

## PAPER

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Cite this: *Environ. Sci.: Processes Impacts*, 2025, 27, 3595

# Distribution of semi-volatile organic compounds, metals, and biological activities in two industrialized cities in Ontario, Canada using passive air sampling

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Industrial emissions contribute to air pollution in industrialized cities in North America, where higher concentrations of chemicals are linked to adverse effects on human health. In the present study, polyurethane foam passive air samplers (PUF-PAS) were deployed over a one-year period in two industrialized cities (5 sites per city – rural, residential, and urban) to determine the spatial and temporal distribution of 30 semi-volatile organic compounds (SVOCs) and 12 metals. Targeted SVOCs included polychlorinated biphenyls (PCBs), flame retardants (PBDEs and TDCPP), and organochlorine pesticides (OCPs; *cis*-chlordane, endosulfan I and 4,4'-DDE), and most pollutants were elevated at industrial locations. The annual average air concentrations of PCBs, PBDEs and OCPs ranged between 17–631 pg m<sup>-3</sup>, while those of the polycyclic aromatic hydrocarbons (PAHs) ranged from 2–42 ng m<sup>-3</sup>. Concentrations of benzo[a]pyrene were greatest during the Winter and Spring, and exceeded the ambient air quality criterion (0.01 ng m<sup>-3</sup>) at all sites (0.03–0.50 ng m<sup>-3</sup>). Iron was the most abundant metal detected, and its spatial distribution likely reflected the presence of steel production. Chemical activated luciferase gene expression (CALUX®) assays for estrogenicity were below detection limits, while anti-androgenicity activity was measured at all sites with the greatest activity observed at locations most impacted by industrial emissions.

Received 26th June 2025  
Accepted 23rd September 2025

DOI: 10.1039/d5em00493d

rsc.li/espi

## Environmental significance

Industrial emissions are primary sources of air contaminants that affect air quality and public health. This study investigates how petrochemical and steel industries influence the distribution of semi-volatile organic compounds (SVOCs), metals, and hormone disruption activity in two industrialized cities in Canada (Sarnia and Hamilton). Using passive air sampling, anti-androgenicity activity was measured in ambient air that could not be explained by regulated contaminants. These findings reveal that conventional monitoring may overlook biologically active contaminants and underestimate exposure. The study also demonstrates that different industries produce distinct chemical profiles in ambient air. Linking environmental contaminants to biological effects offers a transferable approach for assessing air pollution in other industrialized cities.

## 1. Introduction

The World Health Organization (WHO) reports that air pollution causes 7 million deaths each year, posing a growing risk to public health.<sup>1</sup> Industrial and vehicular emissions have been

identified as primary sources of air pollution,<sup>2,3</sup> which consists of a diverse range of chemicals, broadly classified as volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs). Regulatory efforts to manage SVOCs have largely focused on polycyclic aromatic hydrocarbons (PAHs) as well as compounds that are persistent, bioaccumulative, and toxic as defined by the Stockholm Convention on Persistent Organic Pollutants (POPs).<sup>4</sup> Examples include polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polychlorinated naphthalenes (PCNs), polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), and organochlorine pesticides (OCPs).

The cities of Sarnia and Hamilton are heavily industrialized by petrochemical and steel production, respectively, known for their poor air quality, and characterized as having among the

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highest concentrations of (S)VOCs, in Canada.<sup>5</sup> Exposure to air pollution has been linked to health problems such as asthma, upper respiratory tract infection, chronic obstructive pulmonary disease, heart disease, and cancer.<sup>6–10</sup> Other health effects linked with exposure to SVOCs include endocrine disruption, which affects fertility, cognitive ability, obesity, and pregnancy outcomes by altering normal hormone function.<sup>11–13</sup> The studies by Perera *et al.*<sup>14</sup> and Dai *et al.*<sup>15</sup> show that PAH exposure during pregnancy can negatively impact developing fetuses and pregnancy outcomes. In Sarnia, it has been suggested that exposure to airborne endocrine disrupting chemicals (EDCs) could potentially explain the skewed sex ratio among members of the Aamjiwnaang First Nation.<sup>16</sup>

