Assessing Toxicity of Organics in Urban Source Sectors for Air (ATOUSSA)

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Introduction

Urban areas are hotspots of several classes of pollutants with numerous source sectors emitting pollutants to air. Air pollution has been linked to health effects of chronic exposure and there have been studies showing associations of air pollution and mortality or numbers of admissions to hospitals.[1] Known to have adverse effects on human health and environment, gaseous pollutants and particulate matter, used as ambient air quality indicators, are routinely monitored. The mixture of chemicals in air is complex and contains many toxic components including organic pollutants and metals. Knowledge of the composition of the air mixture is essential in revealing potential health risks associated with exposure to urban air. This is the motivation for the ATOUSSA (Assessing Toxicity of Organics in Urban Source Sectors for Air) study initiated in Toronto in 2016.

Sampling under ATOUSSA was conducted in Toronto and the Greater Toronto Area (GTA), the largest city in Canada, at 8 locations from August 2016 to August 2017 for 6 periods of 2 months each, with replicate samplers at each site. The selection of sites (Fig. 1) ranges from one high density commercial site in downtown Toronto representing urban/traffic land-use (WB – Wallberg Bldg); 1 traffic site adjacent to a multi-lane highway (MOECC highway 401 site); 3 low density urban/residential sites (NT-North Toronto; NY-North York; SC/KE-Scarborough); 1 mixed source site located adjacent to traffic/light industry/parkland/residential (DV-Downsview); 1 industrial site located near the steel industry area in Hamilton Harbour / Burlington (HH/BU); and 1 background site situated just offshore of the downtown core (HP-Hanlan's Point). Target analytes included polycyclic aromatic compounds (PACs), organophosphate esters (OPEs), new flame-retardants (NFRs) and polybrominated diphenyl ethers (PBDEs). In addition, a new method for measuring trace metals in PUF disk samples was developed and validated.

Parallel samples were also collected at each site and used for screening and testing sensitive *in vitro* assays. The intention is to explore toxicity indicators that relate to the mixture of chemicals in air and thereby provide an assessment of cumulative toxicity from a range of pollutants and pollutant classes.

Materials and Methods

For assessing the organic pollutants in air, sample deployment, preparation, processing, shipping and storage procedures followed protocols used under the GAPS network and reported in Rauert et al.[2] Field blanks were collected at all sampling sites for assessment of sampling/laboratory contamination and sample results were blank subtracted using the mean analyte concentration detected in blanks. Air concentrations (pg/m^3) were derived from the mass of the chemical (pg) collected on the sampler divided by an effective air sampling volume (m^3) determined using the GAPS Template.[3] Analysis of FRs followed methods reported in Rauert et al. (2018) while PACs were analyzed according to Jariyasopit et al. and Schuster et al.[4,5]

For determination of trace metals, PUF disk underwent an additional pre-cleaning step that involved rinsing with dilute nitric acid. Trace metals were then determined through digestion followed by analysis by ICP-MS.[6]

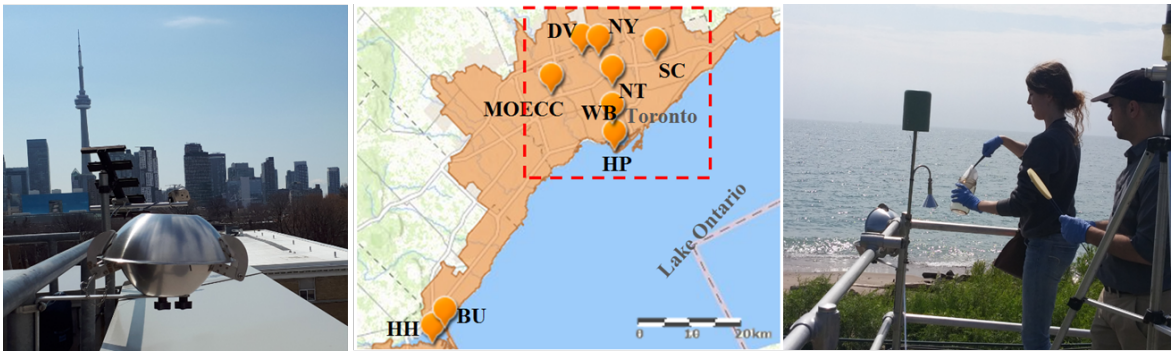

Figure 1: Map of sampling sites under the ATOUSSA study initiated in summer 2016.

