 **(c)**, O_3 **(d)**, NO **(e)** and NO_2 **(f)**.

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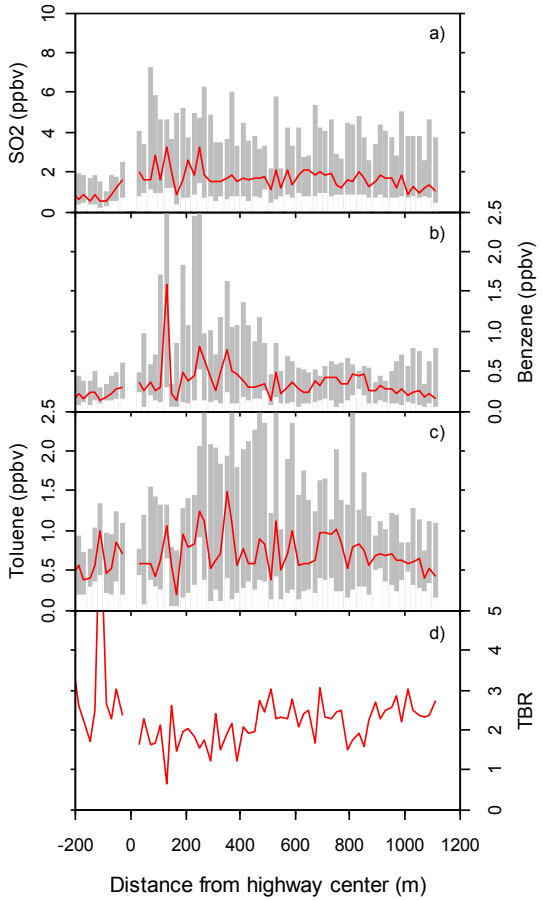

Fig. A2. Median pollution levels (red) line and IQR (grey) at 20 m bins for the entire study for SO_2 **(a)**, benzene **(b)** and toluene **(c)** along the cross section taken on Avenue Marien crossing Highway 40, location is marked in Fig. 4a. The toluene to benzene ratio (TBR) is shown in **(d)**. Only bins with more than 7 measurements are plotted.

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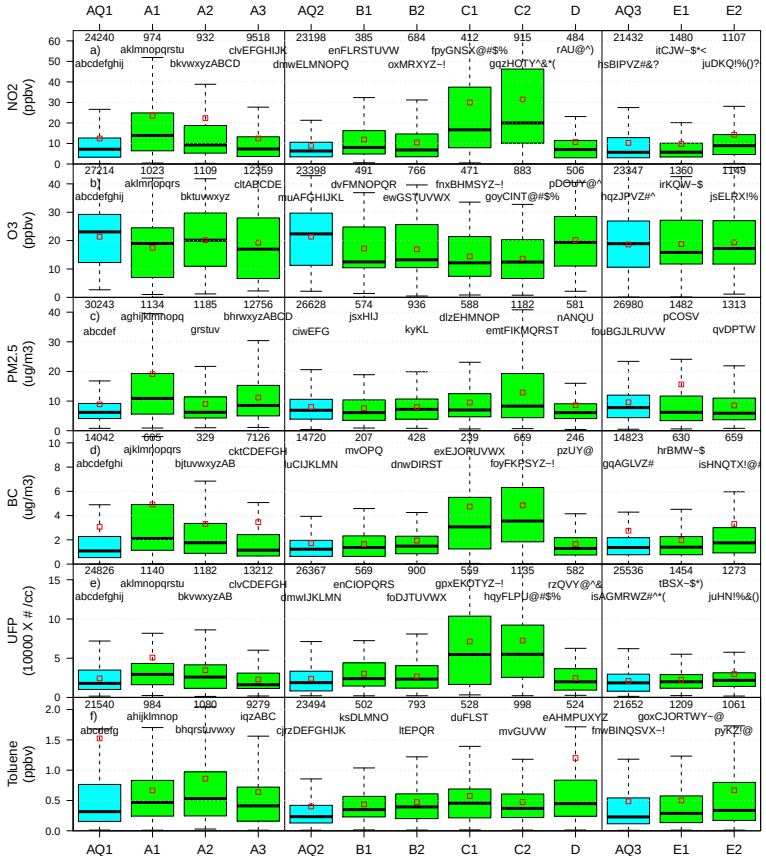

Fig. A3. Same as Fig. 5 with the original 1 s data and letter categories identifying statistically significant differences. Pairs of location with matching letters are significantly different from one another (p-value < 0.05) according to the Wilcoxon Rank Sum test for pairwise group comparsion.

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