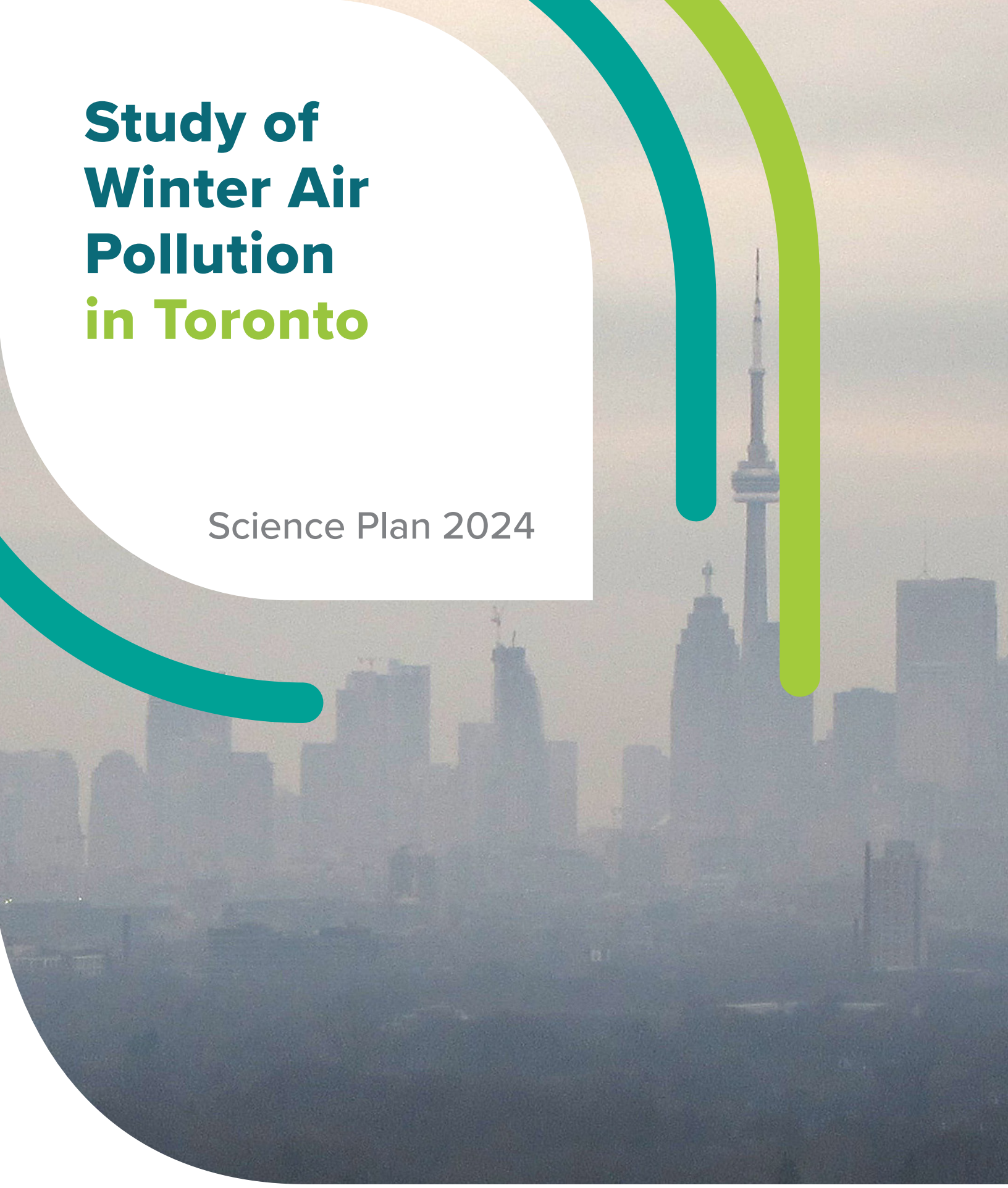
Study of Winter Air Pollution in Toronto

Science Plan 2024



Environment and Climate Change Canada
Environnement et Changement climatique Canada

Canada

Cat. No.: En88-16/2024E-PDF
ISBN: 978-0-660-69347-7
EC23108

Environment and Climate Change Canada
Public Information Centre
Place Vincent Massey building
351 St-Joseph boulevard
Gatineau Quebec K1A 0H3
Toll free: 1-800-668-6767
Email: enviroinfo@ec.gc.ca

Cover photo: © GettyImages

Aussi disponible en français.

Executive Summary

The Study of Winter Air Pollution in Toronto (SWAPIT) is an integrated scientific investigation of urban air quality. It is led by Environment and Climate Change Canada (ECCC) and includes study partners, clients, and stakeholders from federal, provincial, and municipal government agencies and several universities.

SWAPIT aims to advance our understanding of the urban air pollutant mixture. Though much progress has been made in understanding and managing air quality in recent decades, the levels of some pollutants have not fallen as expected. In addition, the mixture of pollutants to which we are exposed simultaneously is a growing concern. The timing of SWAPIT allows for a focus on the relatively under-investigated conditions that are present during winter, and those differ from the rest of the year in terms of the environmental conditions and pollutant emissions.

The SWAPIT Science Plan presents background information about the study, a detailed description of study activities with reference to the scientific literature, and an overview of the tools and activities that will support the generation and communication of SWAPIT's results.

The core questions to be addressed by SWAPIT are:

1. What sources and processes are responsible for the urban air pollutant mixture?
2. What makes up the urban air pollutant mixture and in what quantities?
3. How does the urban air pollutant mixture vary in space and time?
4. How is the urban air pollutant mixture related to human and environmental health risks?

Over ninety scientific and technical experts are involved directly in collecting data and interpreting results under the study. Study activities comprise forty-four sub-projects on urban air quality research topics ranging from the emissions of vehicles that have been parked at cold temperatures to the impacts on urban wildlife from air pollution that is captured by falling snow.

A key component of SWAPIT is a six-week intensive field measurement campaign that will take place from January to March 2024 at several locations in Toronto. Data collected during the campaign will be combined with results of other ongoing efforts to report on the urban air pollutant mixture and improve the scientific and technical tools that we use to understand urban air pollution in Canada's cities.

A Note About Mixing Ratios, Concentrations, and Levels

A key activity in air pollution science involves describing the abundance of pollutants. Abundance can be expressed in several ways, and in the context of air pollution, common descriptors include *mixing ratio*, *concentration*, and *level*. *Mixing ratio* and *concentration* have precise definitions, though both can take several forms, whereas *level* is a less technical term. In this Science Plan, the terms *concentration* and *level* are used most often to describe the abundance of pollutants in air in a generic sense, and *mixing ratio* is used only where specified by the scientist(s) contributing the relevant text.

Table of Contents

List of Figures

List of Tables

Appendices

[This page is intentionally left blank]

Study of Winter Air Pollution in Toronto: Science Plan

"We cannot solve our problems using the same thinking that we used when we created them"
– Albert Einstein

1. Introduction

The Study of Winter Air Pollution in Toronto (SWAPIT) is an integrated scientific investigation of urban air quality. The study aims to advance our understanding of the urban air pollutant mixture, and study timing allows for a focus on the relatively under-investigated conditions that are present during winter at mid-latitudes.

The SWAPIT Science Plan presented herein is divided into three sections. This introduction presents background information about the study and is aimed at non-specialist readers with general knowledge of air quality issues. Second is a detailed description of study activities with reference to the scientific literature for identifying knowledge gaps and justifying how SWAPIT will contribute to bridging them. Finally, the third section describes the tools and activities that will support the generation and communication of SWAPIT's results.

1.1: Study Background

SWAPIT is led by Environment and Climate Change Canada (ECCC) and includes study partners, clients and stakeholders from federal, provincial, and municipal government agencies as well as several universities. Building on initial discussions, the SWAPIT Science Plan Framework was delivered in November 2022. The Framework set out four over-arching questions to be investigated by SWAPIT (see Figure 1).

At the core of SWAPIT is a response to the call for improved characterisation of the urban air pollutant mixture. That call has been expressed by a variety of stakeholders who rely on sound scientific information to carry out research, assessment, policy-making, program development and delivery, and communication. In relation to urban air, such stakeholders have consistently expressed the need to understand the breadth of air pollutants at fine spatial scales, and that need is interpreted in relation to SWAPIT's over-arching questions below.

The improved characterisation of the urban air pollutant mixture can be separated into two components. The first relates to the mixture's chemical constituents, many of which have been studied and managed under separate programs and lack integration as a result. The second characterisation component relates to the variation in individual and combined pollutant levels through space and time. The latter component is increasingly relevant as equity and justice considerations gain prominence in environmental management.

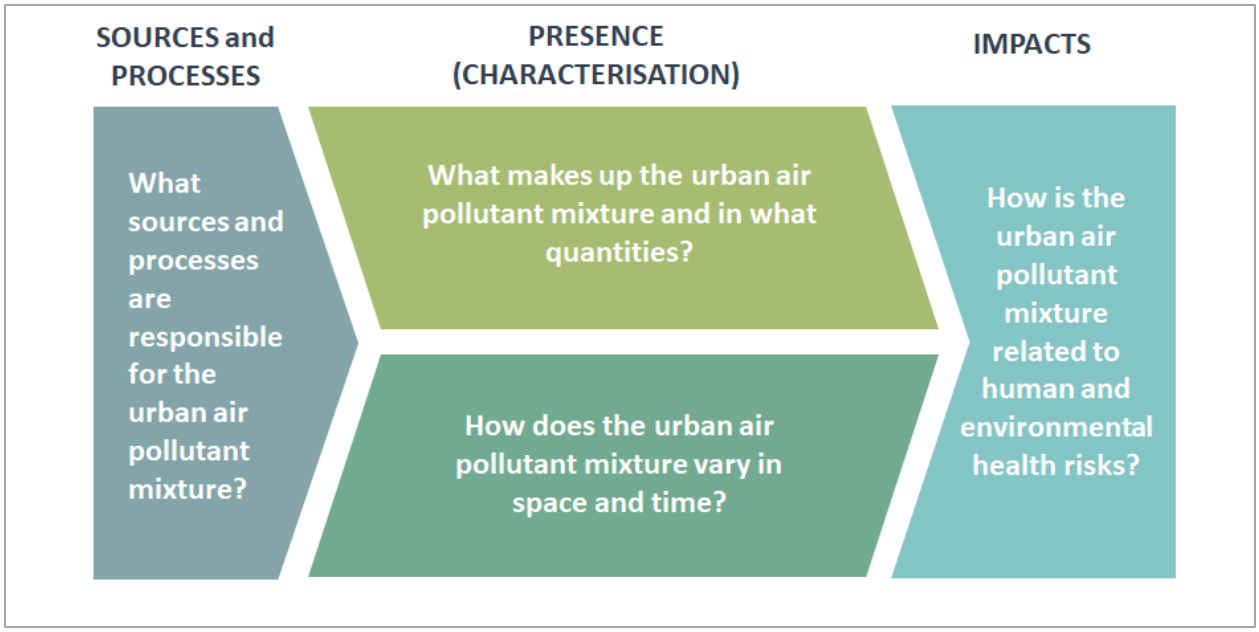


Figure 1: Over-arching questions to be investigated by SWAPIT.

The ultimate value of characterisation lies in its contributions to understanding sources and impacts. Source identification – including differentiating between natural and anthropogenic (human-caused) pollutant releases and among geographic source areas or jurisdictions – is fundamental to the design and implementation of environmental management actions. The complexities of atmospheric fate processes, which drive a variety of physical and chemical transformations, require focused investigations to tie the presence of air pollutants back to their sources and forward to their future forms. Characterising the presence of pollutants in ambient air and atmospheric deposition is also necessary to understand their individual and cumulative effects. The toxicological maxim that "the dose makes the poison" underlies the need for well-characterised ambient pollutant levels, both by individual compound and as mixtures, when determining risks to human and environmental health.

From its inception, SWAPIT has aimed to foster linkages among the silos associated with different pollutant classes and the scientific activities needed to understand the presence, sources, and impacts of the urban air pollutant mixture. Figure 2 depicts the broad classes of pollutants relevant to urban air pollution as distinguished by their main exposure pathways of inhalation or uptake after atmospheric deposition.

The pollutant classes depicted in Figure 2 vary in maturity as individual air quality issues. At a minimum they are each subject to ongoing monitoring and research, and some are also subject to management under domestic and/or international programs. When considered together, however, the urban air pollutant mixture is an issue that is emerging rather than mature. Little is known about the composition and distribution of the mixture as a whole, and no targeted programs have yet been implemented despite ongoing calls for more integrated air pollution research and a greater focus on cumulative effects. In response, SWAPIT has been designed to

accelerate the paradigm shift that is necessary to move from a pollutant-by-pollutant approach to one that is fully integrated for the air pollutant mixture from sources to impacts.

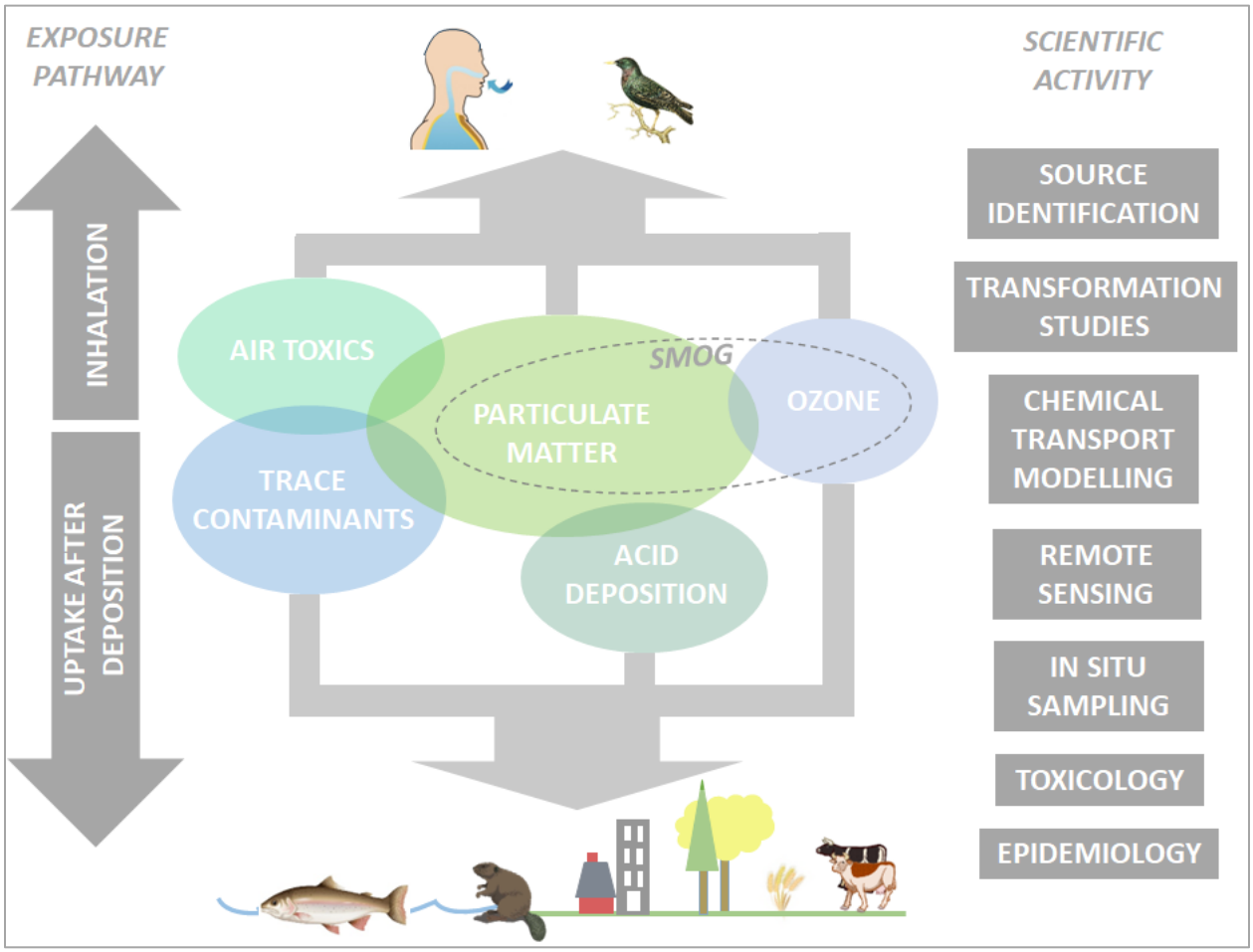


Figure 2: Exposure pathways, pollutants, and scientific activities relevant to SWAPIT.

1.2: Challenges Associated with Considering Air Pollutant Mixtures

As shown in Figure 2, environmental quality can be impaired by the presence of several air pollutants. Differences among pollutants, such as those listed below, preclude a straightforward summation approach to assessing their characteristics as a mixture.

Toxicity endpoints and modes of action.

- The arithmetic sum of air pollutant concentrations is not representative of their potential for cumulative adverse effects. Not all pollutants in a mixture contribute to any given effect, and those that do may behave in antagonistic and/or synergistic ways. The whole can be greater or less than the sum of its parts.

Time scale of ambient concentrations.

- Ambient concentrations are determined by methods that differ depending on the pollutant under consideration. Those methods operate at time scales ranging from seconds to months, and combining results requires adjusting time scales with appropriate consideration of variability and other relevant temporal factors.

Spatial scale of ambient concentrations.

- Similar to the issue of time scale, ambient concentrations are determined at a variety of spatial scales depending on methodology. Satellite measurements and chemical transport models yield concentration information covering areas of several square kilometres within which variability is unknown, whereas the distance over which fixed site measurements are representative is uncertain. Combining results to understand the spatial variability of the air pollutant mixture requires careful consideration and justification of the assumptions used to harmonize spatial scales. This is particularly important when examining urban air due to steep changes in pollutant concentrations over small distances.

Specificity of pollutant identification.

- Ambient characterisation methods target different levels of chemical specificity, and this is true of measurement and chemical transport modelling approaches. Some pollutants are identified as whole molecules (e.g., ozone, benzene), others as aggregate parameters (e.g., particulate matter), and still others as derived quantities based in part on assumptions about atmospheric composition (e.g., aerosol pH) or molecular fragments (e.g., particulate matter composition from aerosol mass spectrometry). Combining information about pollutants in ways that are useful to understanding sources and impacts requires careful attention to the chemical specificity and comparability of different techniques.

Size distribution of particulate pollutants.

- Just as ambient particles exist across a broad range of sizes, so do the pollutants associated with them. Techniques that assess particulate pollutant concentrations do not typically represent the full size range, with cut-offs of 1, 2.5, and 10 μm diameters being most common. The differences in pollutant particle size distributions must be considered when assessing the mixture as a whole in order to understand the potential for inhalation and deposition as well as to credibly tie source emissions to ambient concentrations and impacts.

Multiplicity of sources.

- Many sources contribute to the presence of pollutants in urban air, and determining which sources are most important depends on the pollutant or mixture under

consideration. Increased care is needed to avoid generic expressions such as "air pollution" when specific descriptors would be more accurate. Such care in naming will in turn facilitate the identification of relevant sources and their role in driving the presence and impacts of individual pollutants or their mixtures.

Environmental transformations.

- Time in the atmosphere changes many pollutants through a variety of physicochemical processes, and the resulting transformations can obscure the linkages between sources and impacts. Understanding the pollutant mixture requires detailed knowledge of such transformation processes and how they are affected by environmental conditions and the identity and quantity of pollutants present.

The factors listed above demonstrate some of the challenges that are associated with shifting from a pollutant-by-pollutant focus to one that considers the pollutant mixture. Addressing these factors requires modes of inquiry that are exploratory and descriptive along with the explanatory approaches that drive detailed physicochemical research on individual pollutants or pollutant classes. Success in representing and understanding the mixture will depend on the structure and availability of the shared data set that will be produced under SWAPIT, and this is described further in Section 3.

1.3: The Urban Air Pollution Mixture in Winter

Though ambient monitoring is conducted year-round, detailed studies of urban air pollution have typically focused on summer, particularly when elevated air temperatures and levels of sunshine coincide with stagnant air flow patterns to induce the production of photochemical smog. Such attention to common air pollutants like ozone and particulate matter at the urban scale has not been matched by the regional and global views employed when examining trace contaminants and acidifying substances. As a result, the urban air pollutant mixture is poorly characterised despite detailed understanding of some of its constituents. Examining urban air pollution during the winter season provides a valuable counterpoint to summer studies for reasons associated with weather and pollutant emissions as outlined below.

Meteorological factors affecting urban air pollution.

- Winter is characterised by lower temperatures and solar irradiance compared to summer. These factors drive pollutant emissions from certain sectors (see below) and also affect atmospheric processes such as oxidation, photolysis, and particle/gas partitioning. Scavenging and deposition of pollutants are affected by the phase state of precipitation or fog/cloud droplets, with the relative scavenging efficiency of liquid and frozen forms depending on the physicochemical characteristics of the pollutant in

question. Reduced vegetation in winter decreases the uptake of pollutants from the air, and snow/ice cover reduces volatilisation of semivolatile contaminants from surface water and land. Winter is associated with a shallower and more stable atmospheric boundary layer that can lead to increased airborne pollutant concentrations due to the reduced air volume that receives emissions.

Presence or absence of pollution sources in winter.

- Urban air pollution sources in winter differ from those in warmer periods of the year. The combustion of fossil fuels continues to dominate the heating of indoor spaces in Toronto and many other Canadian cities, and residential wood combustion has additional recreational uses in winter. De-icing agents such as road salt release chlorine and other chemicals that can be pollutants themselves and contribute to the atmospheric chemistry that transforms other emissions to secondary pollutants. Conversely, some pollutant sources, such as wildfires and biogenic emissions from deciduous vegetation, are reduced or absent during winter. Studying air quality under different emissions regimes yields insight into the role of contributing factors which in turn improves our understanding of sources and impacts.

Generalisations have developed about seasonal patterns in pollutant concentrations but these are not always accurate or robust. For example, enhanced ozone and particulate matter concentrations during photochemical smog episodes have led to generalised beliefs about summertime pollution despite greater wintertime concentrations of several pollutants observed at urban locations. Conversely, toxic polycyclic aromatic compounds (PACs) are assumed to have increased airborne concentrations in winter due to heating emissions and decreased vertical mixing, yet that pattern is not observed consistently in the long-term measurement record. Focusing SWAPIT on winter will contribute to a better overall understanding of the urban mixture throughout the year.

2. SWAPIT Science Activities

A SWAPIT Science Planning workshop was held in January 2023 to allow study participants to translate the over-arching questions (Figure 1) into concrete activities. That translation was achieved by using workshop discussions to develop and bridge two related topics: (1) the knowledge gaps relevant to the presence, sources, and impacts of urban air pollutants in winter at mid-latitudes, and (2) the scientific and technical capacity available to SWAPIT from its government and academic participants. Discussions were supported by interactive online tools that allowed participants to provide details of available instrumentation and siting requests for field measurements as well as a linked online mapping tool that shows measurement locations along with pollutant emissions reported through Canada's National Pollutant Release Inventory (NPRI).

2.1: Existing Scientific Infrastructure

In order to ensure the efficient use of resources, SWAPIT science planning has built on existing scientific infrastructure. Additional work under SWAPIT leverages that infrastructure, and the feasibility and relevance of new activities are amplified by the coordinated efforts of the study's participants.

A scan of ongoing air pollution science programs reveals a rich array of efforts relevant to the Greater Toronto-Hamilton Area (GTHA; see Table 1). Positive relationships among government and academic scientists have allowed SWAPIT to build on this strong foundation of ongoing work, and data associated with that work have been offered generously to the SWAPIT effort. In order to accommodate the use of data from both ongoing and new activities, online tools that allow for data reporting and sharing are under development. These are hosted on cloud services that are accessible to study participants from ECCC and partner organizations. A data archive will later be made available to the broader scientific community and general public through the Government of Canada's Open Data portal (see Section 3).

Though several air pollution measurement and research activities are underway in the GTHA, broad differences among target pollutants and measurement scales complicate the development of an integrated understanding of the urban air pollutant mixture. Focused activities under SWAPIT aim to fill gaps in the current scientific landscape – both through measurements conducted during an intensive field sampling campaign in early 2024 and through the analysis of measurement data and other available techniques to improve our understanding of urban air pollutant sources and impacts.

Table 1: Existing air pollution science networks, projects, and platforms relevant to SWAPIT.