Results and Discussion

Flame Retardants (FRs): OPEs concentrations in air were two orders of magnitude higher than both PBDEs and NFRs (Figure 2), which is consistent with the trends reported by Rauert et al. at the global scale.[2] The levels of Σ_9OPEs in Toronto and GTA ranged from 330 to 4150 pg/m^3, with an average of 1750 pg/m^3. Σ_{10}PBDEs concentrations, excluding BDE-209, ranged between 0.9 and 32 pg/m^3 with an average level of 9.2 pg/m^3 whereas the average concentration of NFRs ranged between 3.6 and 20 pg/m^3, with EHTBB as predominant compound in NFR profile.

Spatially, the distribution of FRs was relatively uniform across the GTA across the different site types. The exception were the OPEs that were significantly higher ($p<0.05$) near traffic sources and in the more densely urban areas (Figure 3).

Seasonally, concentrations of OPEs, PBDEs and NFRs were lower in winter months i.e. December 2016 to March 2017 but with no significant difference compared to summer or fall season.

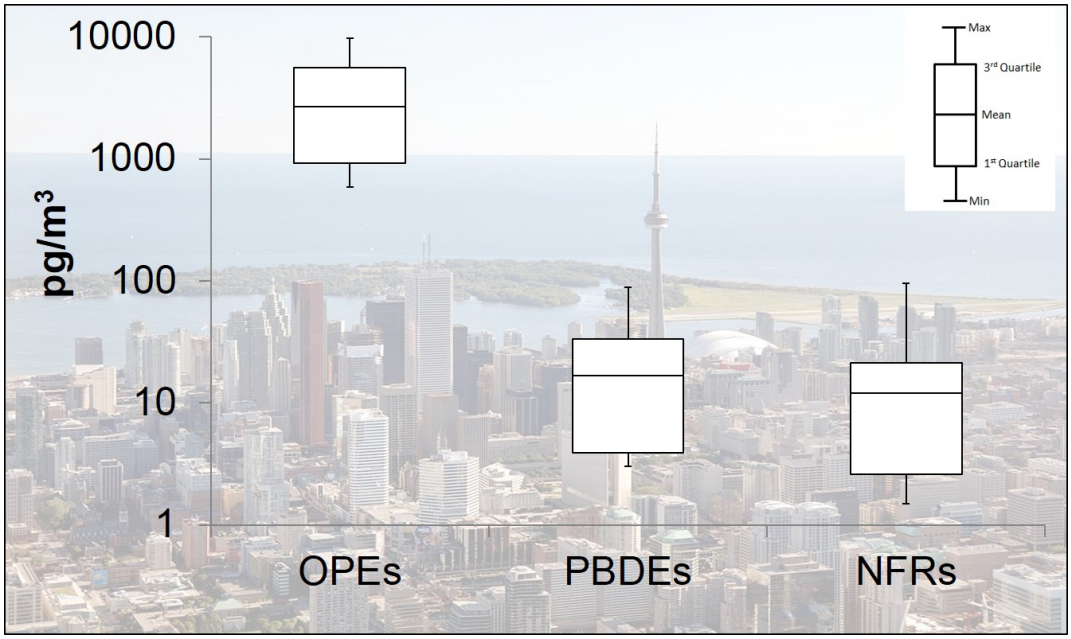

Figure 2: Total concentrations of FRs in Toronto source sector sampling sites (n=8) under the ATOUSSA study derived from PUF disk passive air samplers for the period August-2016 to August-2017.