Several air quality studies, including the Global Atmospheric Passive Sampling (GAPS) monitoring program, have reported on the occurrence of persistent, bioaccumulative, and toxic chemicals, as well as toxic metals, in urban air worldwide.<sup>17–19</sup> In Canada, Jariyasopit *et al.*<sup>20</sup> detected benzo[*a*]pyrene in Toronto with concentrations exceeding 4 to 25 times the regulatory recommendation. As a direct consequence of exposure to air pollution, life expectancy of individuals living in large cities are estimated to be lower.<sup>21,22</sup> Available air quality data reveal that emissions of air contaminants composed mainly of carbon monoxide, nitrogen oxides, sulfur dioxide, VOCs, and particulate matter listed in Canada's national pollutant release inventory (NPRI) exceed  $1.31 \times 10^8$  kg in Sarnia, yet information on the composition of SVOCs and associated risks remains limited.<sup>23</sup> Airborne heavy metal concentration data in both cities are also limited to a study by Olawoyin *et al.*,<sup>24</sup> that recorded unsafe levels of lead (Pb) among nine metals characterized in Sarnia. In Hamilton, a study by Sofowote *et al.*<sup>25</sup> revealed that almost 50% of airborne particulate matter (PM<sub>2.5</sub>) were associated with steel production and vehicular emissions, and their secondary products.

In addition to targeted measurements of known EDCs, chemical activated luciferase gene expression (CALUX) assays allows for the detection of EDCs without prior knowledge of their structure or occurrence.<sup>26</sup> It is an affordable *in vitro* technique that measures the extent to which contaminants bind or activate hormone receptors, such as the aryl hydrocarbon receptor (AhR) targeted by dioxin-like compounds, estrogen receptors (ER), androgen receptors (AR), or thyroid hormone receptors (THR). In Toronto, Klein *et al.*<sup>27</sup> employed CALUX assays, resulting in the detection of elevated AhR and ER disruption activities in outdoor air. While AhR and ER disruption may alter stress response, reproductive health, and promote cancer;<sup>28,29</sup> (anti)AR disruption has been reported to negatively impact fetal development during pregnancy.<sup>30,31</sup> Until now, there has been no efforts to characterize EDC activities in Sarnia and Hamilton.

The objectives of the present study were to: utilize PUF-PAS samplers to analyze for a broad range of SVOCs using gas chromatography-high resolution mass spectrometry (GC-HRMS) over one year in two industrialized cities in Ontario (Sarnia and Hamilton); to investigate the distribution of chemicals and metals in rural, urban, and industrialized areas within each city; and screen for potential biological impacts

using CALUX® assays for estrogenicity and anti-androgenicity. This is the second of two papers investigating the distribution of SVOCs using PUF-PAS in Sarnia and Hamilton, Ontario. By focusing on two industrialized cities (Sarnia and Hamilton) with different industrial profiles (petrochemical and steel), the present study will provide insights into how different types of industry influence SVOCs and metals concentrations across rural, suburban, urban, and industrial areas. As one of Canada's first investigations to integrate air contaminant measurements and anti-androgenicity, it reveals the limitations of routine environmental monitoring that focuses on a narrow range of air contaminants, and consequently do not adequately capture reproductive and developmental health risks. This framework is transferable, linking pollutant profiles with biological metrics to enable adaptable emissions assessments to other industrialized cities.