Network, Project, or Platform	Brief Description	SWAPIT Contact	Lead Agency
NAPS (National Air Pollution Surveillance)	Continuous and integrated ambient air measurements at ground level for ozone and particulate matter (PM) along with their precursors, PM constituents, air toxics, and trace contaminants.	May Siu (ECCC)	ECCC and ON MECP (includes territorial and municipal partners elsewhere in Canada)
CAPMoN (Canadian Air and Precipitation Monitoring Network)	Integrated ambient air and precipitation measurements at ground level with a focus on acid deposition.	Anne Marie Macdonald (ECCC)	ECCC
GAPS (Global Atmospheric Passive Sampling) Network	Integrated passive sampling measurements of trace contaminants over 1-3 month sampling periods at or near ground level.	Tom Harner and Amandeep Saini (ECCC)	ECCC
IMPACT (Improved Assessment and Characterization of Traffic Emissions)	Integrated passive sampling measurements of atmospheric trace gases at ground level + vehicle-based sampling of on-road emissions near ground level.	Greg Evans (University of Toronto)	HEI (Health Effects Institute)
Hamilton Passive Sampling Study	Integrated passive sampling measurements of atmospheric trace gases and air toxics over 1-month sampling periods at or near ground level.	Matthew Adams (University of Toronto Mississauga)	Environment Hamilton and Clean Air Hamilton
ATOUSA (Assessing Toxicity of Organics in Urban Sectors for Air)	Integrated passive sampling measurements of gas- and particle-associated PACs and their transformation products, tire-derived chemicals and other chemicals of emerging concern with linkages to toxicity endpoints.	Sabina Halappanavar (Health Canada) and Tom Harner/Amandeep Saini (ECCC)	Health Canada and ECCC
ECCC Meteorological Research Division Southern Ontario LIDAR Mesonet	Doppler LIDARs measuring winds, turbulence, boundary layer height and aerosol backscatter at 10-minute resolution up to 4 km altitude from ground.	Zen Mariani (ECCC)	ECCC

Network, Project, or Platform	Brief Description	SWAPIT Contact	Lead Agency
Pandonia Global Network	Global network of Pandora spectrometers making measurements of atmospheric trace gases at 20-minute resolution for the total atmospheric column.	Xiaoyi Zhao (ECCC)	NASA and European Space Agency
Aeronet (Aerosol Robotic Network) and AEROCAN (Aerosol Robotic Canadian) Network	Global network of sunphotometers measuring aerosol optical properties in the total atmospheric column. The AErosol RObotic CANadian (AEROCAN) network is a subnetwork of AERONET.	Xiaoyi Zhao (ECCC)	NASA and PHOTONS
COCCON (Collaborative Carbon Column Observing Network)	Global network of ground-based remote sensing instruments measuring greenhouse gases in the total atmospheric column.	Debra Wunch (University of Toronto)	European Space Agency
NDACC (Network for the Detection of Atmospheric Composition Change) – Ultraviolet-Visible (UV-Vis) Working Group	Global network of differential optical absorption spectroscopy (DOAS) observations, including MAX-DOAS for tropospheric trace gas profiling.	Xiaoyi Zhao (ECCC)	BIRA (Belgian Institute for Space Aeronomy)
NDACC (Network for the Detection of Atmospheric Composition Change) – Infrared (IR) Working Group	Global network of ground-based Fourier transform (FTIR) spectroscopy instruments measuring various aerosol and gas-phase pollutants.	Kimberly Strong (University of Toronto)	NASA
TROPOMI	Sun-synchronous satellite-based spectrometers to measure aerosol and various trace gases.	Chris McLinden (ECCC)	European Space Agency
TEMPO	Geostationary satellite-based spectrometer to measure various trace gases.	Chris McLinden (ECCC)	NASA

Network, Project, or Platform	Brief Description	SWAPIT Contact	Lead Agency
ABI on GOES	Geostationary satellite-based imaging radiometer to measure aerosol optical depth (AOD)	Chris Sioris (ECCC)	NOAA
MODIS	Satellite-based radiometer to measure aerosol optical depth (AOD)	Chris Sioris (ECCC)	NASA
CRUISER	Mobile sampling platform for air pollutants with extensive instrument capacity and driving route options.	Ralf Staebler (ECCC)	ECCC
University of Toronto mobile sampling vehicles	Mobile sampling platform for air pollutants with moderate instrument capacity and driving route options.	Greg Evans (University of Toronto)	University of Toronto
Adams Group Sampling Mobile Platform	Mobile sampling platform for air pollutants with modest instrument capacity and flexible driving route options.	Matt Adams (University of Toronto Mississauga)	University of Toronto Mississauga
ECCC Climate Research Division Mobile Greenhouse Gas Measurement Platform	Mobile sampling platform for methane and carbon dioxide throughout Toronto.	Felix Vogel (ECCC)	ECCC
NPRI (National Pollutant Release Inventory)	Inventory of facility-reported releases, disposals and transfers of a broad number of smog pollutants and their precursors, air toxics, and trace contaminants.	Anne Monette (ECCC)	ECCC
APEI (Air Pollutant Release Inventory)	Inventory of estimated releases from all anthropogenic sources for a limited number of smog pollutants and their precursors, air toxics, and trace contaminants.	Lindsay Pratt (ECCC)	ECCC

Network, Project, or Platform	Brief Description	SWAPIT Contact	Lead Agency
JAMS (Joint Air Management Strategy)	State of knowledge overview of multi-pollutant air quality issues in southwestern Ontario with management opportunities derived from historical trends and projection models.	Matthew Parsons (ECCC)	ECCC
GEM	Hydro-meteorological prediction model capable of predicting near-surface meteorological conditions.	Sylvie Leroyer (ECCC)	ECCC
GEM-MACH	Chemical transport model capable of simulating ambient air concentrations and atmospheric deposition for a suite of common air pollutants and air toxics.	Rosa Wu (ECCC)	ECCC

2.2: Overview of the 2024 Intensive Field Measurement Campaign

A key activity under SWAPIT is an intensive field measurement campaign that will take place over six weeks in early 2024 (see Appendix B for calendar). Locations of the fixed ground-based measurements are shown in Figure 3. The majority of locations are existing sites operated by ECCC and/or ON MECP (Ontario Ministry of the Environment, Conservation and Parks) or local universities (University of Toronto and York University).

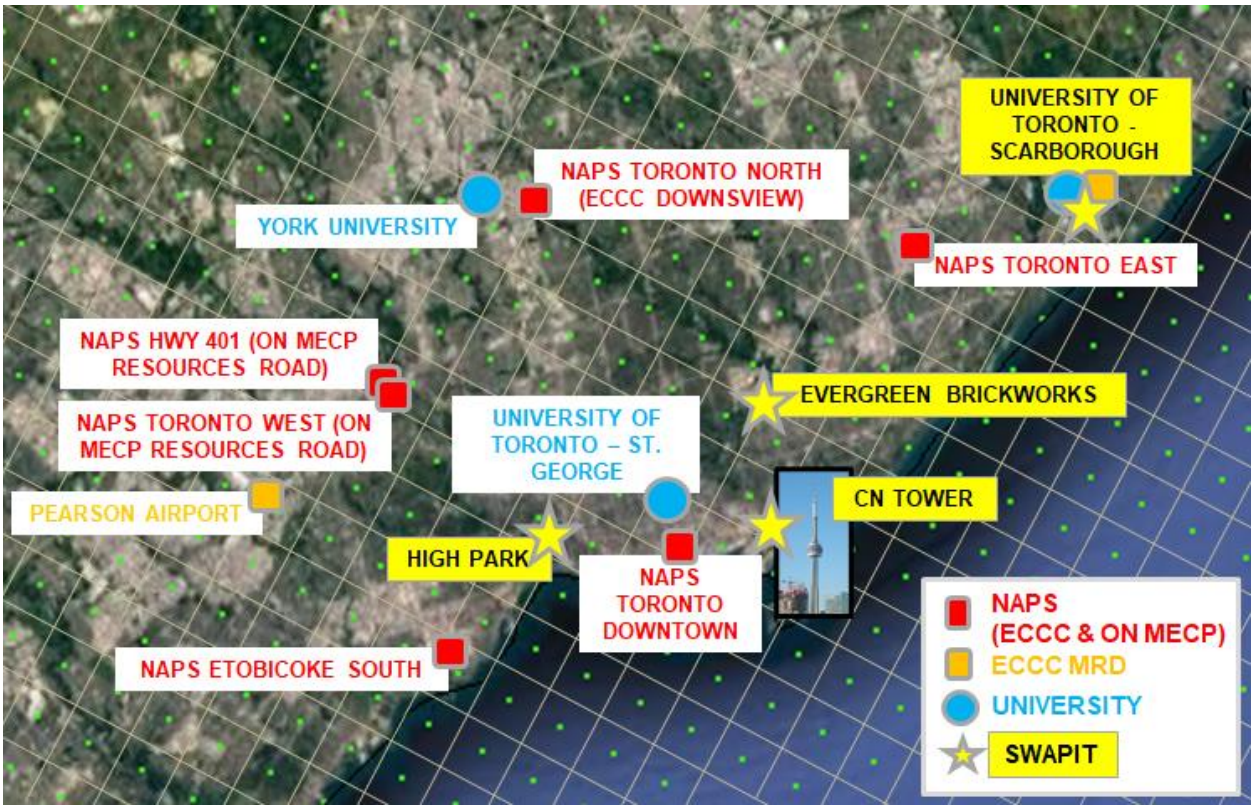


Figure 3: Fixed ground-based measurement sites proposed for 2024 SWAPIT Field Intensive. The background grid represents the 2.5-km model grid for ECCC's chemical transport model, GEM-MACH.

Four temporary measurement locations are planned for the field intensive. Three of these (High Park, Evergreen Brickworks, and the University of Toronto Scarborough (UTSC)) will host ground-based measurements. The latter sites fill spatial gaps in central and east Toronto, represent different land uses (mixed urban, near-road, and downwind urban background, respectively), and enhance a transect along the predominant wintertime wind direction with flows from the southwest. The fourth temporary SWAPIT site will be downtown at the CN Tower. It will allow for measurements at several heights along its support pillar as well as from the roof of its main pod 356 m above ground.

Measurements will be conducted at the fixed sites using active and passive samplers, high-time resolution chemical analysers, and remote sensing instrumentation. Super-intensive measurement periods are also planned for the High Park, Evergreen Brickworks, and UTSC temporary SWAPIT sites. These super-intensives will take place over three consecutive two-week periods during which a highly-instrumented mobile sampling platform (ECCC CRUISER and associated trailers) will be deployed in engine-off stationary sampling mode to supplement the other instrumentation at those sites.

Mobile sampling will be also be conducted during the campaign. Vehicles from the University of Toronto (IMPACT and Adams Mobile Sampling Platform) will examine on-road emissions throughout the city, and differences between cold-start and running vehicle emissions will be investigated at a commuter parking lot through a collaboration between the ECCC CRD and Adams Mobile Sampling Platforms.

Despite technological advances that allow for faster and more chemically resolved measurements, air pollution science continues to seek information at higher spatiotemporal resolution. That drive is particularly relevant in urban areas where substantial differences in air pollutant levels can exist over small spatial scales. Tools at the forefront of efforts to yield highly resolved air pollutant information include space-based (satellite) remote sensing measurements and chemical transport models, and both are important components of SWAPIT.

Compared to ground-based monitoring networks, satellite-based instruments provide air pollutant data at high spatial density. Current satellite pixel areas (e.g., 9 and 25 km^2 for TEMPO and TROPOMI, respectively) allow for a greater number of near-simultaneous measurement locations within a city than do existing ground-based monitors. Nonetheless, the variability in urban air pollution levels may not be captured by satellite-based spatial density, and satellite measurements are further limited to clear sky conditions. Field campaigns with multiple ground-based measurement locations spaced at scales similar to satellite pixel grid sizes are useful for testing the representativeness of satellite measurements. A request for special scans from the newly-launched TEMPO satellite has been met with a positive initial response and will allow for enhanced observations during the SWAPIT field intensive. Given that the field intensive is taking place during the first winter of TEMPO's operation, SWAPIT is providing a unique opportunity to evaluate the new satellite's performance over snow-covered surfaces and other features of its operation. Connections between data collected from ground-based sites and satellite-based instrumentation are being provided in the SWAPIT data sharing and archiving tools to facilitate relevant analyses.

Satellite-based measurements yield data for the total column of air above the Earth's surface. Extracting the concentration at ground level, where most human and ecosystem exposure occurs, requires assumptions about the pollutant's vertical distribution. Those assumptions are often taken from chemical transport models, but the complexity of the urban environment makes thorough ground-truthing difficult. SWAPIT measurements from ground-based vertical profiling instrumentation at several sites as well as multiple elevations at the CN Tower will

provide vertically-resolved air pollutant data with which to evaluate current assumptions and improve the tools that are used to generate them.

Chemical transport models have many uses beyond generating vertical profiles for the air pollutants measured by remote sensing. Such models can simulate air pollutant concentrations at horizontal spatial resolutions finer than those of satellite-based instruments. ECCC's GEM-MACH model is typically configured for grid squares of ~6 km^2 (2.5 km × 2.5 km) but the capability for squares two orders of magnitude smaller (0.06 km^2 = 0.25 km × 0.25 km) is developing rapidly. Chemical transport models are also used to determine the contributions of pollutant sources and locations, and they are additionally used as predictive tools to examine the impacts of management actions and environmental change.

The accuracy of chemical transport model simulations relies on inputs such as meteorology and pollutant emissions as well as representations of the atmospheric processes that transform pollutants in ambient air. Many of these inputs and processes are poorly constrained by existing observations, and the complex interplay among inputs, processes, and numerical and computational factors creates the possibility of compensating errors. Even when model output matches available measurements, rigorous evaluation is necessary to confirm that the output is right for the right reasons. This in turn lends confidence to source attribution and model predictions for which comparative measurements are not available. Through the use of its unprecedented dataset, SWAPIT is uniquely positioned to improve the accuracy of GEM-MACH. This will advance knowledge of the urban air pollutant mixture not only in the GTHA but in other urban areas in Canada and elsewhere.

The preceding text provides a brief summary of the activities planned under the 2024 SWAPIT intensive field sampling campaign. A more complete and detailed description of SWAPIT science activities is presented below through the lens of four study themes: (1) characterisation, (2) sources and processes, (3) impacts, and (4) science tool evaluation and improvement.

2.3: Science Activities Under Theme 1 – Characterisation

A significant SWAPIT contribution will be the production of the most comprehensive snapshot of the air pollutant mixture yet produced throughout a major urban area. Large urban air quality studies have been conducted elsewhere but none has incorporated the range of air pollutants in ambient air, the vertical air column, and atmospheric deposition that are considered in SWAPIT. The breadth of ambient information targeted under SWAPIT requires a variety of data-gathering methods including direct measurements and simulations using chemical transport modelling tools as depicted in Figure 4.

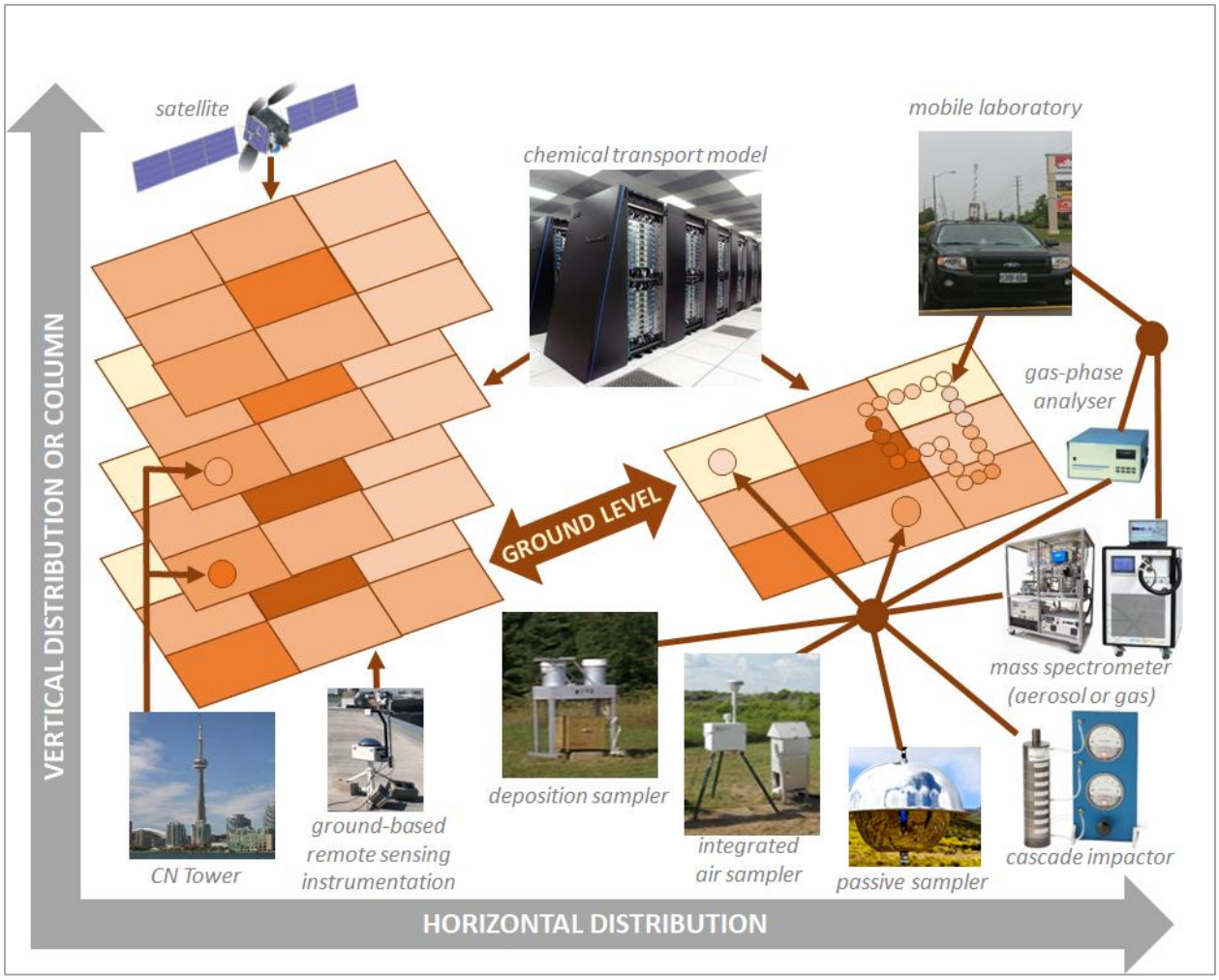


Figure 4: Ambient air pollutant data-gathering methods under SWAPIT.

As an example, Table 2 details select urban air pollutants and the expected availability of simultaneous concentration data as a result of SWAPIT activities.

The most comprehensive coverage will exist for the four pollutants subject to Canada's Air Quality Management System (AQMS): SO_2, NO_2, O_3 and $PM_{2.5}$. Spatiotemporal coverage will be less dense for other air pollutants but will nonetheless allow for simultaneous, collocated measurements of a broad range of pollutants relevant to the urban air pollution mixture.

Table 2: Data availability for select urban air pollutants in SWAPIT.

Platform	SO_2, NO_2, O_3	$PM_{2.5}$	VOCs (speciated)	Metal(loid)s and Trace Elements	PACs	PFAS
Ground-level	9 sites (6 sites for SO_2)	9 sites (mass), 4 sites (speciation)	3 sites (full campaign) + 3 sites (2-week super-intensives)	1 site (full campaign) + 3 sites (2-week super-intensives)	1 site (full campaign) + 3 sites (2-week super-intensives)	3 sites (1 real-time)
Mobile	3 platforms	3 platforms	1 platform	-	-	-
Total column (ground-based)	6 sites	6 sites (estimated from aerosol optical depth)	6 sites (HCHO only)	-	-	-
Total column (space-based)	9 km^2 grid (TEMPO) or 25 km2 (TROPOMI) (vertical column density (VCD))	9 & 25 km^2 grid (aerosol optical depth (AOD))	9 / 25 km^2 grid (vertical column density (VCD) for HCHO only)	-	-	-
Chemical transport model (GEM-MACH)	6 km^2 grid	6 km^2 grid (mass and speciation)	6 km^2 grid (lumped, model output modification needed)	6 km^2 grid (Fe, Cu and Mn only with model output modification)	6 km^2 grid	-

A list of SWAPIT pollutants and precursors that are not typically measured or modelled under existing initiatives (see Table 1) is found below:

- speciated fine particulate matter at high time resolution
- aerosol black and brown carbon at high time resolution
- elemental and organic carbon in size-distributed aerosols
- major ions in size-distributed aerosols
- metal(loid)s in size-distributed aerosols
- metal isotopes in bulk and size-distributed particulate matter
- speciated mercury and isotopes in the gas and particle phases
- polycyclic aromatic compounds (PACs) and *n*-alkanes in size-distributed aerosols
- substituted PACs including alkyl-PACs and oxy-PACs
- speciated volatile organic compounds (VOCs) at high time resolution
- speciated gaseous chlorine compounds at high time resolution
- speciated gaseous nitrogen compounds at high time resolution
- plastics (microplastics, nanoplastics, and tire wear particles)

- plastic/rubber additives (e.g., benzotriazole ultraviolet stabilizers and other PMT [persistent, mobile, and toxic] additives)
- brake wear chemicals
- organophosphate esters
- polyhalogenated carbazoles
- PFAS (per- and polyfluoroalkyl substances).

Output of Theme 1 – Characterisation

Quality-assured data set for multiple pollutants in the urban air mixture available for

- description and analysis of spatiotemporal variation
- investigation of relationships between exposure and socioeconomic factors
- source identification
- improvements to atmospheric phenomenon and process understanding
- chemical transport model evaluation and improvement
- measurement method evaluation and development
- toxicological and epidemiological investigations.

Application of the characterisation data set to the aforementioned activities is described below under Theme 2 (Sources and Processes), Theme 3 (Impacts), and Theme 4 (Science Tool Evaluation and Improvement) as well as in Section 3 (Results: Analysis, Integration, and Communication). The data set will subsequently be made available to the broader scientific community and general public (Section 3) to facilitate additional research and to provide a comprehensive snapshot of current conditions for future retrospective comparisons.

2.4: Science Activities Under Theme 2 – Sources and Processes

Managing pollution requires credible knowledge of its sources and their contributions to ambient air burdens. Because most air pollutants are subject to a variety of atmospheric processes that transform them physically and/or chemically, sources cannot be understood without detailed knowledge of those processes and how they act over the spatiotemporal scales that are relevant to urban systems.

Source information is available through bottom-up inventories such as the National Pollutant Release Inventory (NPRI) and Air Pollutant Emission Inventory (APEI) (see Table 1), and such emissions information is distributed over space and time to arrive at the model-ready inventories that drive chemical transport models such as GEM-MACH. Despite extensive efforts to ensure the quality and completeness of bottom-up inventories, knowledge gaps necessitate the use of estimation methods. Recent experience in the Athabasca oil sands region has identified discrepancies between emissions reported in official inventories or facility reports

and those inferred from ambient conditions for air toxics, volatile organic compounds (VOCs), particulate matter, and greenhouse gases among others (Parajulee and Wania, 2014; Galarneau et al., 2014; Li et al., 2017; Liggio et al., 2019; McLinden et al., 2020; Moussa et al., 2021; You et al., 2021; Wren et al., 2023). These findings are contributing to the improvement of officially-reported releases. Outcomes of the SWAPIT effort will provide similar opportunities to validate and improve official inventories as well as facilitating emission estimates for pollutants that are not among the lists of inventoried compounds.

Important air pollution sources in urban areas include motor vehicle emissions, stationary combustion, industrial releases, pesticide use, cooking emissions, and mobilisation of commercial chemicals such as flame retardants and non-stick coatings from indoor spaces and waste management facilities. Efforts to combat climate change, such as the transition to zero-emission vehicles, are driving a shift in the emissions of important pollutant precursor compounds (McDonald et al., 2018). Meanwhile, the number of commercial chemicals is growing at an increasing rate (Persson et al., 2022), and many are emitted at elevated levels in densely populated areas.

SWAPIT activities aimed at understanding emission sources and the atmospheric processes that modify them are detailed below.

2.4.1: Sources

SWAPIT, through its 2024 intensive field campaign, provides the opportunity for direct measurements of air pollutants at or near their emissions sources. These efforts will include targeted mobile measurements of non-tailpipe emissions while traveling on-road and stationary measurements that will contrast cold-start and running conditions at a commuter parking lot. Stationary source-oriented measurements will contrast particulate matter at near-road environments for two highways with different diesel versus gasoline fleet mixes (Highway 401 and the Don Valley Parkway) and an arterial roadway intersection (Keele Street near York University). Near-road measurements will additionally examine metal isotopes and ammonia, whereas particulate matter from tire wear, which represents an emerging concern as a non-tailpipe vehicle pollutant, will be measured at three fixed sites. Not only will SWAPIT's 2024 intensive field campaign provide direct measurements of near-source air pollutants, study partners will also conduct additional post-measurement analyses to better understand pollutant sources. These efforts will include a comparative analysis of observed pollutants to their release magnitudes and locations reported in official inventories, receptor modelling to understand the contributions of VOC source categories, and analysis of quinones (oxy-PACs) to determine the importance of primary emissions relative to secondary formation.

Project 2.1: Measurements at a commuter parking lot comparing cold-start and running emissions (Lead: Felix Vogel, ECCC Climate Research Division; Collaborators: Sébastien Ars, ECCC

Climate Research Division; Debra Wunch, University of Toronto St. George; Matt Adams, University of Toronto Mississauga)

In previous years, the Climate Research Division (CRD) mobile platform was used to determine CO/CO_2 emission ratios for the moving vehicle fleet in the GTA and Greater Montreal (Ars et al., 2020; Williams et al. 2022). Emission ratios were attributed to different vehicle types using on-board camera footage. This analysis revealed strong discrepancies (lower CO/CO_2 ratios) between reported emission ratios for the on-road transportation sector and the observed emissions of the moving fleet, and these discrepancies are likely driven by cold-start emissions. To correctly allocate CO/CO_2 emission ratios between major roads, where engines and catalysts are typically optimal, and residential areas, where cold-starts occur, it is critical to also assess cold-start emissions in the GTA with direct observations. Within SWAPIT, the ECCC CRD and Adams mobile platforms will be operated in stationary mode to sample air at a commuter parking lot. The platforms will be equipped with instruments able to measure the ratios of CO, CH_4, particulate matter, NO_2, and BTEX to CO_2 for the arriving fleet (morning, warmed engine and catalyst) and departing fleet (afternoon, cold engine and catalyst) over a range of meteorological conditions. .

Project 2.2: Near-road measurements of emissions from an arterial roadway (Lead: Mark Gordon, York University)

Road-dust and non-exhaust emissions have been shown to be dependent on driving conditions (Beji et al., 2020) and winter road treatments have been shown to have extended impact on emissions (Zhu et al., 2012). During SWAPIT, measurements of size-resolved, sub-micron aerosols, in addition to $PM_{2.5}$, will be made at the corner of two urban roads near York University (Keele Street and York Boulevard). Video analysis will provide detailed traffic conditions and the aerosol measurements will be supported by turbulent and diffusion flux measurements. These wintertime measurements will be compared against spring and summer measurements that are being made as part of an unrelated campaign (The CIX - Principal Investigator: Cora Young, York University) as well as wintertime measurements that are being made under SWAPIT near highways with contrasting fleet characteristics (Highway 401 and Don Valley Parkway) to understand the role of varying traffic conditions. As a result, characterisation and model parameterisations of the size distributions and emission rates of road-dust and non-exhaust emissions will be improved.