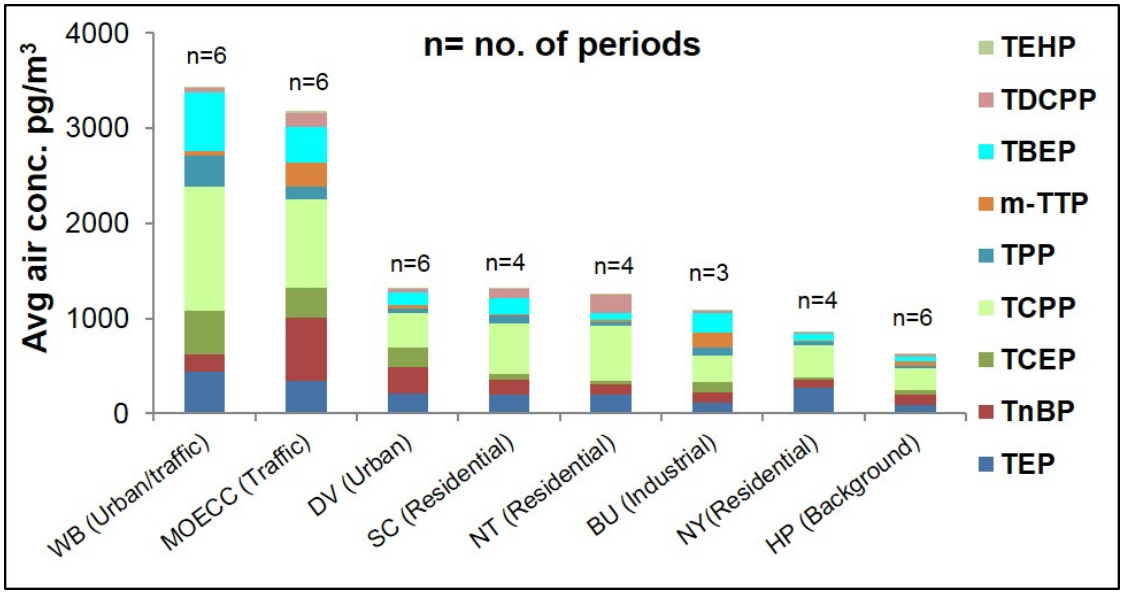

Figure 3: Levels of OPE FRs in air across different source/site types in Toronto for samples collected during August 2016-August 2017 under the ATOUSSA study.

Polycyclic Aromatic Compounds (PACs): Highest concentrations of PACs in air (~20-50 ng/m^3) were observed at the site in Hamilton Harbour (HH) / Burlington (BU), which is impacted by steel industry sources and highway traffic, and the MOECC site located adjacent to the 16-lane Highway 401 that runs across Toronto. Concentrations were also notably elevated at the Wallberg Building site (WB) located in downtown Toronto on the University of Toronto campus and the site in Downsview (DV, mixed traffic/residential/light industry/parkland) located in north Toronto. Levels of alkylated-PACs were about a factor of two higher and followed a similar site profile with the exception the HH/BU site, which exhibited elevated PACs but did not exhibit elevated alk-PACs. Alk-PACs are associated with petrogenic sources (i.e. fossil fuel) whereas PACs are associated with pyrogenic sources e.g wood burning or traffic/industry exhaust. In the oil sands region of Canada alk-PACs are typically 5 times higher than unsubstituted PACs in air.[5]