Project 2.3: Near-road measurements of metal isotopes (Lead: Bridget Bergquist, University of Toronto)

In urban settings it is challenging to quantify sources of metals in aerosols because of the complex mixture of local sources and also regional sources. Traditionally, metals concentrations, correlations and various ratios in aerosols are used to attempt source identification and apportionment. However, many sources do not have distinct suites of metals making these approaches difficult to apply in complex settings. For SWAPIT, the use of metal isotopic measurements in aerosols will be used to aid in source identification. Aerosols, both size fractionated and bulk, will be collected at fixed sites in near-road environments to contrast with samples from different land uses throughout the GTA as well as a reference site that will allow for characterization of regional source isotopic signatures. The isotopic measurements of lead (Pb), copper (Cu), zinc (Zn), and chromium (Cr) will be measured and are expected to display large variations in isotopic compositions that are mostly related to source. Of the metal isotope system, Pb isotopes have the longest history in source apportionment and there are many studies where Pb isotopes in aerosols are successfully used to identify and quantify sources of particulate aerosols. The reason for the success of this metal isotopic system is because it is a radiogenic isotope system and isotopic source differences, due to inherent differences in Pb isotopes based on the age and composition of sources, are very large and easier to measure compared to other metal isotope systems. The other three isotopic systems are stable isotope systems where differences in isotopic compositions are the result of processes in the environment that fractionate isotopes. Because metals undergo different transformations and biogeochemistry in different source materials (i.e., soils, industrial materials, building materials, car exhaust, tire material), sources often have different isotopic compositions. Both Cu and Zn isotopes have been used in urban settings (i.e., San Paulo and London) to differentiate aerosol sources such as tire wear and tear from other industrial sources. Less is known about Cr isotopes in urban aerosols, but this is a metal of concern and Cr isotopes vary enough to be used in groundwater and soil applications. Thus, Cr isotopes is more exploratory. It is anticipated that a multi-metal isotope approach will be a powerful and novel tool in source identification and apportionment of metals in aerosols in Toronto and will also aid in identifying sources of other pollutants associated with similar sources as metals.

Project 2.4: Temporal characterization of tailpipe (TP) and non-tailpipe (NTP) $PM_{2.5}$ near a downtown arterial road (Lead: Greg Evans, University of Toronto; Collaborators: Cheol-Heon Jeong and Yee Ka Wong, University of Toronto)

Receptor modeling based on one-in-three-day filter data collected from 2004-2016 in downtown Toronto has revealed that the concentration of non-tailpipe (NTP) $PM_{2.5}$ has been steadily rising, overtaking primary tailpipe (TP) $PM_{2.5}$ in 2013. In this project, two-hour-time-resolution data data will be collected beside College Street in downtown Toronto in winter and summer 2024, with a mass-spectrometry based Aerosol Chemical Speciation Monitor (ACSM, Aerodyne) and an Xray fluorescence (XRF) based metals monitor (625 Xact, Cooper Environ). The ACSM can measure organic aerosol (OA) and inorganic aerosol (i.e., sulphate, nitrate, and ammonium) while the Xact can measure concentrations of K, Ca, Ti, Mn, Fe, Cu, Zn, Se, Sr, Ba,

and Pb. These data will be combined with existing data in positive matrix factorization to support a higher time-resolution investigation of seasonal differences in NT and NTP $PM_{2.5.}$ This project should provide additional insights into temporal patterns (diurnal, weekend, seasonal) in the ratio of NTP to TP $PM_{2.5}$. Moreover, it may help elucidate factors influencing temporal variability such as how snow and road-salting influence the $PM_{2.5}$ composition and concentration.

Project 2.5: Spatial patterns of tailpipe (TP) and non-tailpipe (NTP) emissions (Lead: Greg Evans, University of Toronto; Collaborators: Cheol-Heon Jeong and Yee Ka Wong, University of Toronto)

As part of a parallel HEI-funded *Improved Assessment and Characterization of Traffic-Related Particulate Emissions* (IMPACT) study, spatial patterns in TP and NTP $PM_{2.5}$ across the greater Toronto Area will be characterized using a combination of fixed-site and mobile monitoring. Through SWAPIT, we will extend this research during the winter of 2024 to increase integration with aspects with other SWAPIT projects (e.g., the influence of snow and road-salting).

Mobile sampling will be conducted using an electric Bolt equipped with high time resolution instruments: $PM_{2.5}$ (TSI DustTrak), PM_{10} (TSI DustTrak), UFP (Testo DiscMini), and Black Carbon (Microaeth). This vehicle will be equipped with two inlets, one on the rear window for measuring pollutant concentrations in the ambient air. A second inlet will measure concentrations of $PM_{2.5}$ and PM_{10} in the rear wheel-well. The difference between these two measurements reflects the addition of pollutants from sources in the wheel-well such as tire dust, brake dust, and resuspension of road dust. For SWAPIT, the Adams mobile sampling platform will also be equipped for wheel-well sampling to allow greater spatial coverage of the city across the routes it follows. In addition, $PM_{2.5}$ and PM_{10} collected on filters from the wheel well will be analysed for markers of brake-wear (Ba, Cu), road dust (Ca, Fe, Na) and tire particles (6 PPD, DPG, DPQ). The Bolt will sample on a route aligned with IMPACT's fixed sites (see below), to investigate sites believed to have contrasting levels of NTP emissions. The sampling route will also be aligned with SWAPIT's fixed sites to support integration with SWAPIT's other projects. Sampling will occur on six to ten days during the SWAPIT field campaign, so that each road segment on the route is sampled at least six times.

We will also deploy at 40 sites, Ultrasonic Personal Air Samplers (UPAS) samplers to collect $PM_{2.5}$ and PM_{10} filters, and Ogawa badges to collect NO_2 and NOx. These samplers will be deployed across near-road sites believed to have contrasting levels of TP and NTP emissions, and ideally different ratios of NTP to TP. The filters from the UPAS will be analysed for markers of brake-wear (Cu, Ba) and road dust resuspension (Ca, Fe). Co-located sampling for $PM_{2.5}$ and PM_{10} using two UPAS will be used to determine the differences between the composition of fine and coarse PM. The NO_2 and NOx data from the Ogawa badges will be used to assess tailpipe emissions. These data will be combined to contrast differences in NTP/TP at the different locations. Additional high time resolution data (5 min) will be collected at half of the sites using a network of 20 AirSENCE devices. AirSENCE is a sensor-based air quality monitoring

technology that uses an array of sensors to measure PM_1, $PM_{2.5}$ and PM_{10}, CO_2, CO, NO_x, and O_3.

Project 2.6: Near-road measurements of atmospheric tire wear particles (Lead: Alex Lee, ECCC Air Quality Research Division; Collaborators: Arthur Chan, University of Toronto; Hayley Hung, ECCC Air Quality Research Division)

Tire wear particles (TWP) have been recognized as one of the major categories of microplastic pollution produced by friction between tires and road surfaces. This non-exhaust particulate matter (PM) can be transported through the air and with runoff leading to environmental pollution and health concerns. Previous studies have reported that TWP can contribute up to a few percentages by mass of airborne PM_{10} and $PM_{2.5}$ (Fussell et al., 2022), and its relative contribution to PM is likely increasing due to various mitigation measures of engine exhaust emissions. A global modeling study has shown that atmospheric transport can be a major pathway of TWP to remote regions (e.g., Arctic) with the magnitude comparable to the total estimated direct and riverine transport of TWP to the ocean (Evangeliou et al., 2020). TWP can also act as a carrier of chemical additives (e.g., 6-PPD) and its transformation products (6PPD-quinone), which are emerging pollutants of concern (Tian et al., 2021).

During SWAPIT, atmospheric PM filter samples will be collected from near-road environments. Mass spectrometry techniques, including pyrolysis-gas chromatography mass spectrometry (Pyr-GC/MS), will be used for measuring tire tread polymer content and tire-derived chemical additives (such as 6-PPD) in filter samples. The results will be analysed with traffic data (e.g., traffic volume and vehicle types) and other co-located gaseous and PM pollutant measurements to improve our understanding on characteristics of fresh TWP emission at near-road environments in wintertime.

Project 2.7: Resolving the wintertime aviation and traffic emissions (Lead: Greg Evans, University of Toronto; Collaborator: Cheol-Heon Jeong, University of Toronto)

Research in several cities has found higher concentrations of ultrafine particles (UFP) in regions around airports. These contributions may arise from emissions from aircrafts, inter-modal shipping of freight, and the higher levels of traffic in the areas surrounding airports. Moreover, concentrations of ultrafine particles from traffic are higher in winter than summer, presumably due to less evaporation and/or increased condensation of volatile components. Finally, both aircraft and traffic also emit other pollutants such as NO_x. While NO_x emissions from vehicles are higher in winter, likely due to poorer performance of the emission treatment systems, little real-world data is available on how winter influences aircraft emissions.

In this project, a Discmini will be deployed at Pearson airport to measure ultrafine particles along with two Ultrasonic Personal Air Samplers (UPAS) samplers to collect PM2.5 and PM10 filters, and an AirSENCE unit to collect high- time-resolution PM_1, $PM_{2.5}$ and PM_{10}, CO_2, CO, NO_x,

and O3 data. These instruments will be used in conjunction with wind direction data to try to separate the contributions to ultrafine particle concentrations of the airport vs. traffic on nearby highway 401. It may also be possible to determine and compare emission factors for these two sources. The filters from the UPAS will be analysed for metals to evaluate the contributions of non-tailpipe emissions.

Project 2.8: Significance of ammonia (NH_3) emissions in vehicle exhaust (Lead: Ralf Staebler, ECCC Air Quality Research Division; Collaborator: Leiming Zhang, ECCC Air Quality Research Division)

Even though on the national scale, NH_3 emissions from vehicles pale in comparison with agricultural emissions, they can be significant on a local / urban scale, particularly near highways, and play an important role in local atmospheric chemistry. These emissions are due primarily to catalytic converters, and received a boost in recent years through the introduction of selective catalytic reduction (SCR) converter requirements for diesel vehicles. Previous measurements near Toronto's Highway 401 (You et al., 2017) found mixing ratios up to 23 ppb through long-path FTIR measurements over the highway, with an average morning peak of 10 ppb. Given the short atmospheric lifetime of NH_3, direct measurements adjacent to Highway 401, coupled with vehicular turbulence measurements, will provide useful data on the relationships between traffic patterns, meteorology and NH_3 concentrations to inform official inventories and improve understanding of aerosol formation in urban areas.

Project 2.9: Comparative analysis of pollutants observed during SWAPIT and reported to the National Pollutant Release Inventory (NPRI) (Lead: Alicia Berthiaume, ECCC National Pollutant Release Inventory – Substance Information Division)

The NPRI is a national inventory of pollutants that are released from institutional point-sources to air, water or land and/or are disposed of on-site or transferred off-site for treatment, recycling or disposal. Legislated under the Canadian Environmental Protection Act (CEPA) (Canada, 1999), the inventory collects the data from qualifying facilities (>7000 in 2021, in >280 industrial sectors), as described in the NPRI reporting requirements (Government of Canada, 2022a), and makes the data publicly available (Government of Canada, 2022b). It is one of over 50 national pollutant release and transfer registries (PRTRs) around the world, whose purpose is both to inform the public about pollutants emissions or disposals on a local to national scale and to support decision-making by various stakeholders/rights holders in the context of the sound management of chemicals (UN ECE, 1998; 2009). Moreover, like other PRTRs globally, the NPRI can directly inform progress towards UN Sustainable Development Goal (SDG) 12, target 12.4 which relates to the sound management of chemicals and wastes by significantly reducing their releases to air, water and soil in order to minimize impacts on human health and the environment (UN, 2015; OECD, 2021). However inventory data quality and comprehensiveness gaps limit its usefulness in this context (Berthiaume, 2021) and thus

research such as SWAPIT can contribute to filling these gaps, improving not only the NPRI but also contributing precedents to improve PRTRs globally and improve tracking of SDG 12. Specifically, SWAPIT substances and measurements will be compared to current NPRI substance lists and reported data to identify substance coverage gaps, and where possible, to: validate local reported annual data, improve estimation methods (i.e., high accuracy and technically/economically feasible for reporters), inform potential improvements to reporting requirements (e.g., threshold adjustments, substance additions), compliance promotion efforts or potential enforcement actions. Also, any linkages made by SWAPIT between inventoried releases and human and/or environmental impacts will be leveraged to situate NPRI data in the context of specific SDG and domestic chemicals management harm minimization goals, and inform regulatory performance measurement.

Project 2.10: Receptor modelling of VOCs using positive matrix factorization (PMF) (Lead: Samar Moussa, ECCC Air Quality Research Division)

Many volatile organic compounds (VOCs) are known or suspected to be air toxics, human carcinogens, irritants and have been linked to various respiratory illnesses. (Gkatzelis et al., 2021) Due to the complexity of the VOCs mixture in ambient air (non-combustion vs combustion sources; primary vs secondary formation), data analysis will be challenging and will therefore entail sophisticated levels of analysis in order to assess the relative contribution of the different VOC sources to the urban air mixture. VOC measurements from the three super-intensive SWAPIT sites (High Park, Evergreen Brickworks, and the University of Toronto Scarborough) will be analysed using Positive Matrix Factorization (PMF) factor analysis to apportion the VOCs emissions. The PMF tool is a bilinear analytic algorithm that separates the time series of various masses to different sources represented by factor profiles, factor time series, and residual signals unresolved by PMF. (Gkatzelis et al. 2021) During SWAPIT, PMF analysis will be performed and different VOC source tracers (e.g. cooking, personal care, traffic, wood burning, etc.) will aid in the assignment of PMF factors to various VOCs categories. Additionally, since multiple sources might exhibit similar temporal and spatial emission patterns, constraints might be used to isolate primary emissions from oxidation processes, and mobile source emission factor profiles from other non-traditional sources. For instance, measurements from NYC have shown that even in an environment that is expected to be primarily dominated by mobile source emissions, there were clear enhancements of VCP (volatile consumer product) tracers such as D5-siloxane and monoterpenes.(Coggon et al. 2021, Gkatzelis et al. 2021) Hence, the PMF analysis described below by Gkatzelis et al. (2021) will be used during SWAPIT for VOC source apportionment. Factor profiles identified by the PMF analysis will be compared to the various VOC profiles used in GEM-MACH (e.g. VCPs, wood burning, cooking, mobile, etc.) and to the profiles in the air pollution emission inventory. The factor contributions from the different VOC sources will be used to assess the overall

importance of the different factors in an urban, wintertime environment and can also be compared to GEM-MACH estimated source contributions.

Project 2.11: Relative contribution of primary and secondary oxy-PACs (quinones) in ambient air (Lead: Andrzej Wnorowski, ECCC Air Quality Research Division; Collaborator: Elisabeth Galarneau, ECCC Air Quality Research Division)

Quinones are oxygen-containing PACs found in the environment from primary emission sources and from secondary transformation of unsubstituted PAHs (Wnorowski 2017). Characterization of quinone fate is important for risk assessment as studies have demonstrated that oxidized species are more harmful and persistent than their parent PAHs (Wang et al., 2011; Bandowe et al., 2014). Their presence as secondary transformation products can also inform our understanding of aerosol aging processes. Following on work conducted in the Athabasca oil sands region (Wnorowski and Charland, 2017; Wnorowski, 2017), quinones will be measured at several SWAPIT sites across PM size fractions including the ultrafine and fine PM that have been the focus of health risk assessments in urban environments. Determination of relationships between quinones and other measured pollutants will determine their contributions to primary and secondary aerosols. The observed quinone profiles will additionally be assessed for use as representative source-specific signatures. Measurements under SWAPIT will provide a reference point for future quinone studies and contribute to the determination of an expanded suite of routinely-monitored PACs as recommended in the recent *State of Knowledge Report on PACs in the Canadian Environment* (Galarneau, 2021). Quinone content of size-distributed PM will additionally inform an evaluation of composition-dependent toxicity through *in vitro* techniques described under Theme 3 (Lead: Errol Thomson, Health Canada).

2.4.2: Atmospheric processes

The urban pollutant mixture arises from a combination of sources. Both local and transported emissions make contributions, and pollutants can be in their original physicochemical form (primary) or transformed (secondary) by a variety of atmospheric processes. Understanding relevant physicochemical transformations is critical to tying observed ambient concentrations back to their sources and forward to their future forms. Under SWAPIT, the measurements aimed at the detailed characterisation conducted under Theme 1 additionally permit investigations of a number of atmospheric processes that are relevant to understanding the urban air pollutant mixture. These include the elucidation of the budgets of nitrogen and chlorine and their impact on the formation of particulate matter. The effect of the shifting VOC mix on the formation of ozone and particulate matter will also be examined. Though brown carbon and acidifying substances have largely been studied away from urban locations, measurements under SWAPIT will contribute to documenting the emerging importance of their urban sources and impacts. Finally, pollutant processing by fog and winter precipitation will be investigated for a variety of pollutants.

Though air pollutants can be transformed chemically from primary to secondary compounds, their atmospheric behaviour also depends on physical phenomena. In order to advance our understanding and modelling capability, SWAPIT activities will investigate the impacts of turbulent kinetic energy, vertical mixing, boundary layer height, and vehicle-induced turbulence as well as mass transfer of semivolatile compounds across the particle size spectrum.

Project 2.12: The budgets of nitrogen- and chlorine-containing compounds and their impact on aerosol formation (Lead: Sumi Wren, ECCC Air Quality Research Division; Collaborators: Jennifer Murphy and Jamie Donaldson, University of Toronto; Jeremy Wentzell, Michael Wheeler, Craig Stroud, Colin Lee, Stefan Miller, and Paul Makar, ECCC Air Quality Research Division).

The wintertime urban atmosphere is characterized by low solar irradiance and low relative humidity (e.g., less sunlight and water vapour to form the OH radical, which is the main summertime driver of the formation of secondary pollutants such as ground-level ozone and the secondary fraction of PM2.5); colder temperatures, which favour multiphase chemical processes and impact gas-particle partitioning; a frequently low and stable boundary layer (which can concentrate pollutants); a different (but not well-constrained) urban VOC composition, driven for example by lower emissions of biogenics such as isoprene and monoterpenes; snow cover; and the application of road de-icing agents (i.e., chloride, sand). These conditions result in a chemical shift in the oxidizing capacity of the atmosphere relative to the summertime (Haskins et al., 2019; Sommariva et al., 2021). These distinct wintertime conditions also impact the controlling mechanisms for particulate matter (PM) formation and its speciation in both the fine mode (PM2.5) and coarse mode (PM10).

However, the importance of atypical radicals and their precursors under these wintertime conditions, in Toronto, which is a mid-latitude, continental (non-marine influenced), urban environment, is not well-understood (i.e., ambient mixing ratios, formation pathways, impact on secondary pollutants) or well-represented in models. These include reactive chlorine radical precursors (e.g., $ClNO_2$, HCl, Cl_2), and HONO, HO_2NO_2 and HCHO, which are photolytic sources of HO_x (=OH + HO_2). Previous work has shown that the multiphase reaction of N_2O_5 with chloride-containing particles to form $ClNO_2$, which photolyzes to form reactive chlorine radicals (Cl), is a significant contributor to the wintertime radical budget in the eastern US (Haskins et al., 2019). Road salt application is a potential source of particulate chloride (Mielke et al., 2011; Kolesar et al., 2018; McNamara et al. 2020) for these multiphase reactions, but its importance is not well constrained nor is it considered in GEM-MACH. Sources of HONO production (e.g., VandenBoer et al., 2014; Chen et al., 2020; Ye et al., 2017) and their relative importance both generally, and particularly in the urban wintertime environment, also remain uncertain. For example, the extent to which renoxification via particle nitrate photolysis (which yields NO_2 and/or HONO) occurs is an open debate (Shi et al., 2021). Similarly, nighttime uptake of NO_2 to aerosol to form particle nitrate and HONO may be erroneously overestimated by chemical

transport models relative to the N_2O_5 hydrolysis pathway (Travis et al., 2022). The detailed measurements planned for SWAPIT provide an opportunity to assess the representation of this chemistry in GEM-MACH.

Ammonium nitrate (NH_4NO_3) is a major component of aerosol mass in the urban wintertime atmosphere (e.g., Womack et al., 2019). Secondary wintertime production of ammonium nitrate is expected to be strongly temperature dependent (via the Henry's law constant of NH_3), however, a good understanding of the factors that impact the gas particle partitioning of total nitrate ($HNO_3 + NO_3^-$) and total NH_x ($NH_3 + NH_4^+$) in the wintertime atmosphere is still lacking. Although wintertime PM2.5 exceedances are found to be mainly driven by high levels of ammonium nitrate, ammonium chloride can also be an important contributor to secondary PM2.5 (Kelly et al., 2013). Open questions include: What size fractions are the particle nitrate and chloride found in and is this correctly represented in GEM-MACH? Does the nitrate interact with the coarse mode? How is particle speciation impacted by road dust emissions and the application of de-icing agents? Is reactive chlorine liberated from particles? How effective are existing mitigation strategies (i.e. decreasing NOx emissions) at decreasing ammonium nitrate (given that its formation is thought to be in a VOC-sensitive regime) (Womack et al., 2019) and what are the impacts of increasing ammonia emissions?

In addition, the pH of aerosol in the winter (pH ~ 3) is higher (moderately acidic) compared to the summer (pH ~ 2). This increase in pH has implications for the uptake of organic acids (e.g., oxalate) and other semivolatile species, and the dissolution of metals (e.g., Fe and Cu) (Tao and Murphy, 2019). How strong is the diurnal cycling of aerosol pH in the winter and can GEM-MACH represent this variability in pH? What is the impact of increasing NH_3 emissions on aerosol pH and aerosol buffering capacity? What other base cations are present and are they correctly represented in GEM-MACH?

A suite of instruments targeting gas and particle phase measurements of inorganic species will be deployed on CRUISER/CAM-2 during the SWAPIT super-intensive sampling periods at High Park, Evergreen Brickworks, and UTSC. An iodide-adduct high-resolution time-of-flight chemical ionization mass spectrometer (Iodide CIMS) will make high time resolution measurements of inorganic gas phase halogen (e.g., Cl_2, HCl, $ClNO_2$, Br_2, HBr, etc.) and nitrogen species (e.g., N_2O_5, HONO, HNO_3, HO_2NO_2, etc.). The instrument will also measure organic acids in addition to HCN and HNCO (both of which are air toxics with poorly constrained wintertime, urban, ambient mixing ratios). Co-located NO_2 (LGR), NO (TECO), and NO_y (second TECO) measurements will allow for closure of much of the odd nitrogen (NOy) budget, and a tunable infrared laser differential absorption spectroscopy (TILDAS) gas phase analyzer will measure NH_3. Particle phase measurements include: integrated, size-resolved inorganic particle composition (anions and cations) from an 11-stage MOUDI (up to PM_{18}); integrated (24-h) PM2.5 (fine-mode) and PM10 (coarse-mode) speciation (ammonium nitrate, ammonium sulphate, metals, organic and elemental carbon) from NAPS samplers (Dąbek- Złotorzyńska et

al., 2011); real-time, high time-resolution measurements of aerosol composition from an AMS (PM_1) – (NH_4^+, SO_4^{2-}, NO_3^-, Cl^-, ORG); and real-time aerosol size distribution (UHSAS, APS). Additionally, regular snow sampling of inorganic ions (via ion chromatography) at a single site for the six-week campaign duration will provide information on the importance of wet and dry deposition as removal processes, and on the concentrations of ions for (photo)chemistry in the different layers of the snowpack and their evolution over time.

Together the gas and particle instrumentation will provide insight into the gas-particle partitioning of total nitrate (HNO_3 + NO_3^-), total NH_x (NH_3 + NH_4^+), and inorganic halogen species, and contribute to the overall characterization of the pollutant mixture. These measurements seek to improve understanding of the formation pathways, ambient mixing ratios, diurnal profiles, and relative importance of inorganic halogen and nitrogen gas phase and particle phase species. Ambient measurements will be interpreted in the context of location, meteorology, and relevant activity data (i.e., application of road salt).

Measured mixing ratios and diurnal profiles will be compared to GEM-MACH outputs of inorganic halogen, nitrogen (NO_x, NO_y, NO_3^-), and NH_4^+/NH_3 species where possible. Modeled and measured VOC diurnal profiles and mixing ratios will be studied for evidence of the impacts of atypical radical chemistry. Additionally, the ambient measurements will be used in an offline heterogeneous inorganic chemistry box model to understand and validate the parametrization of the chemistry (e.g., uptake coefficients, temperature dependencies, assumptions); to determine the importance of including a road salt source of particle chloride, and whether a meteorology-driven emission factor can be derived; and to improve the chemical speciation of road dust speciation and the representation of base cations in the model. The results of these simulations will provide insight into necessary changes to improve GEM-MACH's predictions of particulate matter, ozone, air toxics, and acid deposition.

Project 2.13: The impact of non-exhaust VOCs such as volatile chemical products (VCPs) on organic aerosol formation and ozone forming potential (Lead: Samar Moussa, ECCC Air Quality Research Division; Collaborators: Craig Stroud ECCC Air Quality Research Division; Patrick Hayes, Université de Montréal.)

Volatile organic compounds (VOCs) in urban areas play an important role in the formation of O_3 and secondary organic aerosols (SOA), a major component of $PM_{2.5}$, and therefore have the potential to impact air quality. (McDonald, de Gouw et al. 2018) Regulations of motor vehicle emissions have resulted in declining mixing ratios of NO_x and VOCs in major megacities in North America and Europe. Under the implementation of the Canadian Environmental Protection Act (1999), VOC and NO_x levels decreased by 51% and 40.5% by 2018 across Canada, respectively. However, the reduction in ozone levels in megacities in USA, Europe and Canada is starting to slow down suggesting a shift in the air pollution mixture to one dominated by non-combustion sources that could influence ozone production efficiency.(Khare and Gentner 2018, Coggon, Gkatzelis et al. 2021, Qin, Murphy et al. 2021) With the decline of VOC emissions from

vehicular sources, VOC emissions from non-traditional sources, such as cooking emissions, tire- and brake- wear chemicals, and volatile chemical products (VCPs; used in consumer products, household products, personal care products, etc…), are making a more significant relative contribution to the overall urban VOCs.(McDonald, de Gouw et al. 2018, Gkatzelis, Coggon et al. 2021, Qin, Murphy et al. 2021) Recent studies in Los Angeles have shown that VCPs can contribute as much as 50% to total VOCs in urban areas and as much as 10 ppb of ozone.(Coggon, Gkatzelis et al. 2021) A recent study in NYC has shown that VCP emissions due to fragrances resemble those emitted from summertime forests and accounted for at least 50% of the O_3 attributed to VCPs.(Coggon, McDonald et al. 2018, Coggon, Gkatzelis et al. 2021) Additionally, VCPs and cooking emissions contain a large fraction of oxygenated species with uncertain SOA yields.(Shah, Coggon et al. 2020) McDonald et al have shown that VCPs could be responsible for at least 50% of the organic mass associated with SOA formation.(McDonald, de Gouw et al. 2018)

A full understanding of VOC emissions from non-traditional sources and their transformation products in Canadian ambient air are currently lacking and their contribution to SOA formation and ozone forming potential are underestimated. Additionally, their emissions and chemistry are not well-represented in GEM-MACH and national inventories. There is a knowledge gap in our understanding of how these VOCs affect air quality in urban cities across Canada, especially that more than 80% of Canadians are living in those areas. Hence, it is critical to identify and quantify non-traditional VOC emissions to effectively mitigate air pollution in cities and improve human health for Canadians.

Wintertime measurements will be ideal to estimate non-exhaust VOC emissions because such emissions will not be influenced by biogenic emissions of monoterpenes (VCP tracers for household products and fragrances) and fast secondary oxidation chemistry.

During SWAPIT, a large suite of non-traditional VOCs will be measured during the two-week super-intensive sampling periods at High Park, Evergreen Brickworks, and UTSC, and their contribution to the total VOCs measured will be assessed at the three locations during the study. On-line measurements of VOCs will be conducted using a VOCUS-PTR-TOF with switchable reagent ions (H_3O^+ and NH_4^+) that will be deployed aboard CRUISER.(McDonald, de Gouw et al. 2018, Gkatzelis, Coggon et al. 2021, Gkatzelis, Coggon et al. 2021) The PTR is sensitive to wide range of species including oxygenates, alkenes, aromatics and biogenic species. The use of NH_4^+ as a reagent ion will expand the suite of the measured of oxygenated VOCs (OVOCs).(Khare, Krechmer et al. 2022) Alkanes, alkenes, as well as VOC isomers that cannot be resolved by the PTR-ToF-MS will be measured using an AMA online GC (in collaboration with ON MECP) and offline NAPS VOC-grab samples. The PTR -ToF will be calibrated for a wide range of vehicular and non-traditional VOC tracers (fragrances, solvents, personal care products, cleaning products, cooking emissions, wood burning, vehicles, windshield washer fluids, paint, solvents, etc...). Following the method described by Gkatzelis

et al. 2021, enhancement ratios of tracers to benzene and emission ratios (ER) relative to CO will be calculated.(Gkatzelis, Coggon et al. 2021) The estimated emissions will then be used to evaluate existing non-exhaust VOC emission inventories (e.g. VCPs and VCPy inventory). Additionally, results from SWAPIT ambient measurements will be used to provide GEM-MACH with updated emission rates from non-traditional VOCs sources, and obtain better speciation profiles, which will be used to evaluate their effects on SOA formation and ozone forming potential. Additionally, the measurements could provide GEM-MACH with proper tracers for non-combustion VOCs and could improve the lumping of non-traditional VOCs and OVOCs in the model. Source-specific emission reductions scenarios (e.g. 10%) in GEM-MACH will be performed to derive the source contribution from the difference relative to a base case. Measurement results will be used to modify the model's emission speciation and chemical mechanism to better represent the VCP emissions and OVOC emissions in the model by combining the KPP-generated mechanisms with GEM-MACH.

Project 2.14: Primary emissions and secondary formation of atmospheric brown carbon (Lead: Alex Lee, ECCC Air Quality Research Division; Collaborators: Jon Abbatt, University of Toronto, Craig Stroud and Paul Makar, ECCC Air Quality Research Division).

Black carbon (BC) emitted from combustion sources has been recognized as one of the major short-lived climate forcers in the atmosphere (Bond et al., 2013). Recent modeling studies have revealed that atmospheric brown carbon (BrC), the light absorbing fraction of organic aerosol (OA), can have a strong impact on atmospheric warming, equivalent up to ~50% of the positive radiative forcing caused by ambient BC, in regions with strong BrC emissions (Feng et al., 2013, Wang et al., 2014). However, these results are subject to large uncertainties due to the lack of understanding on their sources, formation processes and atmospheric evolution. While biomass burning has been recognized as the key source of BrC in global scale, there is increasing field evidence that the contributions of other primary sources and secondary processes to BrC in urban environments should not be ignored (Kasthuriarachch et al., 2020, Yan et al., 2017).

During SWAPIT, a soot particle aerosol mass spectrometer (SP-AMS) will be deployed during the two-week super-intensive measurements at High Park, Evergreen Brickworks and UTSC. Due to the unique capability of SP-AMS to detect BC, OA, some metals (e.g., K, V, Ni), and inorganic aerosol simultaneously in a real-time manner, all the measured aerosol species will be integrated into the positive matrix factorization (PMF) analysis for improving source apportionment of both BC and OA (e.g., from local traffic, residential wood burning, secondary formation) at multiple locations. In particular, BC and metal signals can provide insights into the potential origin of fresh/aged combustion-related emissions that cannot be easily resolved based on the conventional PMF approach (Rivellini et al., 2020). Together with the co-located aerosol optical properties measurement, including photoacoustic extinctiometer and multiple wavelength aethalometer, source-specific light absorption properties of primary and secondary urban BrC will be determined in terms of the mass absorption cross-section (MAC) and absorption

Ångström exponent (AAE) (Kasthuriarachch et al., 2020). These parameters can be used as model inputs for evaluating the impacts of urban BrC to the total aerosol light absorption and air quality-climate interaction study.

Project 2.15: Impact of urban emissions on deposition of acidifying substances (Co-leads: Amanda Cole and Jason O'Brien, ECCC Air Quality Research Division; Collaborator: Jennifer Murphy, University of Toronto)

Deposition of nitrogen and sulphur compounds from the atmosphere to the surface can lead to soil and water acidification and eutrophication, with associated impacts on plant growth and diversity. While long-term monitoring sites for wet deposition in Canada were purposely situated to minimize the impact of local emissions, this results in a lack of information about the scale and impact of nitrogen and sulphur deposition on natural and semi-natural areas within and around urban areas. Efforts to fill this gap have begun in some areas of the world (Decina et al., 2020), but data on nitrogen deposition gradients in urban areas in Canada is limited to a single dry deposition gradient study (Zbieranowski and Aherne, 2012). While limited in time, the six weeks of measurements at two SWAPIT wet deposition sites (High Park and UTSC) will allow for a snapshot of NO_3^-, SO_4^{2-} and NH_4^+ wet deposition gradients during the winter when combined with data from existing CAPMoN sites in the area surrounding Toronto. In addition, simultaneous measurements of gas phase NH_3, SO_2, and NO_x, and particle-bound NO_3, SO_4^{2-} and NH_4^+, will allow for estimation of dry deposition fluxes and a quantification of the relative contributions of each of these components to total N and S deposition for comparison with similar measurements in rural and remote areas (Zhang et al., 2008).

Project 2.16: Impact of wet processing (precipitation, clouds, and fog) on urban pollutants and deposition (Lead: Wanmin Gong, ECCC Air Quality Research Division; Collaborators: Michael Wheeler, Paul Makar, Craig Stroud, and Colin Lee, ECCC Air Quality Research Division)

Clouds play an important role in the transport and transformation of atmospheric tracers. Studies have shown that the aqueous-phase formation of sulphate and SOA in cloud and fog droplets can contribute significantly to ambient aerosol mass. The extent to which aqueous-phase processing modifies aerosol characteristics is not well understood, nor are the relevant mechanisms (e.g., mass, chemical composition, hygroscopicity, and oxidation state) (Ervens et al., 2018). Clouds also play a role in atmospheric cleansing when associated with precipitation (i.e., removal of aqueous-phase tracers from cloud through precipitation production, or rainout, and below cloud scavenging of atmospheric tracers by falling hydrometeors, or washout). Wet deposition becomes particularly important in winter at lower temperature for some of the organic contaminants as they partition more from vapour phase to liquid droplets, particles, and snow surfaces (e.g., Lei and Wania, 2004).

The current model representations of cloud processing of gas and aerosol (uptake and partitioning to cloud water and aqueous-phase chemistry) are largely based on (and evaluated for) summer (warm) conditions. Under winter conditions, gas and aerosol partitioning to

supercooled water and ice phase is not well understood; aqueous phase chemistry may be different at cold temperature with different pollutants and pH regimes. For example, studies have indicated that transition metal catalysed oxidation in aqueous phase can be important under winter conditions when photochemical activity is low (Deguillaume et al., 2005; Itahashi et al., 2018). Recently, base cations and aqueous-phase transition metal catalysed oxidation have been added to GEM-MACH. However, there has not been an evaluation on the model representations for processing of gas and aerosol in winter clouds.

Although there is no direct in-cloud sampling planned for the SWAPIT campaign, the precipitation samples collected for wet deposition analysis will consist of both in-cloud scavenging and below-cloud scavenging component. The analysis for inorganic ions and selected organic ions on the precipitation samples collected at the proposed SWAPIT wet deposition sites (and surrounding regional sites), in conjunction with the ambient air measurement of gas and speciated aerosols planned, will shed light on the aqueous-phase processing of urban air pollution mixture in wintertime. In addition, the results from high-resolution GEM-MACH simulations will be compared to the observational SWAPIT data to evaluate and improve model representations of wet processes.

Project 2.17: Fog-pollutant interactions in urban air (Lead: Wanmin Gong, ECCC Air Quality Division; Collaborators: Michael Wheeler, Jason O'Brien, and Amanda Cole, ECCC Air Quality Research Division; Rachel Chang, Dalhousie University)

Fog is often associated with poor visibility which can cause significant disruptions in aviation, marine, and land transportation. In fact, the financial and human losses related to fog and low visibility can be comparable to the losses from other severe weather events (Gultepe et al., 2007). A 30-year fog climatology (1970 – 2004) showed that high frequency of fog formation at Toronto Pearson Airport occurs during the periods of October–November and February–March (Hansen et al., 2007). It is well known that visibility is directly linked to fog droplet number concentration (N_d), which is influenced by the abundance and the physical-chemical characteristics of ambient aerosols (Gultepe et al., 2007). On the other hand, fog also contributes to the aqueous-phase processing of gases and aerosols. A recent investigation on aerosol toxicology conducted in Po Valley during winter fog season found evidence of enhanced toxicity, or increased reactive oxygen species (ROS) activity, in aerosols processed by fog (Decesari et al., 2017). During the SWAPIT campaign, fog droplet number concentration and size distribution will be measured using a fog monitor installed on the CN tower observational deck, along with particle sizers (SMPS and Grimm) to investigate how urban and regional aerosols influence fog formation and characteristics. In addition, an active fog water sampler will be used to collect fog water for chemical analysis of inorganic ions by CAPMoN to elucidate fog processing of urban and regional air pollution. These measurements will be compared with model simulations using a fully coupled version of GEM-MACH to evaluate model representation of aerosol activation and aerosol-cloud interactions. The fog water chemistry measurements will also be used, in conjunction with other SWAPIT ambient air and

precipitation chemistry measurements, to improve our understanding, and the GEM-MACH model representation, of wet processing of gases and aerosols.

Project 2.18: Transformations of PACs deposited with and to snow (Lead: Elisabeth Galarneau, ECCC Air Quality Research Division)

Though GEM-MACH demonstrates high model accuracy for PACs in ambient air (Galarneau et al., 2014; Whaley et al., 2018), modelled deposition does not compare well to available measurements, especially in winter (Whaley et al., 2018). This is further complicated by discrepancies among winter measurements that observe fresh deposition versus the aged snowpack (Tevlin et al., 2021). In order to resolve observed discrepancies, event-based and snowpack PAC measurements will be collocated at SWAPIT sites. Differences between sampling methods will be interpreted in relation to meteorological conditions, snow characteristics, and physicochemical properties across the range of examined PACs in order to improve reported deposition and advance GEM-MACH's ability to model it.

Project 2.19: The evolution of semivolatile toxics across the particle size spectrum (Lead: Elisabeth Galarneau, ECCC Air Quality Research Division)

Polycyclic aromatic compounds (PACs) from the burning of fossil fuels are emitted with fine combustion particles (Alves et al., 2016; Horak et al., 2017; Cheng et al., 2019) whereas they have long been observed across the particle size spectrum in ambient air (e.g., de Maio and Corn, 1966; Van Vaeck and Van Cauwenberghe, 1978). Their particle size evolution appears related to volatility (Pistikopoulos et al., 1990; Offenberg and Baker, 1999) but is not well-understood or represented in chemical transport models. Previous cascade impactor measurements have been hampered by small sample volumes and correspondingly long sampling times, but a novel high-volume cascade impactor system allows for samples on the order of hours. The system will be deployed during SWAPIT with results for PACs and other homologous organic compound groups (e.g., *n*-alkanes) to be assessed relative to non-volatile compounds (e.g., trace metals). Differences among these compound classes will be interpreted in light of the overall particle mass distribution and environmental conditions such as temperature in order to better understand the factors that underlie the evolution of semivolatile compound particle size in ambient air.

Project 2.20: Improving the understanding of turbulent kinetic energy and boundary layer height in urban environments (Lead: Zen Mariani, ECCC Meteorological Research Division; Collaborators: Ralf Staebler, Paul Makar, Craig Stroud, ECCC Air Quality Research Division; Sylvie Leroyer, Stéphane Bélair, ECCC Meteorological Research Division; Mark Gordon, York University)

Verification and evaluation of numerical weather prediction (NWP) model output is crucial for urban areas where surface features and the energy budget differ markedly from natural landscapes. ECCC's GEM NWP model output of turbulent kinetic energy is heavily dependent

upon model parameterization schemes that are influenced by the complex surface roughness and topography in urban environments. Doppler LIDAR observations of turbulence (measured from the surface up to the planetary boundary layer) can be used to perform enhanced verification of GEM turbulent kinetic energy output at unprecedented temporal and spatial resolution. In particular, the lower limits of turbulent kinetic energy from GEM and the effect of vertical mixing in GEM-MACH will be compared to SWAPIT measurements to explore potential improvements to both models.

Boundary layer height (BLH) defines the volume of air within which surface emissions will mix and dilute. Despite its critical role in determining ambient pollutant concentrations, BLH is poorly represented in meteorological and chemical transport models. Doppler LIDAR observations can detect the height of the boundary layer by examining the vertical distribution of velocities. Such LIDAR observations at multiple locations will provide information about the spatiotemporal variability of the boundary layer height across the GTHA and inform the evaluation and improvement of the GEM and GEM-MACH models.

Project 2.21: Investigating impacts of vehicle-induced turbulence in the near-road urban environment (Lead: Ralf Staebler, ECCC Air Quality Research Division; Collaborators: *Zen Mariani, Sylvie Leroyer and Stéphane Belair, ECCC Meteorological Research Division; Paul Makar and Craig Stroud, ECCC Air Quality Research Division; Mark Gordon, York University)*

Vehicle-induced turbulence (VIT) has been shown to play a disproportionate role in the dispersion of traffic-generated pollution (cf. Makar et al., 2021). Previous ECCC campaigns have quantified VIT through mobile measurements with CRUISER in moving traffic, as well as at varying perpendicular distances from a major highway (Gordon et al., 2012). During SWAPIT, VIT will be investigated adjacent to Highway 401 through a combination of stationary measurements. A sonic anemometer will be installed on the roof of the existing NAPS Roadside site trailer facing eastbound traffic on Highway 401 for an *in situ* continuous quantification of turbulence a few metres from the road. These point measurements will anchor the data obtained by a HALO scanning LIDAR, installed on the roof of the NAPS Toronto West site (Upper Garage building), which will provide 3-D maps of all 3 components of the wind, their variances, and turbulent kinetic energy (TKE) in the air above and surrounding the highway. This suite of measurements will be used to characterise VIT and evaluate a recently-developed VIT parameterisation in GEM-MACH for near-road locations.

Project 2.22: *Evaluating meteorological influences on near-road gradients of traffic related pollutants (Lead: Greg Evans, University of Toronto; Collaborator: Cheol-Heon Jeong, University of Toronto)*

Previous research has shown that concentrations of traffic related air pollutants (TRAP) 250m downwind of major roads still exceed those upwind, pointing to the wide footprint of TRAP population exposure around roads. NTP metals were also shown to exhibit a much steeper

roadside gradient than TP pollutants which implies that differences in NTP vs TP exposure may exist within these near-road environments. Moreover, wintertime stagnation events can greatly extend the spatial footprint of the near-road region. Much less is known about vertical gradients of TRAP and even less about how winter stagnation events influence these gradients.

Horizontal TRAP gradients will be investigated during SWAPIT beside highway 401 at the Ontario MECP's Resources Road site. During the winter 2024, we will collect UPAS ($PM_{2.5}$ and PM_{10}) and Ogawa samples at different distance from the roads to compare the gradients in TP (NOx) and NTP (metals) pollutants. AirSENCE units will also be deployed on the two sides of the highway to collect high- time-resolution PM_1, $PM_{2.5}$ and PM_{10}, CO_2, CO, NO_x, and O3 data. Similar data will be collect at a site on Allen Road. The upwind-downwind differences will be used to infer emissions rates from the highway. Additional AirSENCE units may be deployed along the horizontal transect at MECP if electrical power is available. The vertical gradient of TRAP will be studied by deploying small handheld instruments to measure PM2.5 (DustTrak II 8530) and black carbon (MA350), ultrafine particles (Discmini) at three heights on the top (300m), near the middle (150m), and near the bottom (< 30 m) of the CN Tower.

Outputs from Theme 2 – Sources and Processes

- Emission factors, source profiles, and spatiotemporal allocation of releases from vehicle exhaust (cold-start and running), non-exhaust vehicle emissions, and non-exhaust VOCs
- Ground-truthed emission locations for facility-reported NPRI pollutants
- Documented relevance of nitrogen, chlorine and VOC chemistry toward the formation of ozone and secondary particulate matter in winter
- Magnitude of urban contributions to brown carbon and acid deposition
- Impact of snow and fog processing on urban air pollutants
- Improved description of atmospheric turbulence and boundary layer height in the urban environment

2.5: Scientific Activities Under Theme 3 – Impacts

Although the human and environmental health impacts of some air pollutants are well-quantified, the credible ranges of exposures for those impacts remain uncertain and the interaction effects of exposure to multiple pollutants is an active topic of research (Giang et al., 2020; Fazakas et al., 2023). Several SWAPIT activities are aimed at elucidating connections between the characterised urban air pollutant mixture and negative impacts on human or environmental health, and these are summarised below.

Project 3.1: Linking oxidative potential to air toxics and trace contaminants (Co-leads: Tom Harner and Amandeep Saini, ECCC Air Quality Research Division; Collaborators: Pourya Shahpoury, Health Canada and Trent University; Sabina Halappanavar, Health Canada; Xianming Zhang and Cassandra Johannessen, Concordia University; John Liggio, Samar Moussa, Jasmin Schuster and Craig Stroud, ECCC Air Quality Research Division; Mark Parnis, Trent University; Greg Evans, University of Toronto)

Polyurethane foam disk passive air samplers (PUF-PAS), which collect both gas- and particle-associated chemicals have been used in Toronto under the ATOUSA study (2016-2019) to assess several classes of air toxics/contaminants in urban air across different sectors and to establish linkages to toxicity endpoints, including, among others, oxidative stress (Halappanavar et al., 2021). Chemical classes that were measured included PACs (Jariyasopit et al., 2019), flame retardants (Saini et al., 2019) and their transformation products (Liu et al., 2021), trace metals (Gaga et al., 2019), and black carbon (Zhang et al., 2022). Recently, Johannessen et al., (2023) screened these samples for antioxidants and revealed that several tire-additives including DPG, benzotriazoles and benzothiazoles (among others) exhibited high concentrations and were elevated at traffic-influenced sites; in addition, 6PPD and its transformation product, 6PPD-quinone, were detected in air at traffic influenced sites. The 6PPD and its quinone induce acute fish mortality for salmon due to run-off from nearby roadways during rain events (Tian et al., 2020). Concerns have been raised about the occurrence, fate, exposure, and health risks associated with the presence of these tire-derived chemicals and their transformation products in air (Zhang et al., 2022b; Johannessen et al., 2022).

PUF-PAS will be deployed under SWAPIT to assess spatial differences in oxidative potential (OP) across the GTA. [Other toxicity indicators may also be included.] OP is an indicator of PM health and influenced by levels of several chemical classes, including trace metals and quinones (which can include transformation products of PACs and other chemicals). Under SWAPIT, OP will be evaluated from PUF-PAS samplers, instead of the conventional filter samples from active samplers (Shahpoury et al., 2019, 2021, 2022, 2023; Jeong et al., 2020; Weichenthal et al., 2019). This will allow for time-integrated samples from a greater number of sites and is expected to capture the pro-oxidant capacity of both particulate and gaseous chemicals. OP results will be interpreted using aerosol chemical characterization data, e.g., trace metals measured in PUF-PAS. In addition to assessing OP across urban sectors, a key objective of this work is to develop predictive methods for OP based on regression analysis and to test existing models of OP (Lelieveld et al., 2021; Shahpoury et al., 2023b).

Building on the work of Johannessen et al., (2022b, 2023) PUF-PAS samples from SWAPIT sites (including spatial transect studies on the CN Tower and at Highway 401) will be analyzed for a suite of tire-wear chemicals and their transformation products using high resolution LC-Orbitrap (Johannessen et al., 2022). Targeted high resolution screening will be informed by recent experimental data from oxidation experiments by Liggio et al., (in prep.) and Moussa et al., (in

prep.). In addition, non-targeted screening of PUF-PAS samples will be performed and contribute to future interpretation of results (Zhang et al., 2020).

Project 3.2: Oxidative potential of PM from field samples and known sources (Lead: Greg Evans, University of Toronto; Collaborators: Cheol-Heon Jeong, University of Toronto; Tom Harner, ECCC Air Quality Research Division)

Past research has shown that different oxidative potential OP assays respond differentially to different components of PM, with the Ascorbic acid (AA) assay being more responsive to metals, particularly Cu, and the Dithiothreitol (DTT) assay more responsive to organics.

In this project, we will measure the (OP) of PM from field samples collected during SWAPIT and known sources using three assays (AA, GSH, DTT). This analysis will include OP of resuspended road dust collected in the wheel-well of vehicles during mobile sampling and filters collected at fixed sites across the city. The water solubility of the metals in some of these samples will also be evaluated along with the OP for PM samples extracted into water rather than methanol. The OP of the field samples and PM from known sources will be compared to previously measured for ambient PM at 40 sites across Canada. Moreover, the OP values will be compared to values for PUF-PAS samples collected at the same locations (e.g. MECP, Pearson Airport) in SWAPIT Project 3.1.

The oxidative potential of these field samples will also be compared to that for lab samples generated from known sources, such as samples of tires and road dust. These lab-generated samples will also undergo detailed chemical characterization to better understand the chemical compounds contributing the observed OP. We will analyze the metal content of tire slices by XRF and use pyrolysis Gas-chromatography mass spectrometry to samples of styrene butadiene rubber (SBR) and butadiene rubber (BR) to identify mass spectral markers. This same methodology will then be applied to samples of ambient, road dust, and wheel-well PM to hopefully identify and quantify the contributions of tire PM. These lab-based studies will compare multiple methods and potential markers of tire PM that and then apply them to real-world samples from multiple sources with a goal of identifying a surrogate to more easily resolve the contributions of tire-wear PM.

Project 3.3: Assessing in vitro toxicity of air toxics/trace contaminants from near-road and urban background areas (Lead: Errol Thomson, Health Canada: Collaborator: Elisabeth Galarneau, ECCC Air Quality Research Division)

The toxicity of ambient particles depends not only on mass concentrations, but also on their physicochemical characteristics, which in turn are a function of source. Following on work at Canadian locations with various urban and industrial sources (Thomson et al., 2015; 2016), the relative toxic potency of size-fractionated particles collected in the vicinity of contrasting conditions will be examined and related to composition. Size-fractioned airborne particulate matter will be collected by high-volume cascade impactors at sites near fresh vehicle emissions

and further downwind where vehicle emissions have mixed with other urban sources. Sample collection will allow for toxicological analyses and assessment of physicochemical evolution resulting from atmospheric processing. The collected samples will be analysed for pollutants linked to toxicity (e.g., metal(loid)s, polycyclic aromatic compounds, etc.), including chemical tracers for brake and tire wear. Co-located measurements by SWAPIT collaborators will contribute a comprehensive suite of conventional air quality measurements, including the three Air Quality Health Index pollutants (O_3, $PM_{2.5}$ and NO_2), as well as several gas and particle phase compounds. Collaborators will also provide output from fine-scale chemical transport models that depict spatiotemporal variations and thus allow for tracking of emissions and their dispersion. In vitro exposure of relevant lung models will be conducted across a dose-range alongside standard reference materials, and a battery of assays covering cytotoxicity, oxidative stress, inflammatory response, and mRNA profiling will be assessed, with specific additional assays run depending on data needs and/or as guided by the initial screen. Potency estimates will be regressed against particle composition to identify potential determinants of effects.

Project 3.4: Identifying exceedances of health-based air quality guidelines (Lead: Elisabeth Galarneau, ECCC Air Quality Research Division; Collaborator: Amanda Giang, University of British Columbia)

The potential for adverse health effects is often assessed by comparing ambient pollutant concentrations to health-based guidelines. Though no such guidelines exist at the national or federal level, alternate thresholds can be used to examine potential impacts. A variety of air toxics including benzene and other VOCs, PAHs, and metal(loid)s are subject to provincial health-based guidelines. Ontario's Ambient Air Quality Criteria (AAQC) have the largest number of pollutants subject to such limits in Canada (Galarneau et al., 2016). AAQC also include the four CACs managed under the AQMS (SO2, NO2, O3 and PM2.5) for which some threshold values are consistent with Canadian Ambient Air Quality Standards (CAAQS) (CCME, 2022) that incorporate achievability along with health considerations. Ambient concentrations of pollutants subject to relevant guidelines will be assessed for individual exceedances and for cumulative exceedance of the pollutant mixture. For the subset of pollutants that can be simulated using GEM-MACH, the spatial distribution of individual and cumulative exceedance will additionally be developed at fine (2.5 km) resolution. For pollutants without health-based guidelines, SWAPIT data will be interpreted using methods that contextualize pollutants relative to their range of observed concentrations (Soares et al., 2018; Wren et al., 2020) among other techniques, thus allowing for an indication of potential impacts and their differences across the city. Taken together, these measures will provide information about the burden of air pollution at different locations across the city and will additionally allow for interpretation of such burdens relative to local land use, emissions, and demographic characteristics.