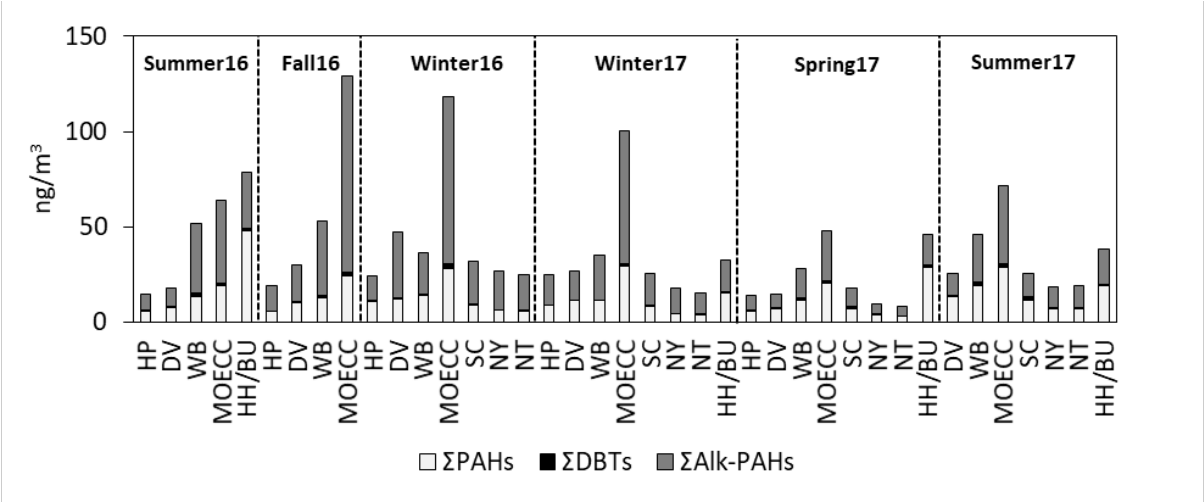

Figure 4: Spatial and seasonal variations of PACs and alkylated PACs across the Greater Toronto Area associated with different source sectors (see Figure 1) for samples collected during 6 sampling periods from August 2016 to August 2017.

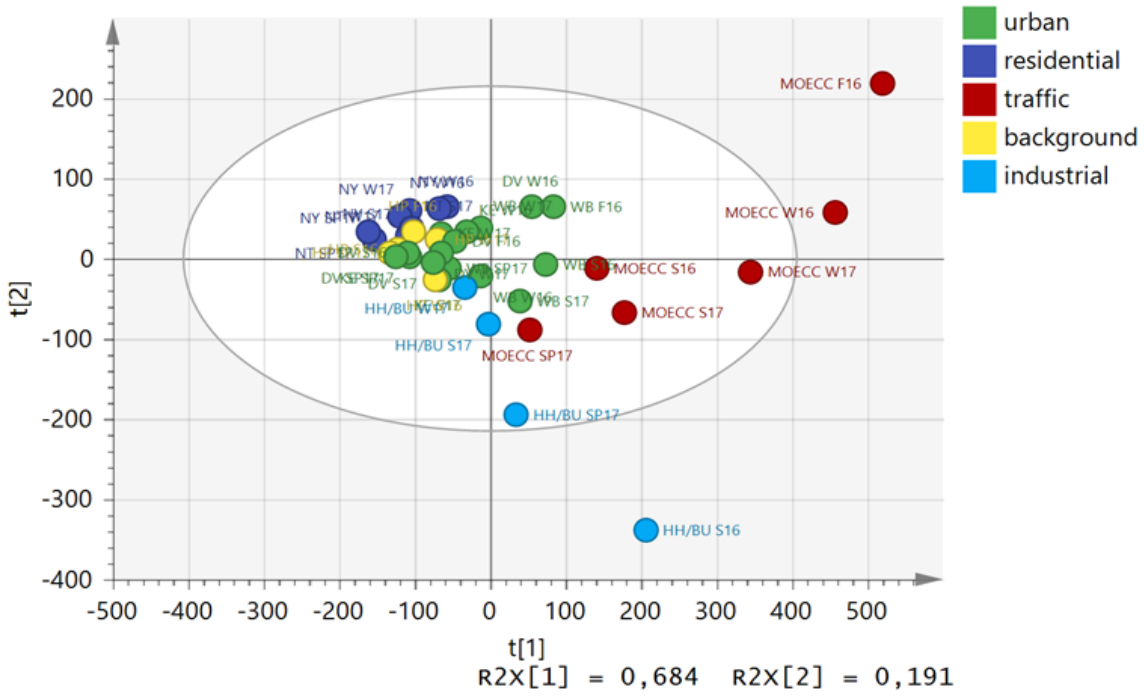

Figure 5: Principal component analysis plots for sampling sites and periods.