Project 3.5: Determining epidemiological relationships between air pollutant exposure and adverse health impacts (Lead: Markey Johnson, Health Canada; Collaborators: Elisabeth Galarneau, ECCC Air Quality Research Division)

Robust spatiotemporal information about pollutant concentrations permits the examination of relationships between adverse health impacts and pollution exposure. The multi-pollutant data sets developed under SWAPIT will be examined for suitability as exposure surfaces for epidemiological investigations, and if appropriate, will be used to further understand disease incidence and impacts as a function of single and multiple pollutant exposure.

Project 3.6: Assessing the effects of snowmelt water on amphibian embryos (Lead: Stacey Robinson, ECCC Ecotoxicology and Wildlife Health Division; Collaborators: Hayley Hung and Elisabeth Galarneau, ECCC Air Quality Research Division; Roxana Suehring, Toronto Metropolitan University)

Atmospheric deposition of air contaminants to snow has been found (e.g., Radke et al. 1980, Franz and Eisenreich 1988, Vasic et al. 2012, Nazarenko et al. 2017) and can follow a gradient with higher concentrations in snow collected closer to pollutant sources (e.g., Kelly et al. 2010). Snowmelt can contribute substantially to ephemeral, and some perennial ponds (Meyer and Wania, 2008 and 2011) that could be used by Canadian native amphibians to breed and develop through aquatic life stages. The effects of snowmelt contaminant mixtures on amphibian fitness-relevant responses has not yet been assessed, however, may be a highly relevant exposure for early life-stages (i.e., embryos) of early spring breeding amphibians in urban areas.

The objective of our study is to assess the effects of snowmelt water collected from urban sites reflecting a gradient of air pollution in the Greater Toronto Area on northern leopard frog (Rana pipiens) embryo hatching success, malformations, survival and gene expression. Specifically, embryos will be exposed to 100% snowmelt water for 96 hours or until hatching, assessed for malformations and changes in gene expression using the novel northern leopard frog EcoToxChip™ (https://www.ecotoxchip.ca/). Assessing the apical and molecular effects of air pollutants in snowmelt will help to understand the risk winter air pollution poses to amphibians using urban aquatic ecosystems.

Project 3.7: Assessing the impact of airborne trace contaminants on urban fish health (Lead: Gérald Tetreault, ECCC Aquatic Contaminants Research Division; Collaborators: Hayley Hung, ECCC Air Quality Research Division; Zhe Lu, Université du Québec à Rimouski; Trevor VandenBoer and Cora Young, York University; Roxana Suehring, Toronto Metropolitan University)

Emerging chemicals that are applied to commercial products, including flame retardants, plasticizers and oil/water spill repellents, are associated with urban populations (Venier et al.,

2019; Rodgers et al., 2023; Li et al., 2017). Many of these chemicals are of concern because they can deposit from the atmsophere into urban aquatic and terrestrial ecosystems and bioaccumulate through the foodweb resulting in adverse effects on urban wildlife (Szabo et al., 2022; Knudtzon et al., 2021) and humans (Domingo and Nadal, 2019). In addition, Tian et al. (2020) reported that a 6-PPD-quinone (6-PPDQ), a transformation product of a common antioxidant applied to tire rubber to prevent degradation and cracking of rubber, induces acute toxicity to coho salmon in the Pacific Northwest. These rubber-derived quinones have been known to be present in runoff-affected receiving waters have also demonstrated effects (reduced hatch success, survival, growth) in lab exposures in fathead minnow (Pimephales promelas) (Prosser et al., 2017). Many other chemicals are added to polymers and plastics, e.g. benzotriazole UV stabilizers (BT-UVs) are added to prevent materials from UV-induced color change or degradation. Little is known about the environmental transport, deposition, fate and impacts of these emerging chemicals in the urban aquatic ecosystem.

During SWAPIT, our team will investigate the air-precipitation-water-sediment-fish interactions of these emerging chemicals to better understand the environmental fate and effects of these substances in an urban setting. Air and precipitation samples will be collected close to urban aquatic systems (e.g. Grenadier Pond, Don River). Simultaneously, water and sediment will be sampled in these aquatic systems, if possible. Atmospheric and aquatic samples will be analysed for per- and polyfluoroalkyl substances (PFASs) (oil/water spill repellents), organophosphate esters (flame retardants and plasticizers), BT-UVs, UV filters (used in sunscreens and personal care products), polyhalogenated carbazoles (PHCZ), tire/ brake wear chemicals including 6-PPD, 6-PPDQ and other plastics/rubber additives, and other persistent, mobile and toxic (PMT) contaminants. Ecotoxicological analysis will be conducted on using 'Fish Embryo Toxicity (FET) Tests Using Tissue Culture Plates' (embryo-development and hatching) (OECD, 2013), to understand the effects of these substances on the urban habitat. Results from this study will allow for the identification and quantification of atmospheric sources, deposition and impacts of commercial chemicals to urban aquatic systems. Further, results can provide atmospheric loadings information for these chemicals to the nearby Great Lakes, North America's most important fresh water resource, which is impacted by contaminants emitted from some of the largest cities in Canada (including Toronto) and the US along its coasts.

Project 3.8: Assessing trace contaminant burden and links to altered health outcomes in semi-aquatic mammals (Lead: Philippe Thomas, ECCC Ecotoxicology and Wildlife Health Division; Collaborators: Esther Attard, Toronto Animal Services)

Recent *in vitro* reports of urban air pollution suggest effects on oxidative stress, pro-inflammatory, and toxicogenomic responses such as transcriptomic effects and cytotoxicity in vertebrate cell lines (Shahriyari et al., 2022; Halappanavar et al. 2021). In turn, this has raised concerns on human and wildlife health impacts from complex mixtures of organic and inorganic contaminants found in urban air pollution. Compounded by the cumulative effects from other

environmental stressors such as wildfire smoke, climate change and habitat degradation and fragmentation in urban parks and greenbelts, urban air pollution can negatively affect mammal species' health, behaviour, distribution, populations, and communities.

Muskrats (*Ondatra zibethicus*) and beaver (*Castor canadensis*) are important semi-aquatic furbearers that are commonly found in urban parks, near marinas and wetlands. Mink (*Neovison vison*) are top trophic level carnivores that prey on fish and readily bioaccumulate environmental pollutants; all of which are endemic to the GTA. In a 2003 study of muskrats living in industrially-disturbed landscapes of northern Ontario, it was found that muskrat tissue concentrations can average 2-times and 3- to 6-times higher than background values and are believed to reflect accumulations resulting from food chain contamination in regional marshes, including levels in Cattails (*Typha latifolia*) stands—their primary food source—and sediments which may be eaten accidentally while feeding (sediment that could be derived in part from atmospheric deposition of airborne particulate matter) (Parker, 2003). Changes in physiological or "health" status from exposure to environmental contaminants can influence how mammal species respond to contaminant mixtures after exposure, with some of the negative consequences of exposure likely amplified by poorer health conditions and impaired metabolic capacity.

In collaboration with Toronto Animal Services, cadavers of muskrat, beaver and mink are collected from locations across Toronto. After a brief examination, and administration of pentobarbital (if euthanasia is necessary) by the on-staff DVM, carcasses are frozen at -20^{o}C until necropsies and tissue samples are collected at the National Wildlife Research Centre (ECCC-Carleton University, Ottawa, ON). Through these necropsies, we will collect morphometric data (i.e., weight, length, gonadosomatic index, hepatosomatic index etc.) and tissue samples (liver and muscle) to measure contaminants of concern to SWAPIT, but also to obtain DNA for molecular genetic analyses. In female animals, the uteri will be collected to assess pregnancy status through visual identification of fetuses in utero or by counting placental scars. Any fetuses will also be collected for contaminant analysis. If possible, ovaries will be freeze-clamped and stored in liquid nitrogen (where possible) for histology and ovarian damage evaluations and DNA sequencing.

<u>Lung Damage and RNA-Seq:</u> Recent studies have highlighted an association between exposure to urban air pollution, PM2.5 and lung damage. In fact, persistent endoplasmic reticulum stress is a mechanism that causes lung damage under PM2.5 exposure. The gene Nrf2 facilitates lung injury during PM2.5 exposure and CYP2E1 metabolism is involved in this process. Upstream and downstream genes in this pathway such as GRP94 are also impacted by PM2.5 exposure with cascading effects on inflammatory and oxidative stress in the lung (Ding et al. 2021). To determine the molecular pathways involved in some of the biological effects measured in collected mammals, we will perform RNA-Seq (McMaster Genome Facility) in lung tissue from animals with high (i.e., tissue residues above the 90th centile) and low (i.e., tissue residues

below the 10th centile) contaminant of concern exposure. Information from the RNA-Seq analyses will provide the basis for pathway analysis, gene set, and Gene Ontology enrichment analysis using the Database for Annotation, Visualization and Integrated Discovery suite, including examination of regulatory pathways defined in the Kyoto Encyclopedia of Genes and Genomes Pathways. This approach will allow us to identify the deregulated genes, genome-wide, in the lung of animals with SWAPIT contaminant of concern exposure relative to a less-exposed reference group. We will perform gene ontology analysis of the deregulated genes to find similarities and differences in molecular pathways and functional networks that are disrupted with each exposure paradigm. As routinely done in other studies, we will confirm the genome-wide gene expression data by randomly selecting 5-10% of the identified targets and subjecting them to single-gene validation assays by reverse transcriptase real-time PCR (RT-PCR). These data will inform future mechanistic studies, and will provide the necessary information on biomarkers of early biological effect, useful to urban air pollution monitoring programs.

Ovarian damage: To examine if exposure to contaminants of concern to SWAPIT results in adverse effects to ovaries, we will examine changes in ovarian weight and ovarian histopathology using techniques well established by our group. We will determine the amount of follicular atresia (TUNEL), the number of primary, growing, and antral follicles and the presence of cystic follicles or rete ovarii. Ovaries will be immuno-stained for markers of proliferation (Ki67), angiogenesis (CD31, VEGF, VEGFR2, bFGF), and apoptosis (TUNEL). We will also determine the number of primordial follicles; this is a marker of germ cell depletion (ovarian reserve) which is thought to predict reproductive life-span.

Outputs of Theme 3 – Impacts

- Linked measures of toxicity and ambient pollutant concentrations
- Spatiotemporal distribution of health-based guideline exceedances
- Burdens of disease and adverse impacts from air pollution exposure in humans including vulnerable populations
- Relationships between pollutant exposure and adverse effects in amphibians, fish, and semi-aquatic mammals

2.6: Scientific Activities Under Theme 4 - Science tool evaluation and improvement

Large air quality studies present opportunities to evaluate and improve the tools that scientists use to measure and understand air pollution. Such opportunities are being facilitated under SWAPIT to further develop techniques that measure plastics and mercury in air at ground level. Collocated measurements for common air pollutants are also providing opportunities to

evaluate satellite-based measurements and chemical transport models with unprecedented spatiotemporal density. The field campaign's measurement strategy allows for sub-grid variability to be assessed in satellite pixel and model grid squares that contain multiple fixed measurement sites as well as additional locations accessible to mobile sampling platforms. The assessment of estimated vertical distributions is also possible because of vertically-resolved measurements that will inform the accuracy of procedures that derive ground-level concentrations from total column measurements.

Project 4.1: Evaluation of techniques for measurement of airborne mercury in urban environments (Lead: Alexandra Steffen, ECCC Air Quality Research Division; Collaborators: Katrina MacSween and Geoff Stupple, ECCC Air Quality Research Division; Bridget Bergquist, University of Toronto)

Mercury is subject to the international Minamata Convention on Mercury, which includes obligations to monitor and evaluate the effectiveness of emission reduction measures (UNEP 2013). Mercury is introduced to the atmosphere from both natural emissions (e.g., volcanoes, weathering of mercury-containing rock) and anthropogenic releases (e.g., coal combustion, metal mining and processing), as well as re-emission of previously deposited anthropogenic and natural sources (Streets et al., 2017, Amos et al., 2013). The relative contributions of these sources remain uncertain. Recent advances in mercury isotopes characterization have led to the development of techniques for identifying what these potential source contributions are. Mercury in the atmosphere exists in gaseous form as both Gaseous elemental mercury, GEM and Reactive Gaseous Mercury, RGM) and or it may bind with particulates of varying size (Particulate bound mercury, PHg). Measurements of reactive mercury and particulate bound mercury are difficult due to small concentration and uncertainties in measurement techniques.

As a pollutant of global concern, mercury has been measured at a variety of locations with substantial scientific effort directed toward remote regions susceptible to long-range atmospheric transport (Pirrone et al., 2010, Amos et al., 2013). Less attention has been paid to mercury's behaviour in urban air despite concentrations known to be elevated above typical background (Liu et al., 2007; Nie et al., 2020, Lynam & Keeler, 2006). Local emission sources, and the unique air flow patterns and terrain of the urban environment influence the dispersion and chemistry of atmospheric mercury. In the GTHA, mercury was detected near sources reporting to the NPRI though the quantitative relationships between reported emissions and measured ambient concentrations were not consistent (McLagan et al., 2018). The development of the commercially available mercury passive air sampler (MerPAS), that utilises a sulphur impregnated activated carbon as a sorbent for gaseous elemental mercury, allows for accurate measurement of GEM with greater spatial coverage and without the need for power or intensive infrastructure (Mclagan et al., 2016). Mercury passive air samplers will be deployed at six SWAPIT measurement sites to determine the spatial distribution of GEM across the GTA. They will additionally allow for assessing variability among the SWAPIT measurement locations

which represent different land uses and sources than the facility-directed measurements conducted by McLagan et al. (2018). Samplers will also be deployed up the CN tower to provide insight into the vertical distribution of mercury within the urban boundary layer. The MerPAS has also been identified as a suitable method for use in determining isotopic characterisation (Szponar et al., 2020), which will be used to determine local and regional sources of mercury and possible transformations the mercury has undergone with in the urban atmosphere and the spatial variability of these factors between the SWAPIT sites.

In addition to the passive sampling noted above, collocated measurements of speciated mercury in the gas and particle phases will be conducted adjacent to Highway 401 using two techniques, if possible. The purpose of these measurements is to determine how the combination of the urban environment and winter boundary conditions influence the speciation of mercury. Additionally, to understand if the use of road salt, ozone and OH radicals and winter meteorology produce similar chemical reactions to those observed in the High Arctic that cause the rapid conversion of GEM to RGM and PHg (Steffen et al., 2008). The first technique is using the Tekran 1130 and 1135 inlet system, which is a commercially available system for the separation, preconcentration and measurement of reactive and particulate mercury species, respectively. The second technique compares the results from two separate inlets that measure the total atmospheric mercury (high temperature pyrolyzer inlet) and gaseous elemental mercury (CEM filtered inlet), which can then be used to derive the sum of reactive and particulate mercury species. This new dual channel methodology has been field tested in Alert, NU, Canada, and similar systems have been used in aircraft measurements campaigns (Jaffe et al., 2014). The application of salts on road surfaces and high occurrence of particulates may be leading to localized mercury chemistry. The NAPS Toronto West site, with collocated mercury speciation measurements will help provide further proof of method and an understanding of how the urban environment influences atmospheric mercury's chemistry and behaviour.

Project 4.2: Connecting sources of microplastics and microfibers to their presence in air and aquatic systems (Lead: Liisa Jantunen, ECCC Air Quality Research Division; Collaborator: Miriam Diamond, University of Toronto)

Measuring microplastics in the atmospheric related samples is still an emerging field of investigation. Method comparisons in urban, urban highway, sub-urban, rural and agricultural land use areas have been underway for the last 2 years in anticipation of SWAPIT. Methods being compared are high-volume air sampling, bulk deposition (Nipher gauge and bottle and funnel), wet-only deposition and passive (slides with a sticky adhesive and moss bags) and have been deployed at four land use types. During SWAPIT the urban sites will expand to include High Park and Pearson International Airport. These data will be used to determine the best way to sample air for microplastics and how the different sampling approaches compare. These

results will be modeled to identify sources and the mechanisms of air transport and fate in support of mitigation strategy development.

Project 4.3: Satellite aerosol optical depth measurements to identify sources of urban aerosol (Lead: Chris Sioris, ECCC Air Quality Research Division)

Aerosol optical depth (AOD) measurements from MODIS (Moderate Resolution Imaging Spectroradiometer) and the Advanced Baseline Imager (ABI) on GOES (Geostationary Operational Environmental Satellite) will be used to identify urban sources of aerosol. The ABI AOD retrieval approach was designed for dark vegetation (Kaufman et al., 1997) and tends to struggle in urban areas where the relationship between surface reflectance in the visible and at 2 µm is quite different than over dark vegetation. The ABI AOD retrieval over land is essentially tuned to succeed over dark vegetation by exploiting this spectral relationship. Nevertheless, ABI has revealed aerosol hotspots near the intersection of the 401 and Don Valley Parkway and near Pearson airport. GOES AOD has 5 minute temporal resolution, which can be useful for tracking the movement of an aerosol plume back in time to its point of origin. Satellite aerosol measurements during the SWAPIT field intensive will be used to examine the spatial variability of PM. Results will be compared with other measurement and modelling techniques used during the SWAPIT campaign in order to increase certainty and identify potential improvements.

Project 4.4: Validating the vertical distribution of common air pollutants using Pandora at the CN Tower (Lead: Xiaoyi Zhao, ECCC Air Quality Research Division; Collaborators: Vitali Fioletov, Ihab Abboud, Jonathan Davies, Akira Ogyu, Reno Sit, and Sum Chi Lee, ECCC Air Quality Research Division)

High concentrations of total column and surface NO_2 in Toronto's downtown area were studied and reported (Zhao et al., 2020, 2022; Griffin et al., 2020). However, the vertical distribution of NO_2 and other air pollutants, such as HCHO, is still not well known. Alofted layers of air pollutants could have a strong impact on satellite and surface monitoring measurements' comparison and agreement (i.e., alofted pollutants can be detected by satellite column measurements, but could not be sampled by surface monitoring instruments). Moreover, previous work shows the agreement between remote sensing and GEM-MACH modelled surface NO_2 has a larger bias in the winter time, mostly due to modelling issues with boundary layer height in cold seasons (Zhao et al., 2019). This work will utilize Pandoras in downtown Toronto at different altitudes (310 m at CN Tower and 120 m at UTSG) to provide detailed vertical structure changes of air pollutants, to address these questions. The vertical profile and column observations of NO_2 and HCHO from other Pandora sites in the Toronto area will be used to provide the ground truth for satellite validation and verification work. We are aiming to improve the understanding of how to link satellite observations with nose-height level air quality.

Project 4.5: Evaluation of wintertime measurements from the newly-launched TEMPO satellite (Lead: Debora Griffin, ECCC Air Quality Research Division; Collaborators: Chris McLinden and Sumi Wren, ECCC Air Quality Research Division)

TEMPO (Zoogman et al., 2017) has recently been launched (April 7, 2023) with operational measurements anticipated to start in October 2023. Validation is crucial for new satellite instruments to determine the accuracy and precision of the observations. SWAPIT observations will be used to help validate TEMPO data, particularly its ability to capture spatial gradients through the GTA, as well as its ability to capture diurnally variation on timescales of one hour and shorter. This will be done by comparing TEMPO retrievals at both operational and SWAPIT-specific time resolutions to data from a combination of dense surface stations (including 6 Pandoras), multiple mobile platforms (including mobile MAX-DOAS), ground-based HCHO measurements (TILDAS – Tunable Infrared Laser Differential Absorption Spectrometer) and output from Canadian AQ models run at TEMPO pixel and sub-pixel resolution, 2.5 km to 250 m. Another important aspect of TEMPO validation relates to snow cover. Throughout the campaign period there will be intermittent snow cover which provides an excellent opportunity to evaluate the performance of TEMPO for snow/snow-free/mixed conditions.

Project 4.6: Non-Exhaust Vehicle Emissions and Representation in GEM-MACH (Lead: Ali Katal, ECCC Air Quality Research Division; Collaborators: Junhua Zhang, Craig Stroud and Samar Moussa, ECCC Air Quality Research Division)

As vehicle combustion emissions slowly decrease over time, non-combustion emissions are gaining in importance in terms of impact on air quality (volatile chemical products, non-combustion vehicle emissions). Air quality models must also adapt to the change in chemical speciation associated with these new emission types. ECCC PIRD developers are creating new emission inventories for volatile chemical products using the US EPA VCPy model. In this project, GEM-MACH emissions will be processed with this new inventory. The GEM-MACH chemical mechanism will also be updated to better represent oxygenated VOCs, long chain alkanes, windshield washer, tire and brake wear emissions. Dust emissions also need better constraints for urban land use as a function of recent and current meteorology. Road construction dust is a challenge to model as it is intermittent but can be important. Road salt emission estimates will be developed based on usage data provided by relevant municipal and provincial agencies.

Project 4.7: Aqueous Chemistry and Oxidative Potential in GEM-MACH (ARQI Lead: Alex Lupu, ECCC Air Quality Research Division; Collaborators: Craig Stroud, Kenjiro Toyota, Tom Harner and Amandeep Saini, ECCC Air Quality Research Division; Pourya Shahpoury, Health Canada and Trent University)

Heath studies have shown the importance of particle oxidative potential (OP) in $PM_{2.5}$ toxicity. Particle-phase oxidants can react with antioxidants on the human lung surface to form reactive

oxygen species (ROS). Incorporating the capability to model OP in GEM-MACH is timely to use and expand on the SWAPIT measurement data set and to address future needs. The GEM-MACH OP capability will build on observed correlations between OP and measured particle composition as well as on results of chemical box modelling and will have a basis in developing updates to modelled aqueous chemistry and the incorporation of OP-relevant trace metal components (Fe, Cu) in GEM-MACH.

Surface heterogeneous reactions will also be added to GEM-MACH. The surfaces in question include the cold built environment (with or without snow) and cold particle surfaces. Dry deposition of N_2O_5 can produce $ClNO_2$ and/or Cl_2 if the surface contains road salt. The yields of $ClNO_2$ and Cl_2 may depend on the acidity of the surface, ambient humidity (or the wetness of the surface), temperature and co-existent contaminants (organic compounds). Gaseous HCl and particulate chloride previously deposited to the surface may also be recycled via surface reactions associated with the dry deposition of N_2O_5. NO_2 surface reactions forming HONO and HNO_3 will also be assessed for urban surface and particle surfaces. All of these reactions contribute to the pool of radicals that are available in the atmosphere for promoting the formation of ozone and secondary particulate matter, and the relevance of these reactions may be unique to wintertime when OH radical production is reduced.

Project 4.8: Proof of concept for inverse emission modelling with GEM-MACH (Lead: Shuzhan Ren, ECCC Air Quality Research Division; Collaborators: Debora Griffin and Michael Sitwell, ECCC Air Quality Research Division)

The typical use of GEM-MACH simulates ambient pollutant concentrations based on emissions, meteorology, and atmospheric processes. The relationship between emissions and ambient concentrations can be summarized mathematically as a Hamiltonian operator, and that operator can be combined with measurements, preliminary emission maps, and a statistical method (Bayesian Inversion) to better refine the emissions estimates. The technique is best-suited to moderate to long-lived chemical species (CO_2, CH_4, CO, NO_x, BC, SO_2) with wintertime chemical lifetimes longer than ~6-hours at the urban scale. Measurements that are simultaneous, hourly and spatially distributed are most appropriate, and these can be from surface instrumentation or satellites as long as the satellite data are sensitive to surface layer concentrations. Based on available measurements from the SWAPIT field campaign, proof of concept of inverse emission modelling with GEM-MACH will be tested for CO, CH_4 and NO_x.

Project 4.9: Improvements to modelling of the boundary layer and deposition using GEM-MACH (Lead: Craig Stroud, ECCC Air Quality Research Division; Collaborators: Shuzhan Ren, Ali Katal, Paul Makar, Wanmin Gong, ECCC Air Quality Research Division; Sylvie Leroyer and Stéphane Belair, ECCC Meteorological Research Division)

GEM-MACH primary emitted pollutant predictions are highly sensitive to surface roughness layer meteorology (~ 100m). The most important parameter is vertical diffusivity. Winter as opposed to summer, and nighttime as opposed to daytime, can result in the concentration of

emitted pollutants near the surface. Chemical transport models typically use sub-grid scale mixing parameterizations as the model cannot resolve fine scale flow of turbulent eddies. The vertical measurements collected under SWAPIT will provide constraints when testing different mixing scheme parameterizations at the different model spatial scales for urban areas. For moderate to long-lived species, the boundary layer (BL) height is also important at providing a cap on mixing into the free troposphere. Recent versions of GEM have focused on improving BL height predictions. These will be assessed during SWAPIT to test whether they are sufficient for urban air quality predictions. Model results will be compared to LIDAR scans and gradients observed at the CN tower and ON MECP Resources Road.

Air pollutants are removed from the atmosphere by precipitation through two mechanisms: in-cloud condensation and below-cloud wash out. The precipitation phase state and cold cloud processes are important in determining wintertime wet deposition. Wintertime sulfate aerosol is currently overpredicted on regional scales. Cold season precipitation phase state can also be assessed with SWAPIT measurements. Recent cold season wet scavenging parameterizations, which are dependent on drop phase state, have been introduced into GEM-MACH and their importance on wintertime PM2.5 will be assessed using the data set collected during the SWAPIT field campaign.

Project 4.10: Evaluation of ultrafine particle modelling in GEM-MACH with MOSAIC (Lead: Ashu Dastoor, ECCC Air Quality Research Division; Collaborator: Kirill Semeniuk, ECCC Air Quality Research Division)

An updated particle nucleation scheme for GEM-MACH is being developed with MOSAIC (Model for Simulating Aerosol Interactions and Chemistry). Particle size distributions in the ultrafine mode (D<100 nm) will be compared to measurements from the SWAPIT field campaign to evaluate the accuracy of the new scheme.

Project 4.11: GEM-MACH model evaluation by source factors (Lead: Mahtab Majdzadeh, ECCC Air Quality Research Division; Collaborators: Craig Stroud, Kenjiro Toyota and Paul Makar, ECCC Air Quality Research Division)

Air quality models are often evaluated for summertime conditions due to the higher levels of oxidants compared to winter. Air quality models are also typically evaluated for generic categories like east versus west, or for an entire data set which hides offsetting biases. Positive matrix factorization (PMF) can separate air masses sampled at a location based on their source. GEM-MACH output for pollutant concentrations and particle size distributions will be evaluated against SWAPIT measurements that have been separated by source factors determined by PMF to identify model biases for certain source types. The model will also be evaluated for families of chemical species such as organic carbon, reactive chlorine, and reactive nitrogen. These quantities are better conserved and their relative fractional speciation can be assessed and compared to model output.

Project 4.12: Source sector apportionment using GEM-MACH (Lead: Craig Stroud, ECCC Air Quality Research Division, Collaborators: Junhua Zhang and Samar Moussa, ECCC Air Quality Research Division)

Source-specific tracers (e.g., residential wood combustion, volatile chemical products, food cooking) and their associated emission factors will be added to GEM-MACH along with their associated chemistry. By comparing model output to measurements conducted under SWAPIT, the magnitude of uncertainties in the underlying emission inventories will be determined. The model will subsequently be run to determine the impact of small emission reductions (e.g., 10%) to evaluate changes to source apportionment and end-point sensitivities (e.g. $PM_{2.5}$ changes).

Project 4.13: Evolution of horizontal resolution from 2.5 km to 250 m using GEM-MACH with the Town Energy Balance (TEB) (Lead: Craig Stroud, ECCC Air Quality Research Division; Collaborators: Paul Makar, Ali Katal, and Shuzhan Ren, ECCC Air Quality Research Division)

Chemical transport modelling continues to evolve to finer spatial resolutions in part to support the assessment of sources and impacts within urban areas (e.g., transportation sources such as rail yards, truck hubs, and airports, or inequities among neighbourhoods). Very high resolution models can resolve individual sources and provide improved emission estimates when using inverse modelling. SWAPIT data for a variety of air toxics (e.g., benzene, toluene, black carbon, metals) and for common air pollutants and greenhouse gases from cold-start vehicle measurements will be used to develop and evaluate 1) emission maps, 2) surface mixing schemes, and 3) high resolution land use maps able to capture changes in roughness length at 250 m horizontal resolution. The model development and evaluation will also assist in determining whether surface data assimilation for moisture and heat is necessary beyond the current finest resolution is 2.5 km.

Project 4.14: Improvements to wintertime physical processes in GEM at the urban scale (Lead: Sylvie Leroyer, ECCC Meteorological Research Division; Collaborators: Stéphane Bélair; ECCC Meteorological Research Division)

GEM uses surface data assimilation in order to apply realistic hydro-meteorological conditions such as snow fraction and soil moisture at the initial time but the current method is not fully adapted to urban areas. Data gathered during SWAPIT such as snow cover evolution photographs will be used to improve it. Surface and near-surface weather forecasting in GEM (including in TEB) such as air temperature, snow and water budgets over the different urban covers (streets, gardens, rooftops) will be assessed with measurements from the campaign leading to possible improvements related to modeling and surface data assimilation in

wintertime. These results will be analyzed considering the land-use characteristics in the models and in the data obtained through SWAPIT.

Outputs of Theme 4 – Science tool evaluation and improvement

- Improved ground-based measurement techniques for mercury and plastics
- Validated remote sensing measurements based on deployments of ground-based instruments at altitude or with novel satellite-based platforms
- New chemical transport capability for ultrafine particles, trace metals, and oxidative potential
- Enhanced chemical transport modelling using GEM-MACH based on improvements to the representation of winter emissions, aqueous chemistry, and deposition
- Proof of concept for inverse emission modelling using GEM-MACH
- Improved meteorological modelling with GEM based on improvements to representations of turbulence, planetary boundary layer height, and wintertime physical processes
- Increase in horizontal resolution from 2.5 km to 250 m for meteorological and chemical transport modelling using GEM and GEM-MACH, respectively

3: Results: Analysis, Integration, and Communication

SWAPIT will make substantial contributions to understanding the presence, sources, and impacts of the urban air pollutant mixture based on new data and linkages to ongoing efforts. Key to fulfilling the study's potential are straightforward access to data and the fostering of opportunities for collaboration among SWAPIT partners.

3.1: Data Acquisition and Management

The SWAPIT Steering Committee (see Appendix D) includes two leadership positions that oversee data issues. The first relates to data acquisition and the second to data management, though both work together closely. These data issues have been fundamental to SWAPIT planning since the study's outset when the list of sites and instruments was first developed and subsequently refined. Sharing of SWAPIT data is carried out on a free online platform for ease of access by study partners. That platform – the shared SWAPIT Google Drive - holds planning documents such as the evergreen project Gantt chart as well as presentations and recordings from workshops and the SWAPIT Science Talks.

Leading up to and during the 2024 SWAPIT field intensive, participants involved in conducting and supporting measurements will use BAND to communicate. BAND is free to use, and its app and browser versions are navigable from cell phones and computers. Messages regarding meteorological conditions and general sampling plans will be broadcast to all participants each day, and information sharing among participants connected to specific sites or platforms will occur through sub-group discussions on an "as needed" basis. An online Google Forms logging system will also be implemented to allow participants to report conditions, problems, and other relevant information that can be accessed by others to assist in revising sampling plans and interpreting data collected during the field campaign.

Data from measurements, model runs, and subsequent analyses will be shared using a multi-faceted approach. During the field campaign and for a limited time afterward, each investigator in charge of a sampler, instrument, inventory, model or other data set will share data (or a link to data held by programs external to SWAPIT) through a dedicated folder on the SWAPIT Google Drive to which partners will have read-only access. For data produced by ECCC instruments, long-term internal data storage is available with back-up capability. This mechanism is not available for data external to ECCC, and alternative storage methods are being identified. A final data archive will be made available through ECCC's Open Data Portal for use by the broader scientific community and interested public.

3.2: Data Analysis and Integration

SWAPIT results can be viewed as a collection of outputs that arise from the overall characterisation data set described in Section 2.3 (Theme 1) and the science activities described in Sections 2.4-2.6 (Themes 2-4). Activities were developed to bridge relevant knowledge gaps as identified in the scientific literature and using tools and resources available to SWAPIT partners.

Those ideas and plans aim to make numerous novel contributions, with many collaborating scientists associated with more than one science activity. Though such plans are based on expert opinion, uncertainty is inherent due to the impossibility of knowing *a priori* what study observations will reveal and what the state of available resources will be in subsequent years. In order to prioritize data analysis and integration activities, SWAPT partners will be engaged through a series of themed workshops to be held in the years following the 2024 intensive field campaign. These workshops will gather relevant experts to determine how joint science activities should move forward to contribute novel findings within available resource constraints.

Workshop topics to be explored include

- Sharing samples for chemical and toxicological analyses
- Delivering an authoritative ambient observation data set for individual and combined air pollutant concentrations
- Linking ambient air, deposition, and terrestrial/aquatic systems through SWAPIT data
- Supplying observed source-specific emission factors, ratios, and profiles to inventory developers and documenting resulting inventory improvements
- Using the SWAPIT data set for a comprehensive multi-factor evaluation of GEM-MACH
- Prioritising process improvements to GEM and GEM-MACH including comparison to pre-SWAPIT performance
- Prioritising GEM-MACH runs for source apportionment and emissions scenarios
- Conducting epidemiological analyses for acute and chronic exposure estimates from ambient observations, model output, or new exposure surfaces using land use regression or other techniques
- Preparing omnibus publications on key multi-component and cross-disciplinary topics (e.g., representing vertical mixing in urban areas; particulate matter composition and sources across the size spectrum, etc.)

3.3: Communication of Results

SWAPIT communications will aspire to a standard no lower than excellent, and seek to reach the scientific community, clients and stakeholders, and the general public.

For the scientific community, excellence will entail publication of peer-reviewed articles in high-quality journals that are reputable and not affiliated with publishers who engage in predatory

practices. Open access publishing is encouraged whenever possible whereas "salami" publishing (viz., splitting results across multiple papers to inflate publication statistics) is discouraged for financial and ethical reasons. Presentation of results at high-quality academic conferences is also encouraged as a means of communicating with the scientific community. Plans are underway for special sessions at meetings of the American Geophysical Union (AGU) and the Society for Environmental Toxicology and Chemistry (SETAC), and further opportunities for dissemination of scientific results will be identified by collaborating scientists.

For communications to clients, stakeholders, and the general public, a formal Communications Plan is under development by ECCC and will include consultation with partner organizations. Once complete, the plan will be available on the shared SWAPIT Google Drive.

3.4: Applicability to Other Locations

Toronto is Canada's largest city with a population expected to reach 10 million by 2046 (Ontario, 2022). Though this provides a solid justification for selecting Toronto as the site of ECCC's first integrated urban air pollution study, the location was chosen in part because of the air quality research capacity that is present there among the federal and provincial governments and local universities. This choice was rooted in practical considerations, not least of which was minimising study costs. Nonetheless, SWAPIT efforts beyond the 2024 field campaign will aim to ensure that new knowledge and enhanced science tools serve the improvement of air quality in other urban areas of Canada and elsewhere.

Recent amendments to the Canadian Environmental Protection Act (CEPA) enshrine the right to a healthy environment, and the forthcoming implementation framework will account for the consideration of principles such as environmental justice and intergenerational equity (Canada, 2023). Though implementation will not be a scientific research activity, it will require credible scientific information and tools to support it. The outcomes of SWAPIT – including new ways to represent the air pollutant mixture and the fine-scale variations of its impacts across urban areas – are aligned with the scientific needs associated with delivering on the commitments of the amended CEPA at locations beyond Toronto and the GTHA.

Acknowledgements

Pollution – as a pillar of the triple planetary threat and an indicator of societal disparities – continues to cause concern. Much progress has been made by using a pollutant-by-pollutant approach to study and manage environmental pollution, yet the impact of real-world pollutant mixtures is a growing preoccupation. It is within this context that SWAPIT was born. By no means having all the answers, SWAPIT is nonetheless advancing the shift required to address the complexities associated with air pollution in cities. Such advances are never easy or tidy, and the combined efforts of a great number of people were needed to develop this first-generation attempt at tackling urban air pollution science in Canada.

The managers of ECCC's Air Quality Processes Research Section have been pivotal to SWAPIT's development, from the initial approval and support of the study by Stewart Cober to the tireless vision translation and team-building of Alexandra (Sandy) Steffen to the ongoing practical supports facilitated by Kathy Hayden. Rosa Wu, manager of ECCC's Modelling and Integration Research Section, was an early supporter of the study's goals and vision, and she provided helpful strategic advice for moving the study forward amid initial uncertainties about its scope and approach. Zoe Davis, Matt Cooper and Matt Parsons in ECCC's Air Quality Program Office also provided valuable advice and context to support SWAPIT's goals.

The SWAPIT leadership team, including the Steering Committee as well as the leads for fixed sites and mobile platforms, has proven itself repeatedly with accomplishments that have been both grounded and creative. The team was formed in part with the goals of improving representation by women and giving leadership experience to younger staff. Both groups have convincingly demonstrated their worth alongside seasoned male colleagues who openly shared their expertise.

As valuable as management support and leadership have been, SWAPIT is ultimately a collaboration of scientific and technical experts. Over ninety such experts from several government agencies and nine universities have agreed to share measurements, data and interpretation under the SWAPIT banner despite no formal mandate or budget. This is a remarkable outcome and demonstrates how stepping outside the status quo can pay enormous dividends.

Special thanks to Yushan Su and Chris Charron for facilitating measurements at the Ontario Ministry of the Environment, Conservation and Parks site at Resources Road. We are also deeply grateful to High Park, the Evergreen Brickworks, the University of Toronto Scarborough, and the CN Tower for entertaining the idea of sampling at their sites, and to Josée Lafontaine for her efforts in drafting agreements with our partners.

References

Alves C.A. et al. (2016) Polycyclic aromatic hydrocarbons (PAHs) and their derivatives (oxygenated-PAHs, nitrated-PAHs and azaarenes) in size-fractionated particles emitted in an urban road tunnel. Atm. Res. 180:128–137.

Amos, H. M., Jacob, D. J., Streets, D. G., & Sunderland, E. M. (2013). Legacy impacts of all-time anthropogenic emissions on the global mercury cycle. *Global Biogeochemical Cycles*, *27*(2), 410–421. https://doi.org/10.1002/gbc.20040

Ars, S., Vogel, F., Arrowsmith, C., Heerah, S., Knuckey, E., Lavoie, J., Lee, C., Mostafavi Pak, N., Phillips, J.L., Wunch, D. (2020) Investigation of the Spatial Distribution of Methane Sources in the Greater Toronto Area Using Mobile Gas Monitoring Systems. Environ. Sci. Technol. 54:15671-15679.

Bandowe, B.A.M., Meusel, H., Huang, R.-J., Ho, K., Cao, J., Hoffmann, T., Wilcke, W., 2014. PM2.5-bond oxygenated PAHs, nitro-PAHs and parent-PAHs from the atmosphere of a Chinese megacity: seasonal variation, sources and cancer risk assessment. Sci. Total Environ. 473, 77-87.

A. Beji, K. Deboudt, S. Khadari, B. Muresan, P. Flament, M. Fourmentin, L. Lumière (2020) Non-exhaust particle emissions under various driving conditions: Implications for sustainable mobility, Transportation Research Part D: Transport and Environment, (81) 102290

Berthiaume A. 2021. Use of the National Pollutant Release Inventory in environmental research: a scoping review. Environmental Reviews. 293 doi: https://doi.org/10.1139/er-2020-0122

Bond, T. C.; Doherty, S. J.; Fahey, D. W.; Forster, P. M.; Berntsen, T.; Deangelo, B. J.; Flanner, M. G.; Ghan, S.; Kä rcher, B.; Koch, D.; Kinne, S.; Kondo, Y.; Quinn, P. K.; Sarofim, M. C.; Schultz, M. G.; Schulz, M.; Venkataraman, C.; Zhang, H.; Zhang, S.; Bellouin, N.; Guttikunda, S. K.; Hopke, P. K.; Jacobson, M. Z.; Kaiser, J. W.; Klimont, Z.; Lohmann, U.; Schwarz, J. P.; Shindell, D.; Storelvmo, T.; Warren, S. G.; Zender, C. S. Bounding the Role of Black Carbon in the Climate System: A Scientific Assessment. J. Geophys. Res. Atmos. 2013, 118 (11), 5380−5552.

Canada (1999) Canadian Environmental Protection Act 1999 S.C. 1999, c 33. Retrieved on 05 05, 2023 from: https://laws-lois.justice.gc.ca/eng/acts/c-15.31/

Canada. (2023) National Air Pollution Surveilance (NAPS) program, https://www.canada.ca/en/environment-climate-change/services/air-pollution/monitoring-networks-data/national-air-pollution-program.html.

Canada (2023) Bill S-5: Strengthening environmental protection for a healthier Canada act. https://www.canada.ca/en/environment-climate-change/news/2023/06/bill-s-5-strengthening-environmental-protection-for-a-healthier-canada-act.html; last accessed 2023-06-26.

CCME (Canadian Council of Ministers of the Environment). (2022) Air. https://ccme.ca/en/current-activities/air; last accessed 2022-Nov-04.

Chen, D., Huey, L. G., Tanner, D. J., Li, J., Ng, N. L., and Wang, Y. (2017) Derivation of Hydroperoxyl Radical Levels at an Urban Site via Measurement of Pernitric Acid by Iodide Chemical Ionization Mass Spectrometry, Environ. Sci. Technol., 51: 3355-3363, 10.1021/acs.est.6b05169, 2017.

Chen, Q., Edebeli, J., McNamara, S. M., Kulju, K. D., May, N. W., Bertram, S. B., Thanekar, S., Fuentes, J. D., Pratt, K. A. (2019) HONO, particulate nitrite, and snow nitrite at a midlatitude urban site during wintertime, ACS Earth Space Chem., 3: 811 – 822.

Cheng, Y. et al. (2019) Size-segregated emission factors and health risks of PAHs from residential coal flaming/smoldering combustion. *Environ. Sci. Pollut. Res*. 26:31793 - 31803.

Coggon, M. M., G. I. Gkatzelis, B. C. McDonald, J. B. Gilman, R. H. Schwantes, N. Abuhassan, K. C. Aikin, M. F. Arend, T. A. Berkoff, S. S. Brown, T. L. Campos, R. R. Dickerson, G. Gronoff, J. F. Hurley, G. Isaacman-VanWertz, A. R. Koss, M. Li, S. A. McKeen, F. Moshary, J. Peischl, V. Pospisilova, X. Ren, A. Wilson, Y. Wu, M. Trainer and C. Warneke (2021). "Volatile chemical product emissions enhance ozone and modulate urban chemistry." Proceedings of the National Academy of Sciences **118**(32): e2026653118.

Coggon, M. M., B. C. McDonald, A. Vlasenko, P. R. Veres, F. Bernard, A. R. Koss, B. Yuan, J. B. Gilman, J. Peischl, K. C. Aikin, J. DuRant, C. Warneke, S.-M. Li and J. A. de Gouw (2018). "Diurnal Variability and Emission Pattern of Decamethylcyclopentasiloxane (D5) from the Application of Personal Care Products in Two North American Cities." Environmental Science & Technology **52**(10): 5610-5618.

Dąbek- Złotorzyńska, E., Dann, T. F., Martinelango, P. K., Celo, V., Brook, J. R., Mathieu, D., Ding, L., Austin, C. C. (2011) Canadian National Air Pollution Surveillance (NAPS) PM2.5 speciation program: Methodology and PM2.5 chemical composition for the years 2003 – 2008. Atmos. Environ., 43 (3), 673 – 686. https://www.sciencedirect.com/science/article/pii/S135223101000899X?via%3Dihub

Decesari, S., Sowlat, M. H., Hasheminassab, S., Sandrini, S., Gilardoni, S., Facchini, M. C., et al. (2017). Enhanced toxicity of aerosol in fog conditions in the Po Valley, Italy. Atmospheric Chemistry and Physics, 17(12), 7721–7731. https://www.atmos-chem-phys.net/17/7721/2017/.

Decina, Stephen M., Lucy R. Hutyra, and Pamela H. Templer (2020). Hotspots of nitrogen deposition in the world's urban areas: a global data synthesis. *Frontiers in Ecology and the Environment* 18.2: 92-100.

Deguillaume, L., Leriche, M., Desboeufs, K., Mailhot, G., George, C., & Chaumerliac, N. (2005). Transition metals in atmospheric liquid phases: Sources, reactivity, and sensitive parameters. Chemical Reviews, 105(9), 3388–3431. https://doi.org/10.1021/cr040649c.

DeMaio, L. and M. Corn. (1966) Polynuclear aromatic hydrocarbons associated with particulates in Pittsburgh air. *J. Air Poll. Control Assoc.* 16:67-71.

Domingo, J. L.; Nadal, M. Human exposure to per- and polyfluoroalkyl substances (PFAS) through drinking water: A review of the recent scientific literature. Environ. Res. 2019, 177, 108648.

Ervens, B., Sorooshian, A., Aldhaif, A. M., Shingler, T., Crosbie, E., Ziemba, L., Campuzano-Jost, P., Jimenez, J. L., and Wisthaler, A.: Is there an aerosol signature of chemical cloud processing?, Atmos. Chem. Phys., 18, 16099–16119, https://doi.org/10.5194/acp-18-16099-2018, 2018.

Evangeliou, N.; Grythe, H.; Klimont, Z.; Heyes, C.; Eckhardt, S.; Lopez-Aparicio, S.; Stohl, A., Atmospheric transport is a major pathway of microplastics to remote regions. Nature Communications 2020, 11, (1), 3381.

Feng, Y.; Ramanathan, V.; Kotamarthi, V. R. Brown Carbon: A Significant Atmospheric Absorber of Solar Radiation. Atmos. Chem. Phys. 2013, 13 (17), 8607−8621.

Franz, T.P., Eisenreich, S.J. 1998. Snow scavenging of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in Minnesota. Environ. Sci. Technol., 32:1771-1778, 10.1021/es970601z

Fussell, J. C.; Franklin, M.; Green, D. C.; Gustafsson, M.; Harrison, R. M.; Hicks, W.; Kelly, F. J.; Kishta, F.; Miller, M. R.; Mudway, I. S.; Oroumiyeh, F.; Selley, L.; Wang, M.; Zhu, Y., A Review of Road Traffic-Derived Non-Exhaust Particles: Emissions, Physicochemical Characteristics, Health Risks, and Mitigation Measures. Environ.Sci.Technol. 2022, 56, (11), 6813-6835.

Gaga, E.O., Harner, T., Dąbek- Złotorzyńska, E., Celo, V., Evans, G., Jeong, C-H., Halappanavar, S., Jariyasopit, N., Su, Y. Polyurethane Foam (PUF) Disk Samplers for Measuring Trace Metals in Ambient Air. Environ. Sci. Technol. Letters 2019, 6, 545-550.

Galarneau, E., Makar, P.A., Zheng, Q., Narayan, J., Zhang, J., Moran, M.D., Bari, M.A., Pathela, S., Chen, A., Chlumsky, R. (2014) PAH concentrations simulated with the AURAMS-PAH chemical transport model over Canada and USA. Atmos. Chem. Phys. 14:4065-4077.

Galarneau, E., Hollebone, B.P., Yang, Z. and Schuster, J., 2014. Preliminary measurement-based estimates of PAH emissions from oil sands tailings ponds. Atmospheric Environment, 97: 332-335.

Galarneau, E. et al., 2016. Air toxics in Canada measured by the National Air Pollution Surveillance (NAPS) program and their relation to ambient air quality guidelines. Journal of the Air & Waste Management Association, 66(2): 184-200.

Galarneau, E. (2021) Polycyclic aromatic compounds in the Canadian environment: overview of results and knowledge gaps from the special issue. *Environ. Pollut.* **285**:117607.

Giang, A, Castellani, K. (2020) Cumulative air pollution indicators highlight unique patterns of injustice in urban Canada. *Environ. Res. Lett.* **15**:124063.

Gkatzelis, G. I., M. M. Coggon, B. C. McDonald, J. Peischl, K. C. Aikin, J. B. Gilman, M. Trainer and C. Warneke (2021). "Identifying Volatile Chemical Product Tracer Compounds in U.S. Cities." Environmental Science & Technology **55**(1): 188-199.

Gkatzelis, G. I., M. M. Coggon, B. C. McDonald, J. Peischl, J. B. Gilman, K. C. Aikin, M. A. Robinson, F. Canonaco, A. S. H. Prevot, M. Trainer and C. Warneke (2021). "Observations Confirm that Volatile Chemical Products Are a Major Source of Petrochemical Emissions in U.S. Cities." Environmental Science & Technology **55**(8): 4332-4343.

Gkatzelis, G. I., M. M. Coggon, B. C. McDonald, J. Peischl, K. C. Aikin, J. B. Gilman, M. Trainer and C. Warneke (2021). "Identifying Volatile Chemical Product Tracer Compounds in U.S. Cities." Environmental Science & Technology **55**(1): 188-199.

Gordon, M., Staebler, R. M., Liggio, J., Makar, P. A., Li, S.-M., Wentzell, J., Lu, G., Lee, P., and Brook, J. R.: Measurements of enhanced turbulent mixing near highways, J. Appl. Meteorol. Clim., 51, 1618–1632, 2012.

Government of Canada. 2022. Canada Gazette, Part I, Volume 156, Number 7: Supplements - Notice with respect to the substances in the National Pollutant Release Inventory for 2022, 2023 and 2024. Retrieved 08 11, 2022, from https://www.gazette.gc.ca/rp-pr/p1/2022/2022-02-12/html/sup1-eng.html

Government of Canada. 2022. Explore National Pollutant Release Inventory data. Retrieved 08 12, 2022, from https://www.canada.ca/en/environment-climate-change/services/national-pollutant-release-inventory/tools-resources-data/exploredata.html

Griffin, D., McLinden, C. A., Racine, J., Moran, M. D., Fioletov, V., Pavlovic, R., Mashayekhi, R., Zhao, X., and Eskes, H.: Assessing the Impact of Corona-Virus-19 on Nitrogen Dioxide Levels

over Southern Ontario, Canada, Remote Sens., 12, 4112, https://doi.org/10.3390/rs12244112, 2020.

Gultepe, I., Tardif, R., Michaelides, S.C., Cermak, J., Bott, A., Bendix, J., Müller, M.D., Pagowski, M., Hansen, B., Ellrod, G., Jacobs, W., Toth, G., Cober, S.G. (2007). Fog Research: A Review of Past Achievements and Future Perspectives. Pure appl. geophys. 164, 1121–1159. https://doi.org/10.1007/s00024-007-0211-x

Halappanavar, S., Wu, D., Boyadzhiev, A., Solorio-Rodriguez, S., Williams, A., Jaroyasopit, N., Saini, A., Harner, T. Toxicity screening of air extracts representing different source sectors in the city of Toronto: In vitro oxidative stress, pro-inflammatory response, and toxicogenomic analysis. Mutation Research - Genetic Toxicology and Environmental Mutagenesis 2021, 872, 503415.

Hansen, B., I. Gultepe, P. King, G. Toth, and C. Mooney, 2007: Visualization of seasonal-diurnal climatology of visibility in fog and precipitation at Canadian airports. Preprints, 16th Conf. on Applied Climatology, San Antonio, TX, Amer. Meteor. Soc., P1.3. [Available online at http://ams.confex.com/ams/87ANNUAL/techprogram/paper_117973.htm.] https://collaboration.cmc.ec.gc.ca/science/arma/climatology/

Haskins, J. D. et al., (2019) Anthropogenic control over wintertime oxidation of atmospheric pollutants, Geophys. Res. Lett., 46: 14826 – 14835.