Principal Component Analysis. Principal component analysis was performed using SIMCA 14.1 on 39 observations (samples) categorized by seasons and sites. Variables are target analyte concentrations in which alk-PAHs were grouped as alk-NAPs, alk-PHEs/ANTs, alk-FLUs, alk-FLAs/PYRs, alk-BTCs. The variables that contained numbers of non-detects greater than 25% of total observations were excluded from the analysis. Figure 5 provides an overview of spatial variation associating with different source sectors for air. The first and second factors (x-axis) represent 68.4% and 19.1%, respectively, of the explained variance level. The two dominant source sites are separated from the others – the MOECC site which is heavily impacted by highway traffic, and the HH/BU sites that is impacted by industrial sources in Hamilton Harbour, including steel manufacturing. It is noteworthy that the HH/BU sample from summer 2016 is separated from the cluster. This reflects a change in the sampling location during the course of the study. In summer 2016 the site was located closer to the industrial sources and then moved to a new long-term location about 4 km away starting in Winter 2017 (Fig. 1).

Toxicity Assessment: A variety of *in vitro* methods are being applied to the replicate passive air sample extracts for assessing a range of toxicity endpoints (e.g. mutagenicity, cytotoxicity, oxidative stress). The aim is to explore correlations between toxicity indicators and concentration levels of different compound classes associated with different source sectors for air. Ultimately, this can lead to toxicity indicator maps that represent the mixture of chemicals in air (Figure 5).

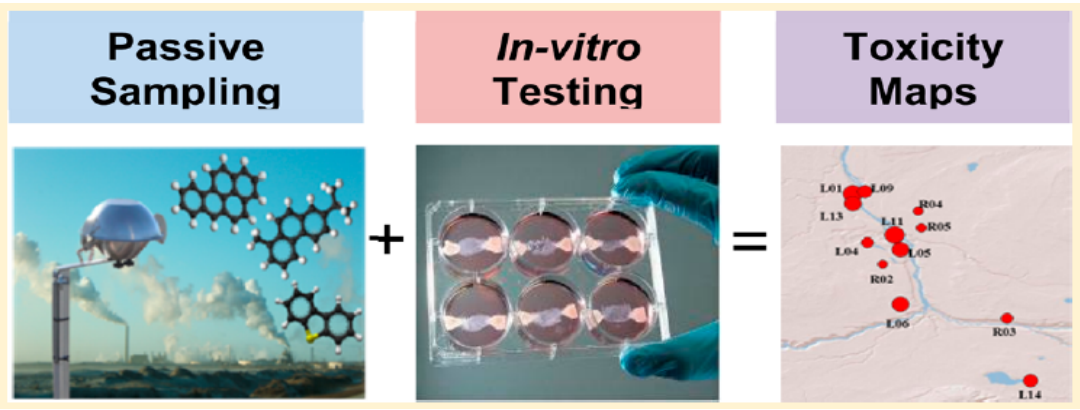

Figure 5: Conceptual diagram for the "toxicity indicator mapping" approach.

Trace metals in air using PUF-PAS: New methodology has been developed and validated for the measurement of trace elements in air using PUF-PAS. The approach has been applied to the ATOUSSA study samples to reveal new information on time-weighted levels of metals in air.[6] These data will be linked to results of organic pollutants and to new methods being explored for assessing toxicity indicators for mixtures of chemicals in air.

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