Healy, R.M., Sofowote, U., Su, Y., Debosz, J., Noble, M., Jeong, C.-H., Wang, M., Hilker, N., Evans, G.J., Doerksen, G., Jones, K., Munoz, A. (2017) Ambient measurements and source apportionment of fossil fuel and biomass burning black carbon in Ontario. Atmos. Environ. 161:34-47.

Horak et al. (2017) PAH emissions from old and new types of domestic hot water boilers. Environ. Pollut. 225:31-39.

Itahashi, S.; Yamaji, K.; Chatani, S.; Hayami, H.: Refinement of Modeled Aqueous-Phase Sulfate Production via the Fe- and Mn-Catalyzed Oxidation Pathway. Atmosphere 2018, 9, 132. https://doi.org/10.3390/atmos9040132

Jaffe DA, Ambrose JL, Gratz L, Jaegle L, Shah V, Selin NE, Song S, Giang A. Aircraft Observations of Mercury over the US: The Nomadss Experiment. InAGU Fall Meeting Abstracts 2014 Dec (Vol. 2014, pp. B52B-02).

Jariyasopit, N., Tung, P., Su, K., Halappanavar, S., Evans, G.J., Su, Y., Khoomrung, S., Harner, T. Polycyclic aromatic compounds in urban air and associated inhalation cancer risks: A case study targeting distinct source sectors. Environmental Pollution 2019, 252, 1882-1891.

Jeong, C.-H., Traub, A., Huang, A., Hilker, N., Wang, J. M., Herod, D., Dąbek- Złotorzyńska, E., Celo, V. and Evans, G. J.: Long-term analysis of PM2.5 from 2004 to 2017 in Toronto: Composition, sources, and oxidative potential. 2020. Environ. Pollut., 263, 114652.

Joe, P., and Coauthors, 2018: The Environment Canada Pan and Parapan American Science Showcase Project. Bull. Amer. Meteor. Soc., 99, 921–953, https://doi.org/10.1175/BAMS-D-16-0162.1.

Kasthuriarachchi, N. Y.; Rivellini, L. H.; Adam, M. G.; Lee, A. K. Y., Light Absorbing Properties of Primary and Secondary Brown Carbon in a Tropical Urban Environment. Environmental Science and Technology 2020, 54, (17), 10808-10819.

Kelly, E.N., Schindler, D.W., Hodson, P.V., Short, J.W., Radmanovich, R., Nielsen, C.C., 2010. Oil sands development contributes elements toxic at low concentrations to the Athabasca River and its tributaries. Proc. Natl. Acad. Sci. U. S. A. 107 (37), 16178–16183. https://doi.org/10.1073/pnas.10087541

Kelly, K. E., Kotchenruther, R., Kuprov, R., Silcox, G. D. (2013) Receptor model source attributions for Utah's Salt Lake City airshed and the impacts of wintertime secondary ammonium nitrate and ammonium chloride aerosol. Journal of the Air & Waste Management Association, 63(5):575–590

Khare, P. and D. R. Gentner (2018). "Considering the future of anthropogenic gas-phase organic compound emissions and the increasing influence of non-combustion sources on urban air quality." Atmos. Chem. Phys. **18**(8): 5391-5413.

Khare, P., J. E. Krechmer, J. E. Machesky, T. Hass-Mitchell, C. Cao, J. Wang, F. Majluf, F. Lopez-Hilfiker, S. Malek, W. Wang, K. Seltzer, H. O. T. Pye, R. Commane, B. C. McDonald, R. Toledo-Crow, J. E. Mak and D. R. Gentner (2022). "Ammonium adduct chemical ionization to investigate anthropogenic oxygenated gas-phase organic compounds in urban air." Atmos. Chem. Phys. **22**(21): 14377-14399.

Johannessen, C., Liggio, J., Zhang, X., Saini, A., Harner, T. Composition and transformation chemistry of tire-wear derived organic chemicals and implications for air pollution. Atmospheric Pollution Research 2022, 13, 101533.

Johannessen, C., Saini, A., Zhang, X., Harner, T. Air monitoring of tire-derived chemicals in global megacities using passive samplers. *Environmental Pollution* 2022b, 314, 120206.

Johannessen. C., Saini, A., Zhang, X., Harner, T. Screening study of tire-derived organic chemicals in urban air at the source-sector scale. 2023 (In Preparation)

Kaufman, Y.J., Andrew E. Wald, Lorraine A. Remer, Bo-Cai Gao, Rong-Rong Li, and Luke Flynn (1997) The MODIS 2.1- m Channel—Correlation with Visible Reflectance for Use in Remote Sensing of Aerosol. IEEE Trans. Geosci. Remote Sens. 35:1286-1298.

Knudtzon, N. C.; Thorstensen, H., Ruus, A., Helberg, M., Bæk, K., Enge, E. K., Borgå, K. Human exposure to per- and polyfluoroalkyl substances (PFAS) through drinking water: A review of the recent scientific literature. Environ. Int. 2021, 152, 106478

Kolesar, K. R., Mattson, C. N., Peterson, P. K., May, N. W., Prendergast, R. K., Pratt, K. (2018) Increases in wintertime PM2.5 sodium and chlorine linked to snowfall and road salt application. Atmos. Environ., 177: 195 – 202.

Lei, Ying D., Wania, F. (2004) Is rain or snow a more efficient scavenger of organic chemicals?, Atmospheric Environment, Volume 38, Issue 22, 2004, Pages 3557-3571, ISSN 1352-2310, https://doi.org/10.1016/j.atmosenv.2004.03.039.

Lelieveld, S., Wilson, J., Dovrou, E., Mishra, A., Lakey, P. S. J., Shiraiwa, M., Pöschl, U. and Berkemeier, T.: Hydroxyl Radical Production by Air Pollutants in Epithelial Lining Fluid Governed by Interconversion and Scavenging of Reactive Oxygen Species. 2021, Environ. Sci. Technol., 55, 14069–14079.

Leroyer, S., Bélair, S., Souvanlasy, V., Vallée, M., Pellerin, S., & Sills, D. (2022). Summertime Assessment of an Urban-Scale Numerical Weather Prediction System for Toronto. *Atmosphere*, *13*(7), 1030. https://doi.org/10.3390/atmos13071030

Li, S..-M., Leithead, A., Moussa, S.G., Liggio, J., Moran, M.D., Wang, D., Hayden, K., Darlington, A., Gordon, M., Staebler, R., Makar, P.A., Stroud, C.A., McLaren, R., Liu, P.S.K., O'Brien, J., Mittermeier, R.L., Zhang, J., Marson, G., Cober, S.G., Wolde, M., Wentzell, J.J.B. (2017) Differences between measured and reported volatile organic compound emissions from oil sands facilities in Alberta, Canada. PNAS 114:E3756-E3765

Li, W. L.; Ma, W. L.; Zhang, Z. F.; Liu, L. Y.; Song, W. W.; Jia, H. L.; Ding, Y. S.; Nakata, H.; Minh, N. H.; Sinha, R. K.; Moon, H. B.; Kannan, K.; Sverko, E.; Li, Y. F. Occurrence and Source Effect of Novel Brominated Flame Retardants (NBFRs) in Soils from Five Asian Countries and Their Relationship with PBDEs. Environ. Sci. Technol. 2017, 51, 11126-11135.

Liggio, J., Li, S.-M., Staebler, R.M., Hayden, K., Darlington, A., Mittermeier, R.L., O'Brien, J., McLaren, R., Wolde, M., Worthy, D., Vogel, F. (2019) Measured Canadian oil sands CO_2 emissions are higher than estimates made using internationally recommended methods. Nature Communications 10:1863.

Liu, Q., Li., L., Zhang, X., Saini, A., Li, W., Hung, H., Hao, C., Li, K., Lee, P., Wentzell, J.J.B., Huo, C., Li., S-M., Harner, T., and Liggio, J. Uncovering global-scale risks from commercial chemicals in air. Nature 2021, 600, 457-461.

Lyapustin, A., Y. Wang, I. Laszlo, R. Kahn, S. Korkin, L. Remer, R. Levy, and J. S. Reid (2011), Multiangle implementation of atmospheric correction (MAIAC): 2. Aerosol algorithm, J. Geophys. Res., 116, D03211, doi:10.1029/2010JD014986.

Lynam MM, Keeler GJ. Source–receptor relationships for atmospheric mercury in urban Detroit, Michigan. Atmospheric Environment. 2006 Jun 1;40(17):3144-55.

Makar, P. A., Stroud, C., Akingunola, A., Zhang, J., Ren, S., Cheung, P., and Zheng, Q.: Vehicle-induced turbulence and atmospheric pollution, Atmos. Chem. Phys., 21, 12291–12316, https://doi.org/10.5194/acp-21-12291-2021, 2021.

McDonald, B. C., J. A. de Gouw, J. B. Gilman, S. H. Jathar, A. Akherati, C. D. Cappa, J. L. Jimenez, J. Lee-Taylor, P. L. Hayes, S. A. McKeen, Y. Y. Cui, S.-W. Kim, D. R. Gentner, G. Isaacman-VanWertz, A. H. Goldstein, R. A. Harley, G. J. Frost, J. M. Roberts, T. B. Ryerson and M. Trainer (2018). "Volatile chemical products emerging as largest petrochemical source of urban organic emissions." Science **359**(6377): 760-764.

McLagan D S, Mitchell C P J, Huang H, Lei Y D, Cole A S, Steffen A, Hung H and Wania F. 2016. A high-precision passive air sampler for gaseous mercury Environ. Sci. Technol. Lett. 3 24–9

McLinden, C.A., [1,2], Cristen L F Adams[3], Vitali Fioletov[1], Debora Griffin[1], Paul A Makar[1], Xiaoyi Zhao[1], Andrew Kovachik[1,4], Nolan Dickson[1,4], Cassandra Brown[3], Nicolay Krotkov[5], Can Li[5,6], Nicolas Theys[7], Pascal Hedelt[8] and Diego G Loyola[8] (2020) Inconsistencies in sulfur dioxide emissions from the Canadian oil sands and potential implications. *Environ. Res. Lett.* **16** 014012.

McNamara. S. M. et al. (2020) Observation of road salt aerosol driving inland wintertime atmospheric chlorine chemistry, ACS Cent. Sci., 6: 684 – 694.

Meyer, T., Wania, F. 2008. Organic contaminant amplification during snowmelt. Water Res., 42: 1847-1865, 10.1016/j.watres.2007.12.016

Meyer, T., Wania, F. 2011. Modeling the elution of organic chemicals from a melting homogeneous snow pack. Water Res., 45:3627-3637, 10.1016/j.watres.2011.04.011

Moussa, S.G., Staebler, R.M., You, Y., Leithead, A., Yousif, M.A., Brickell, P., Beck, J., Jiang, Z., Liggio, J., Li, S.-M., Wren, S.N., Brook J.R., Darlington, A., Cober, S.G. (2021) Fugitive Emissions of Volatile Organic Compounds from a Tailings Pond in the Oil Sands Region of Alberta. E*nviron. Sci. Technol.* 55:12831–12840.

Nazarenko, Y., Fournier, S., Kurien, U, Rangel-Alvarado, R.B., Nepotchatykh, O., Seers, P., Ariya, P.A. 2017. Role of snow in the fate of gaseous and particulate exhaust pollutants from gasoline-powered vehicles. Environmental Pollution 223: 665-675. https://doi.org/10.1016/j.envpol.2017.01.082

Offenberg, J.H., Baker, J.E. (1999) Aerosol size distributions of polycyclic aromatic hydrocarbons in urban and over-water atmospheres. *Environ. Sci. Technol.* 33:3324-3331.

Ontario (2022) Ontario population projections. https://www.ontario.ca/page/ontario-population-projections; last accessed 2022-Nov-04.

Organisation for Economic Cooperation and Development. 2013. Test no. 236: Fish embryo acute toxicity (FET) test. OECD Publishing.

Organisation for Economic Cooperation and Development. 2021. Using PRTR Information to Evaluate Progress Towards the Sustainable Development Goal 12, OECD Series on Pollutant Release and Transfer Registers, No. 25, OECD Publishing, Paris. Retrieved on 8 December 2021 from https://www.oecd.org/chemicalsafety/pollutant-release-transfer-register/using-prtr-information-evaluate-progress-towards-sustainable-development-goal-12.pdf

Parajulee, A.; Wania, F. (2014) Evaluating officially reported polycyclic aromatic hydrocarbon emissions in the Athabasca oil sands region with a multimedia fate model. *PNAS* DOI: 10.1073/pnas.1319780111.

Pirrone N, Cinnirella S, Feng X, Finkelman RB, Friedli HR, Leaner J, Mason R, Mukherjee AB, Stracher GB, Streets DG, Telmer K. Global mercury emissions to the atmosphere from anthropogenic and natural sources. Atmospheric Chemistry and Physics. 2010 Jul 2;10(13):5951-64.

Pistikopoulos, P., H.M. Wortham, L. Gomes, S. Masclet-Beyne, E. Bon Nguyen, P.A. Masclet and G. Mouvier. (1990) Mechanisms of formation of particulate polycyclic aromatic hydrocarbons in relation to the particles size distribution: effects on meso-scale transport. *Atmos. Environ.* **24A**:2573-2584.

Prosser RS, Parrott JL, Galicia M, Shires K, Sullivan C, Toito J, Bartlett AJ, Milani D, Gillis PL, Balakrishnan VK. 2017. Toxicity of sediment-associated substituted phenylamine antioxidants on the early life stages of Pimephales promelas and a characterization of effects on freshwater organisms. Environmental Toxicology Chemistry 36: 2730−2738. DOI: 10.1002/etc.3828

Qin, M., B. N. Murphy, K. K. Isaacs, B. C. McDonald, Q. Lu, S. A. McKeen, L. Koval, A. L. Robinson, C. Efstathiou, C. Allen and H. O. T. Pye (2021). "Criteria pollutant impacts of volatile chemical products informed by near-field modelling." Nature Sustainability **4**(2): 129-137.

Radke, L.F., Hobbs, P.V., Eltgroth, M.W. 1980. Scavenging of aerosol particles by precipitation. J. Appl. Meteorol., 19:715-722, 10.1175/1520-0450(1980)019<0715:SOAPBP>2.0.CO;2

Rivellini, L. H.; Adam, M. G.; Kasthuriarachchi, N.; Lee, A. K. Y., Characterization of carbonaceous aerosols in Singapore: Insight from black carbon fragments and trace metal ions detected by a soot particle aerosol mass spectrometer. Atmospheric Chemistry and Physics 2020, 20, (10), 5977-5993.

Rodgers, T.F.M., Giang, A., Diamond, M. L., Gillies, E., Saini, A. Field-Based Distribution and Bioaccumulation Factors for Cyclic and Aliphatic Per- and Polyfluoroalkyl Substances (PFASs) in an Urban Sedentary Waterbird Population. Nat. Comm. 2023, 14, 1175.

Saini, A., Clarke, J., Jariyasopit, N., Rauert, C., Schuster, J.K., Halappanavar, S., Evans, G., Su, Y., Harner, T. Flame Retardants in Urban Air: A Case Study in Toronto Targeting Distinct Source Sectors. Environmental Pollution 2019, 247, 89-97.

Shah, R. U., M. M. Coggon, G. I. Gkatzelis, B. C. McDonald, A. Tasoglou, H. Huber, J. Gilman, C. Warneke, A. L. Robinson and A. A. Presto (2020). "Urban Oxidation Flow Reactor Measurements Reveal Significant Secondary Organic Aerosol Contributions from Volatile Emissions of Emerging Importance." Environmental Science & Technology **54**(2): 714-725.

Shahpoury, P., Harner, T., Lammel, G., Lelieveld, S., Tong, H., and Wilson, J.: Development of an antioxidant assay to study oxidative potential of airborne particulate matter, Atmos. Meas. Tech. 2019, 12, 6529–6539.

Shahpoury P., Zhang Z.W., Arangio A., Celo V., Dąbek- Złotorzyńska E., Harner T., Nenes A. The influence of chemical composition, aerosol acidity, and metal dissolution on the oxidative potential of fine particulate matter and redox potential of the lung lining fluid. Environment International. 2021, 148, 106343.

Shahpoury, P. et al. (+20 authors). Inter-comparison of oxidative potential metrics for airborne particles identifies differences between acellular chemical assays. Atmospheric Pollution Research 2022, 13, 101596.

Shahpoury, P., Lelieveld, S., Johannessen, C., Berkemeier, T., Celo, V., Dąbek- Złotorzyńska, E., Harner, T., Lammel, G., Nenes, A., Aerosol acidity, ligand complexation, and soluble metals influence the oxidative potential of fine particulate matter in urban environments. 2023 (in preparation)

Shahpoury, P., Lelieveld, S., Srivastava, D., Baccarini, A., Mastin, J., Berkemeier, T., Celo, V., Dąbek- Złotorzyńska, E., Harner, T., Lammel, G., Nenes, A.: Aerosol acidity and ligand

complexation regulate the temporal changes in solubility of transition metals and oxidative burden of fine aerosols particles; a multi-year Canadian perspective. 2023 (In-preparation)

Shi, Q., Tao, Y., Krechmer, J. E., Heald, C. L., Murphy, J. G., Kroll, J. H., Ye, Q. (2021). Laboratory Investigation of Renoxification from the Photolysis of Inorganic Particulate Nitrate. Environ. Sci. Technol., 55, 854 – 861. https://pubs.acs.org/doi/pdf/10.1021/acs.est.0c06049

Soares, J., Makar, P.A., Aklilu, Y., Akingunola, A. (2018) The use of hierarchical clustering for the design of optimized monitoring networks. Atmos. Chem. Phys. 18:6543–6566.

Sommariva, R., Crilley, L. R., Ball, S. M., Cordell, R. L., Holliz, L. D. J., Bloss, W. J., Monks, P. S. (2021) Enhanced wintertime oxidation of VOCs via sustained radical sources in the urban atmosphere, Environ. Pollut., 274: 116563 (doi: 10.1016/j.envpol.2021.116563)

Steffen A, Douglas T, Amyot M, Ariya P, Aspmo K, Berg T, Bottenheim J, Brooks S, Cobbett F, Dastoor A, Dommergue A. A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow. Atmospheric Chemistry and Physics. 2008 Mar 12;8(6):1445-82.

Strawbridge, K. B., Travis, M. S., Firanski, B. J., Brook, J. R., Staebler, R., and Leblanc, T.: A fully autonomous ozone, aerosol and nighttime water vapor lidar: a synergistic approach to profiling the atmosphere in the Canadian oil sands region, Atmos. Meas. Tech., 11, 6735–6759, https://doi.org/10.5194/amt-11-6735-2018, 2018.

Streets DG, Horowitz HM, Jacob DJ, Lu Z, Levin L, Ter Schure AF, Sunderland EM. Total mercury released to the environment by human activities. Environmental science & technology. 2017 Jun 6;51(11):5969-77.

Szabo, D.; Moodie, D.; Green, M. P.; Mulder, R. A.; Clarke, B. Field-Based Distribution and Bioaccumulation Factors for Cyclic and Aliphatic Per- and Polyfluoroalkyl Substances (PFASs) in an Urban Sedentary Waterbird Population. Environ. Sci. Technol. 2022, 56 (12), 8231-8244.

Szponar N, McLagan DS, Kaplan R J, Mitchell CP J, Wania F, Steffen A and Bergquist B A 2020 Isotopic characterization of atmospheric gaseous elemental mercury by passive air sampling Environ. Sci. Technol. 54 10533–43.

Tao, Y. and Murphy, J. C. (2019) The Mechanisms Responsible for the Interactions among Oxalate, pH, and Fe Dissolution in PM2.5, *ACS Earth Space Chem*, 3, 10, 2259 – 2265. https://pubs.acs.org/doi/abs/10.1021/acsearthspacechem.9b00172

Tevlin, A., Galarneau, E., Zhang, T., Hung, H. (2021) Polycyclic aromatic compounds (PACs) in the Canadian environment: ambient air and deposition. Environ. Poll. 271:116232.

Tian, Z.; Zhao, H.; Peter, K. T.; Gonzalez, M.; Wetzel, J.; Wu, C.; Hu, X.; Prat, J.; Mudrock, E.; Hettinger, R.; Cortina, A. E.; Biswas, R. G.; Kock, F. V. C.; Soong, R.; Jenne, A.; Du, B.; Hou, F.; He, H.; Lundeen, R.; Gilbreath, A.; Sutton, R.; Scholz, N. L.; Davis, J. W.; Dodd, M. C.; Simpson, A.; McIntyre, J. K.; Kolodziej, E. P., A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon. Science 2021, 371, (6525), 185-189.

Thomson EM, Breznan D, Karthikeyan S, MacKinnon-Roy C, Charland JP, Dąbek- Złotorzyńska E, Celo V, Kumarathasan P, Brook JR, Vincent R. Cytotoxic and inflammatory potential of size-fractionated particulate matter collected repeatedly within a small urban area. Part Fibre Toxicol. 2015 Jul 16;12:24. doi: 10.1186/s12989-015-0099-z. PMID: 26178321; PMCID: PMC4502610.

Thomson EM, Breznan D, Karthikeyan S, MacKinnon-Roy C, Vuong NQ, Dąbek- Złotorzyńska E, Celo V, Charland JP, Kumarathasan P, Brook JR, Vincent R. Contrasting biological potency of particulate matter collected at sites impacted by distinct industrial sources. Part Fibre Toxicol. 2016 Dec 1;13(1):65. doi: 10.1186/s12989-016-0176-y. PMID: 27906031; PMCID: PMC5134226.

Travis, K. R., Crawford, J. K, Chen, G., Jordan, C. E., Nault, B. A., Kim, H., et al. (2022). Limitations in representation of physical processes prevent successful simulation of PM2.5 during Korus-AQ. *Atmos. Chem. Phys*., 22, 7933-7958. https://doi.org/10.5194/acp-22-7933-2022

United Nations. 2015. A/RES/70/1 - Transforming our world: the 2030 agenda for sustainable development. United Nations. Retrieved 02 12 2021 from: https://www.un.org/ga/search/view_doc.asp?symbol=A/RES/70/1&Lang=E

United Nations Economic Commission for Europe (1998) Aarhus Convention on Access to Information, Public Participation in Decision-making and Access to Justice in Environmental Matters. Retrieved on 05 09, 2023 from: https://unece.org/DAM/env/pp/documents/cep43e.pdf

United Nations Economic Commission for Europe (2009). Kyiv Protocol on Pollutant Release and Transfer Registries. Retrieved on 05 09, 2023 from: https://unece.org/DAM/env/pp/prtr/Protocol%20texts/PRTR_Protocol_e.pdf

United Nations Environment Program, 2013 Minamata convention on mercury: Text and annexes United Nations Environmental Programme (UNEP) 1–67 Geneva, Switzerland http://hdl.handle.net/20.500.11822/8541).

Vandenboer, T. C., Markovic, M. Z., Sanders, J. E., Ren, X., Pusede, S. E., Browne, E. C., Cohen, R. C., Zhang, L., Thomas, J., Brune, W. H., Murphy, J. G. (2014) Evidence of nitrous acid (HONO) reservoir at the ground surface in Bakersfield, CA, during CalNex 2010, J. Geophys. Res. Atmos., 119: 9093 – 9106.

Van Vaeck, L. and K. Van Cauwenberghe. (1978) Cascade impactor measurements of the size distribution of the major classes of organic pollutants in atmospheric particulate matter. *Atmos. Environ.* **12**:2229-2239.

Vasić, M.V., Mihailović, A., Kozmidis-Luburić, U., Nemes, T., Ninkov, J., Zeremski-Škorić, T., Antić, B. 2012. Metal contamination of short-term snow cover near urban crossroads: correlation analysis of metal content and fine particles distribution. Chemosphere, 86:585-592, 10.1016/j.chemosphere.2011.10.023

Venier, M.; Salamova, A.; Hites, R. A. How to distinguish urban vs. agricultural sources of persistent organic pollutants? Curr. Opin. Environ. Sci. Health 2019, 8, 23-28.

Wang, W., Jariyasopit, N., Schrlau, J., Jia, Y., Tao, S., Yu, T.W., Dashwood, R.H., Zhang, W., Wang, X., Simonich, S.L., 2011. Concentration and photochemistry of PAHs, NPAHs, and OPAHs and toxicity of PM2.5 during the Beijing Olympic games. Environ. Sci. Technol. 45 (16), 6887-6895.

Wang, X.; Heald, C. L.; Ridley, D. A.; Schwarz, J. P.; Spackman, J. R.; Perring, A. E.; Coe, H.; Liu, D.; Clarke, A. D. Exploiting Simultaneous Observational Constraints on Mass and Absorption to Estimate the Global Direct Radiative Forcing of Black Carbon and Brown Carbon. Atmos. Chem. Phys. 2014, 14 (20), 10989−11010.

Weichenthal, S., Shekarrizfard, M., Traub, A., Kulka, R., Al-Rijleh, K., Anowar, S., Evans, G., Hatzopoulou, M.: Within-city spatial variations in multiple measures of PM2.5 oxidative potential in Toronto, Canada. 2019. Environ. Sci. Technol. 53, 2799–2810.

Whaley, C.H., Galarneau, E., Makar, P.A., Akingunola, A., Gong, W., Gravel, S., Moran, M.D., Stroud, C., Zhang, J., Zheng, Q. (2018) GEM-MACH-PAH (rev2488): a new high-resolution chemical transport model for North American polycyclic aromatic hydrocarbons and benzene. Geosci. Model Dev. 11: 2609-2632.

Williams, J.P., Ars, S., Vogel., F., Regehr, A., Kang, M. (2022) Differentiating and mitigating methane emissions from fugitive leaks from natural gas distribution, Historic Landfills, and Manholes in Montréal, Canada. *Environ. Sci.Technol.* 56: 16686–16694

Womack, C. C., McDuffie, E. E., Edwards, P. M., Bares, R., de Gouw, J. A., Docherty, K. S., et al. (2019). An odd oxygen framework for wintertime ammonium nitrate aerosol pollution in urban areas: NOx and VOC control as mitigation strategies. Geophysical Research Letters, 46, 4971–4979. https:// doi.org/10.1029/2019GL082028

Wnorowski, A. (2017) Characterization of the ambient air content of parent polycyclic aromatic hydrocarbons in the Fort McKay region (Canada). Chemosphere, 174, 371–379.

Wnorowski, A., Charland, J.-P. (2017). Profiling quinones in ambient air samples collected from the Athabasca region (Canada). Chemosphere 189, 55–66.

Wren, S., Mihele, C.M., Lu, G., Jiang, Z., Wen, D., Hayden, K., Mittermeier, R.L., Staebler, R.M., Cober, S.G., Brook, J.R. (2020) Improving insights on air pollutant mixtures and their origins by enhancing local monitoring in an area of intensive resource development. *Environ. Sci. Technol.* 54:14936–14945.

Wren, S.N., McLinden, C.A., Griffin, D., Li, S.,-M., Cober, S.G., Darlington, A., Hayden, K., Mihele, C., Mittermeier, R.L., Wheeler, M., Wolde, M., Liggio, J. (2023) Aircraft and satellite observations reveal historical gap between top–down and bottom–up CO_2 emissions from Canadian oil sands. PNAS Nexus 2:pgad140.

Xu, J., Zhang, M., Ganji, A., Mallinen, K., Wang, A., Lloyd, M., Venuta, A., Simon, L., Kang, J., Gong, J., Zamel, Y., Weichenthal, S., and Hatzopoulou, M. (2022) Prediction of Short-Term Ultrafine Particle Exposures Using Real-Time Street-Level Images Paired with Air Quality Measurements. Environ. Sci. Technol 56:12885-12897.

Yan, C.; Zheng, M.; Bosch, C.; Andersson, A.; Desyaterik, Y.; Sullivan, A. P.; Collett, J. L.; Zhao, B.; Wang, S.; He, K.; Gustafsson, Ö . Important Fossil Source Contribution to Brown Carbon in Beijing during Winter. Sci. Rep. 2017, 7, 43182.

Ye, C., Zhang, N., Gao, H., Zhou, X. (2017) Photolysis of particulate nitrate as a source of HONO and NOx, Environ. Sci. Technol., 51: 6849 – 6856.

You, Y., Staebler, R. M., Moussa, S. G., Su, Y., Munoz, T., Stroud, C., Zhang, J., and Moran, M. D.: Long-path measurements of pollutants and micrometeorology over Highway 401 in Toronto, Atmos. Chem. Phys., 17, 14119–14143, https://doi.org/10.5194/acp-17-14119-2017, 2017.

You, Y. Samar G. Moussa, Lucas Zhang, Long Fu, James Beck, and Ralf M. Staebler (2021) Quantifying fugitive gas emissions from an oil sands tailings pond with open-path Fourier transform infrared measurements. Atmos. Meas. Tech. 14:945–959.

Zbieranowski, Antoni L., and Julian Aherne (2012). Ambient concentrations of atmospheric ammonia, nitrogen dioxide and nitric acid across a rural–urban–agricultural transect in southern Ontario, Canada. *Atmospheric Environment* 62: 481-491.

Zhang, H., S. Kondragunta, I. Laszlo, and M. Zhou, Improving GOES Advanced Baseline Imager (ABI) aerosol optical depth (AOD) retrievals using an empirical bias correction algorithm, Atmos. Meas. Tech., 13, 5955–5975, 2020.

Zhang, L., Vet, R., O'Brien, J. M., Mihele, C., Liang, Z., & Wiebe, A. (2009). Dry deposition of individual nitrogen species at eight Canadian rural sites. *Journal of Geophysical Research: Atmospheres*, *114*(D2).

Zhang. W. Z., Shahpoury, P., Zhang, W., Harner, T., Huang, L. A new method for measuring airborne carbonaceous particles using PUF disk passive samplers. Chemosphere 2022, 299, 134323.

Zhang, X., Saini, A., Hao, C., Harner, T. Passive Air Sampling and Nontargeted Analysis for Screening POP-like Chemicals in the Atmosphere: Opportunities and Challenges. Trends in Anal Chem. 2020, 132, 116052.

Zhang, Y., Xu, C., Zhang, W., Qi, Z., Song, Y., Zhu, L., Dong, C., Chen, J., Cai, Z. p-Phenylenediamine Antioxidants in PM2.5: The Underestimated Urban Air Pollutants. Environ. Sci. Technol. 2022b 56, 11, 6914–6921.

Zhao, X., Griffin, D., Fioletov, V., McLinden, C., Davies, J., Ogyu, A., Lee, S. C., Lupu, A., Moran, M. D., Cede, A., Tiefengraber, M., and Müller, M.: Retrieval of total column and surface NO_2 from Pandora zenith-sky measurements, Atmos. Chem. Phys., 19, 10619–10642, https://doi.org/10.5194/acp-19-10619-2019, 2019.

Zhao, X., Griffin, D., Fioletov, V., McLinden, C., Cede, A., Tiefengraber, M., Müller, M., Bognar, K., Strong, K., Boersma, F., Eskes, H., Davies, J., Ogyu, A., and Lee, S. C.: Assessment of the quality of TROPOMI high-spatial-resolution NO_2 data products in the Greater Toronto Area, Atmos. Meas. Tech., 13, 2131–2159, https://doi.org/10.5194/amt-13-2131-2020, 2020.

Zhao, X., Fioletov, V., Alwarda, R., Su, Y., Griffin, D., Weaver, D., Strong, K., Cede, A., Hanisco, T., Tiefengraber, M., McLinden, C., Eskes, H., Davies, J., Ogyu, A., Sit, R., Abboud, I., and Lee, S. C.: Tropospheric and Surface Nitrogen Dioxide Changes in the Greater Toronto Area during the First Two Years of the COVID-19 Pandemic, Remote Sens., 14, 1625, https://doi.org/10.3390/rs14071625, 2022.

D. Zhu, H.D. Kuhns, J.A. Gillies, V. Etyemezian, S. Brown, A.W. Gertler, Analysis of the effectiveness of control measures to mitigate road dust emissions in a regional network (2012) Transportation Research Part D: Transport and Environment, (17) 332-340.

P. Zoogman, et al.: Tropospheric emissions: Monitoring of pollution (TEMPO), JQSRT, Volume 186, 2017, Pages 17-39, https://doi.org/10.1016/j.jqsrt.2016.05.008.

,

Appendices

Appendix A: Authors and Contributors

Lead Author

Elisabeth Galarneau, Environment and Climate Change Canada, Air Quality Research Division

Contributors - Environment and Climate Change Canada

Ihab Abboud, Air Quality Research Division
Stéphane Belair, Meteorological Research Division
Alicia Berthiaume, National Pollutant Release Inventory - Substance Information Division
Elisa Boutzis, Air Quality Research Division
Valbona Celo, Air Quality Research Division
Amanda Cole, Air Quality Research Division
Matthew Cooper, Air Quality Program Office
Ewa Dąbek- Złotorzyńska, Air Quality Research Division
Andrea Darlington, Air Quality Research Division
Ashu Dastoor, Air Quality Research Division
Jonathan Davies, Air Quality Research Division
Zoe Davis, Air Quality Program Office
Andrew Elford, Air Quality Research Division
Vitali Fioletov, Air Quality Research Division
Bernard Firanski, Air Quality Research Division
Wanmin Gong, Air Quality Research Division
Debora Griffin, Air Quality Research Division
Tom Harner, Air Quality Research Division
Katherine Hayden, Air Quality Research Division
Hayley Hung, Air Quality Research Division
Liisa Jantunen, Air Quality Research Division
Ali Katal, Air Quality Research Division
Alex Lee, Air Quality Research Division
Colin Lee, Air Quality Research Division
Sum Chi Lee, Air Quality Research Division
Sylvie Leroyer, Meteorological Research Division
John Liggio, Air Quality Research Division
Alex Lupu, Air Quality Research Division
Anne Marie Macdonald, Air Quality Research Division
Katrina MacSween, Air Quality Research Division
Mahtab Majdzadeh, Air Quality Research Division
Paul Makar, Air Quality Research Division
Zen Mariani, Meteorological Research Division
Chris McLinden, Air Quality Research Division
Cristian Mihele, Air Quality Research Division
Stefan Miller, Air Quality Research Division
Samar Moussa, Air Quality Research Division

Authors and Contributors (continued)

Contributors – Environment and Climate Change Canada (continued)

Jason O'Brien, Air Quality Research Division
Akira Ogyu, Air Quality Research Division
Matthew Parsons, Air Quality Program Office
Shuzhan Ren, Air Quality Research Division
Stacey Robinson, Ecotoxicology and Wildlife Health Division
Amandeep Saini, Air Quality Research Division
Jasmin Schuster, Air Quality Research Division
Kirill Semeniuk, Air Quality Research Division
Andrew Sheppard, Air Quality Research Division
Chris Sioris, Air Quality Research Division
Reno Sit, Air Quality Research Division
Michael Sitwell, Air Quality Research Division
May Siu, Air Quality Research Division
Ralf Staebler, Air Quality Research Division
Alexandra Steffen, Air Quality Research Division
Craig Stroud, Air Quality Research Division
Geoffrey Stupple, Air Quality Research Division
Gérald Tetreault, Aquatic Contaminant Research Division
Philippe Thomas, Ecotoxicology and Wildlife Health Division
Kenjiro Toyota, Air Quality Research Division
Felix Vogel, Climate Research Division
Jeremy Wentzell, Air Quality Research Division
Michael Wheeler, Air Quality Research Division
Luc White, Air Quality Research Division
Andrzej Wnorowski, Air Quality Research Division
Sumi Wren, Air Quality Research Division
Rosa Wu, Air Quality Research Division
Junhua Zhang, Air Quality Research Division
Leiming Zhang, Air Quality Research Division
Xiaoyi Zhao, Air Quality Research Division

Contributors – Health Canada

Sabina Halappanavar, Environmental Health Science and Research Bureau
Markey Johnson, Water and Air Quality Bureau
Pourya Shahpoury, Environmental Health Science and Research Bureau
Errol Thomson, Environmental Health Science and Research Bureau

Contributors – Concordia University

Cassandra Johannessen, Department of Chemistry and Biochemistry (Ph.D. student)
Xianming Zhang, Department of Chemistry and Biochemistry

Authors and Contributors (continued)

Contributor – Dalhousie University
Rachel Chang, Department of Physics and Atmospheric Science

Contributor – Toronto Metropolitan University
Roxana Suehring, Department of Chemistry and Biology

Contributor – Trent University
Mark Parnis, Department of Chemistry

Contributor – Université de Montréal
Patrick Hayes, Département de chimie (Department of Chemistry)

Contributor - Université du Québec à Rimouski
Zhe Lu, Institut des sciences de la mer (Department of Marine Science)

Contributor – University of British Columbia
Amanda Giang, Institute of Resources, Environment and Sustainability

Contributors - University of Toronto
Jonathan Abbatt, Department of Chemistry (St. George)
Matthew Adams, Department of Geography, Geomatics and Environment (Mississauga)
Bridget Bergquist, Department of Earth Sciences (St. George)
Arthur Chan, Department of Chemical Engineering and Applied Chemistry (St. George)
Miriam Diamond, Department of Earth Sciences (St. George)
Jamie Donaldson, Department of Physical and Environmental Sciences (Scarborough)
Greg Evans, Department of Chemical Engineering and Applied Chemistry (St. George)
Cheol-Heon Jeong, Department of Chemical Engineering and Applied Chemistry (St. George)
Jennifer Murphy, Department of Chemistry (St. George)
Kim Strong, Department of Physics (St. George)
Yee Ka Wong, Department of Chemical Engineering and Applied Chemistry (St. George) (PDF)
Debra Wunch, Department of Physics (St. George)

Contributors – York University
Mark Gordon, Department of Earth and Space Science and Engineering
Trevor VandenBoer, Department of Chemistry
Cora Young, Department of Chemistry

Contributor – City of Toronto
Esther Attard, Toronto Animal Services

Appendix B: Calendar for Intensive Field Measurement Campaign in Early 2024

Month (2024)	Sun	Mon	Tue	Wed	Thu	Fri	Sat
January	14	15	16	17	18	19	20
		INSTALLATION	INSTALLATION	INSTALLATION	INSTALLATION	INSTALLATION	
January	21	22	23	24	25	26	27
		INSTALLATION	INSTALLATION	INSTALL CRUISER AT HIGH PARK	**FIRST DAY OF SAMPLING**		
January/February	28	29	30	31	1	2	3
February	4	5	6	7	8	9	10
				TAKE DOWN CRUISER FROM HIGH PARK	INSTALL CRUISER AT DVP		
February	11	12	13	14	15	16	17
February	18	19	20	21	22	23	24
					TAKE DOWN CRUISER FROM DVP	INSTALL CRUISER AT UTSC	
February/March	25	26	27	28	29	1	2
March	3	4	5	6	7	8	9
					LAST DAY OF SAMPLING	TAKE DOWN CRUISER FROM UTSC + DECOMMISSIONING	
March	10	11	12	13	14	15	16
		DECOMMISSIONING	DECOMMISSIONING	DECOMMISSIONING	DECOMMISSIONING	DECOMMISSIONING	

NAPS Sampling Day (1 in 3) only
NAPS Sampling Day (1 in 3 & 1 in 6)

High Park Super-Intensive
DVP Super-Intensive
UTSC Super-Intensive

Appendix C: Summary of SWAPIT Science Activities Under Themes 2, 3 and 4

Theme 2: Sources and Processes

Project 2.1: Measurements at a commuter parking lot comparing cold-start and running emissions (Lead: Felix Vogel, ECCC Climate Research Division; Collaborators: Sébastien Ars, ECCC Climate Research Division; Debra Wunch, University of Toronto St. George; Matt Adams, University of Toronto Mississauga)

Project 2.2: Near-road measurements of emissions from an arterial roadway (Lead: Mark Gordon, York University)

Project 2.3: Near-road measurements of metal isotopes (Lead: Bridget Bergquist, University of Toronto)

Project 2.4: Temporal characterization of tailpipe (TP) and non-tailpipe (NTP) $PM_{2.5}$ near a downtown arterial road (Lead: Greg Evans, University of Toronto; Collaborator: Cheol-Heon Jeong and Yee Ka Wong, University of Toronto)

Project 2.5: Spatial patterns of tailpipe (TP) and non-tailpipe (NTP) emissions (Lead: Greg Evans, University of Toronto; Collaborator: Cheol-Heon Jeong and Yee Ka Wong, University of Toronto)

Project 2.6: Near-road measurements of atmospheric tire wear particles (Lead: Alex Lee, ECCC Air Quality Research Division; Collaborators: Arthur Chan, University of Toronto; Hayley Hung, ECCC Air Quality Research Division)

Project 2.7: Resolving the wintertime aviation and traffic emissions (Lead: Greg Evans, University of Toronto; Collaborator: Cheol-Heon Jeong, University of Toronto)

Project 2.8: Significance of ammonia (NH_3) emissions in vehicle exhaust (Lead: Ralf Staebler, ECCC Air Quality Research Division; Collaborator: Leiming Zhang, ECCC Air Quality Research Division)

Project 2.9: Comparative analysis of pollutants observed during SWAPIT and reported to the National Pollutant Release Inventory (NPRI) (Lead: Alicia Berthiaume, ECCC National Pollutant Release Inventory – Substance Information Division)

Project 2.10: Receptor modelling of VOCs using positive matrix factorization (PMF) (Lead: Samar Moussa, ECCC Air Quality Research Division)

Project 2.11: Relative contribution of primary and secondary oxy-PACs (quinones) in ambient air (Lead: Andrzej Wnorowski, ECCC Air Quality Research Division; Collaborator: Elisabeth Galarneau, ECCC Air Quality Research Division)

Project 2.12: The budgets of nitrogen- and chlorine-containing compounds and their impact on aerosol formation (Lead: Sumi Wren, ECCC Air Quality Research Division; Collaborators: Jennifer Murphy and Jamie Donaldson, University of Toronto; Jeremy Wentzell, Michael Wheeler, Craig Stroud, Colin Lee, Stefan Miller, and Paul Makar, ECCC Air Quality Research Division).

Project 2.13: The impact of non-exhaust VOCs such as volatile chemical products (VCPs) on organic aerosol formation and ozone forming potential (Lead: Samar Moussa, ECCC Air Quality Research Division; Collaborators: Craig Stroud ECCC Air Quality Research Division; Patrick Hayes, Université de Montréal.)

Project 2.14: Primary emissions and secondary formation of atmospheric brown carbon (Lead: Alex Lee, ECCC Air Quality Research Division; Collaborators: Jon Abbatt, University of Toronto, Craig Stroud and Paul Makar, ECCC Air Quality Research Division).

Project 2.15: Impact of urban emissions on deposition of acidifying substances (Co-leads: Amanda Cole and Jason O'Brien, ECCC Air Quality Research Division; Collaborator: Jennifer Murphy, University of Toronto)

Project 2.16: Impact of wet processing (precipitation, clouds, and fog) on urban pollutants and deposition (Lead: Wanmin Gong, ECCC Air Quality Research Division; Collaborators: Michael Wheeler, Paul Makar, Craig Stroud, and Colin Lee, ECCC Air Quality Research Division)

Project 2.17: Fog-pollutant interactions in urban air (Lead: Wanmin Gong, ECCC Air Quality Division; Collaborators: Michael Wheeler, Jason O'Brien, and Amanda Cole, ECCC Air Quality Research Division; Rachel Chang, Dalhousie University)

Project 2.18: Transformations of PACs deposited with and to snow (Lead: Elisabeth Galarneau, ECCC Air Quality Research Division)

Project 2.19: The evolution of semivolatile toxics across the particle size spectrum (Lead: Elisabeth Galarneau, ECCC Air Quality Research Division)

Project 2.20: Improving the understanding of turbulent kinetic energy and boundary layer height in urban environments (Lead: Zen Mariani, ECCC Meteorological Research Division; Collaborators: Ralf Staebler, Paul Makar, Craig Stroud, ECCC Air Quality Research Division; Sylvie Leroyer, Stéphane Bélair, ECCC Meteorological Research Division; Mark Gordon, York University)

Project 2.21: Investigating impacts of vehicle-induced turbulence in the near-road urban environment (Lead: Ralf Staebler, ECCC Air Quality Research Division; Collaborators: *Zen*

Mariani, Sylvie Leroyer and Stéphane Belair, ECCC Meteorological Research Division; Paul Makar and Craig Stroud, ECCC Air Quality Research Division; Mark Gordon, York University)

Project 2.22: *Evaluating meteorological influences on near-road gradients of traffic related pollutants (Lead: Greg Evans, University of Toronto; Collaborator: Cheol-Heon Jeong, University of Toronto)*

Theme 3: Impacts

Project 3.1: Linking oxidative potential to air toxics and trace contaminants (Co-leads: Tom Harner and Amandeep Saini, ECCC Air Quality Research Division; Collaborators: Pourya Shahpoury, Health Canada and Trent University; Sabina Halappanavar, Health Canada; Xianming Zhang and Cassandra Johannessen, Concordia University; John Liggio, Samar Moussa, Jasmin Schuster and Craig Stroud, ECCC Air Quality Research Division; Mark Parnis, Trent University; Greg Evans, University of Toronto)

Project 3.2: Oxidative potential of PM from filed samples and known sources (Lead: Greg Evans, University of Toronto; Collaborators: Cheol-Heon Jeong, University of Toronto; Tom Harner, ECCC Air Quality Research Division)

Project 3.3: Assessing in vitro toxicity of air toxics/trace contaminants from near-road and urban background areas (Lead: Errol Thomson, Health Canada: Collaborator: Elisabeth Galarneau, ECCC Air Quality Research Division)

Project 3.4: Identifying exceedances of health-based air quality guidelines (Lead: Elisabeth Galarneau, ECCC Air Quality Research Division; Collaborator: Amanda Giang, University of British Columbia)

Project 3.5: Determining epidemiological relationships between air pollutant exposure and adverse health impacts (Lead: Markey Johnson, Health Canada; Collaborators: Elisabeth Galarneau, ECCC Air Quality Research Division)

Project 3.6: Assessing the effects of snowmelt water on amphibian embryos (Lead: Stacey Robinson, ECCC Ecotoxicology and Wildlife Health Division; Collaborators: Hayley Hung and Elisabeth Galarneau, ECCC Air Quality Research Division; Roxana Suehring, Toronto Metropolitan University)

Project 3.7: Assessing the impact of airborne trace contaminants on urban fish health (Lead: Gérald Tetreault, ECCC Aquatic Contaminants Research Division; Collaborators: Hayley Hung, ECCC Air Quality Research Division; Zhe Lu, Université du Québec à Rimouski; Trevor VandenBoer and Cora Young, York University; Roxana Suehring, Toronto Metropolitan University)

Project 3.8: Assessing trace contaminant burden and links to altered health outcomes in semi-aquatic mammals (Lead: Philippe Thomas, ECCC Ecotoxicology and Wildlife Health Division; Collaborators: Esther Attard, Toronto Animal Services)

Theme 4: Science tool evaluation and improvement

Project 4.1: Evaluation of techniques for measurement of airborne mercury in urban environments (Lead: Alexandra Steffen, ECCC Air Quality Research Division; Collaborators: Katrina MacSween and Geoff Stupple, ECCC Air Quality Research Division; Bridget Bergquist, University of Toronto)

Project 4.2: Connecting sources of microplastics and microfibers to their presence in air and aquatic systems (Lead: Liisa Jantunen, ECCC Air Quality Research Division; Collaborator: Miriam Diamond, University of Toronto)

Project 4.3: Satellite aerosol optical depth measurements to identify sources of urban aerosol (Lead: Chris Sioris, ECCC Air Quality Research Division)

Project 4.4: Validating the vertical distribution of common air pollutants using Pandora at the CN Tower (Lead: Xiaoyi Zhao, ECCC Air Quality Research Division; Collaborators: Vitali Fioletov, Ihab Abboud, Jonathan Davies, Akira Ogyu, Reno Sit, and Sum Chi Lee, ECCC Air Quality Research Division)

Project 4.5: Evaluation of wintertime measurements from the newly-launched TEMPO satellite (Lead: Debora Griffin, ECCC Air Quality Research Division; Collaborators: Chris McLinden and Sumi Wren, ECCC Air Quality Research Division)

Project 4.6: Non-Exhaust Vehicle Emissions and Representation in GEM-MACH (Lead: Ali Katal, ECCC Air Quality Research Division; Collaborators: Junhua Zhang, Craig Stroud and Samar Moussa, ECCC Air Quality Research Division)

Project 4.7: Aqueous Chemistry and Oxidative Potential in GEM-MACH (ARQI Lead: Alex Lupu, ECCC Air Quality Research Division; Collaborators: Craig Stroud, Kenjiro Toyota, Tom Harner and Amandeep Saini, ECCC Air Quality Research Division; Pourya Shahpoury, Health Canada and Trent University)

Project 4.8: Proof of concept for inverse emission modelling with GEM-MACH (Lead: Shuzhan Ren, ECCC Air Quality Research Division; Collaborators: Debora Griffin and Michael Sitwell, ECCC Air Quality Research Division)

Project 4.9: Improvements to modelling of the boundary layer and deposition using GEM-MACH (Lead: Craig Stroud, ECCC Air Quality Research Division; Collaborators: Shuzhan Ren, Ali Katal, Paul Makar, Wanmin Gong, ECCC Air Quality Research Division; Sylvie Leroyer and Stéphane Belair, ECCC Meteorological Research Division)

Project 4.10: Evaluation of ultrafine particle modelling in GEM-MACH with MOSAIC (Lead: Ashu Dastoor, ECCC Air Quality Research Division; Collaborator: Kirill Semeniuk, ECCC Air Quality Research Division)

Project 4.11: GEM-MACH model evaluation by source factors (Lead: Mahtab Majdzadeh, ECCC Air Quality Research Division; Collaborators: Craig Stroud, Kenjiro Toyota and Paul Makar, ECCC Air Quality Research Division)

Project 4.12: Source sector apportionment using GEM-MACH (Lead: Craig Stroud, ECCC Air Quality Research Division, Collaborators: Junhua Zhang and Samar Moussa, ECCC Air Quality Research Division)

Project 4.13: Evolution of horizontal resolution from 2.5 km to 250 m using GEM-MACH with the Town Energy Balance (TEB) (Lead: Craig Stroud, ECCC Air Quality Research Division; Collaborators: Paul Makar, Ali Katal, and Shuzhan Ren, ECCC Air Quality Research Division)

Project 4.14: Improvements to wintertime physical processes in GEM at the urban scale (Lead: Sylvie Leroyer, ECCC Meteorological Research Division; Collaborators: Stéphane Bélair; ECCC Meteorological Research Division)

Appendix D: SWAPIT Leadership Team

SWAPIT Steering Committee (SWAPIT SC)

SWAPIT SC Position	Name(s)
Principal Investigator	Elisabeth Galarneau
Technical Planning and Operations	Andrew Sheppard
Fixed Sites	Jasmin Schuster, Kenny Yan
Mobile and Portable Platforms	Sébastien Ars, Colin Lee
Chemical Transport Modelling	Elisa Boutzis, Ali Katal, Craig Stroud
Data Acquisition	Andrew Elford
Data Management	Bernard Firanski
Project Management and Logistics	Andrea Darlington, Sandro Leonardelli, Stoyka Netcheva
Administration	Keta Joshi

SWAPIT Site Coordinators

Site	Name(s)
CN Tower	Raymon Atienza
Evergreen Brickworks	Samar Moussa
High Park	Gang Lu
Lester B. Pearson International Airport	Zen Mariani
Super-Intensive Portable Package	Jeremy Wentzell, Sumi Wren
University of Toronto Scarborough	Cecilia Shin

SWAPIT Mobile Platform Coordinators

Mobile Platform	Name
ECCC CRD Platform	Felix Vogel
Adams Group Platform	Matt Adams*
Evans Group Platform	Cheol-Heon Jeong **

** University of Toronto Mississauga*

*** University of Toronto St. George*