## 2. Materials and methods

### 2.1 Chemicals and standards

The following classes of contaminants were analyzed in the present study including polychlorinated biphenyls (PCB-28, -52, -101, -118, -153, -138, and -180), halogenated flame retardants (PBDE-28, -47, -99, -153, and TDCPP), organochlorine pesticides (endosulfan I, *cis*-chlordane, and 4,4'-DDE), and polycyclic aromatic hydrocarbons (acenaphthene, acenaphthylene, anthracene, benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*g,h,i*]perylene, chrysene, dibenz[*a,h*]anthracene, fluoranthene, fluorene, indeno[1,2,3-*c,d*]pyrene, naphthalene, phenanthrene, pyrene). A detailed list of all the targeted analytes and their corresponding internal standards is provided in Table S1a. Authentic standards including, *cis*-chlordane, endosulfan I, and 1,1-dichloro-2,2-bis(4-chlorophenyl)ethene (4,4'-DDE) were obtained from Cambridge Isotope Laboratories (Tewksbury, MA, USA); tris(1,3-dichloro-2-propyl)phosphate (TDCPP), 2,4,4'-trichlorobiphenyl (PCB-28), 2,2',5,5'-tetrachlorobiphenyl (PCB-52), 2,2',4,5,5'-pentachlorobiphenyl (PCB-101), 2,3',4,4',5-pentachlorobiphenyl (PCB-118), 2,2',4,4',5,5'-hexachlorobiphenyl (PCB-153), 2,2',3,4,4',5'-hexachlorobiphenyl (PCB-138), 2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB-180), 2,4,4'-tribromodiphenyl ether (PBDE-28), 2,2',4,4'-tetrabromodiphenyl ether (PBDE-47), 2,2',4,4',5-pentabromodiphenyl ether (PBDE-99), and 2,2',4,4',5,5'-hexabromodiphenyl ether (PBDE-153) were obtained from Wellington Laboratories (Guelph, ON, Canada); and PAHs acenaphthene, acenaphthylene, anthracene, benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*g,h,i*]perylene, chrysene, dibenz[*a,h*]anthracene, fluoranthene, fluorene, indeno[1,2,3-*c,d*]pyrene, naphthalene, phenanthrene, and pyrene were obtained from Sigma-Aldrich (St. Louis, MO, USA). Internal standards of <sup>13</sup>C<sub>10</sub>-chlordane, <sup>13</sup>C<sub>12</sub>-DDE, <sup>13</sup>C<sub>9</sub>-endosulfan, D<sub>10</sub>-phenanthrene, D<sub>12</sub>-benzo[*a*]pyrene and D<sub>12</sub>-perylene, and injection standard D<sub>10</sub>-anthracene, were obtained from Cambridge Isotope Laboratories (Tewksbury, MA, USA). <sup>13</sup>C<sub>12</sub>-PCBs (-28, -52, -101, 118, -153, -138, and -180) and <sup>13</sup>C<sub>12</sub>-PBDEs (-47 and -99) were obtained from Wellington Laboratories (Guelph, ON, Canada). Solvents, namely acetone, *n*-hexane,



Table 1 Coordinates and classification of sampling locations

| City     | Sampling sites           | Classification | Description  | Coordinates  |              |
|----------|--------------------------|----------------|--|--------------|--------------|
|          |                          |                |  | Latitude     | Longitude    |
| Sarnia   | S_North                  | Residential    | Near highway   | 42°59'25.0"N | 82°23'43.3"W |
|          | S_East                   | Residential    |  | 42°58'11.1"N | 82°22'17.9"W |
|          | S_Central                | Industrial     |  | 42°57'41.6"N | 82°24'25.1"W |
|          | S_Southeast <sup>a</sup> | Rural          |  | 42°53'06.0"N | 82°16'49.4"W |
|          | S_Aamjiwnaang (AFN)      | Residential    |  | 42°54'45.2"N | 82°25'00.6"W |
| Hamilton | H_North                  | Urban          | Industrially influenced<br>Isthmus, near marina<br>Lakeside (Lake Ontario)<br>Downtown<br>Near highway | 43°18'01.3"N | 79°48'10.5"W |
|          | H_East                   | Industrial     |  | 43°15'57.6"N | 79°46'42.4"W |
|          | H_Central                | Urban          |  | 43°15'31.6"N | 79°51'38.0"W |
|          | H_West                   | Residential    |  | 43°15'27.0"N | 79°54'28.3"W |
|          | H_South                  | Residential    |  | 43°14'27.6"N | 79°53'22.1"W |

<sup>a</sup> Approximate location.

and toluene (HPLC grade) were obtained from Sigma-Aldrich (St. Louis, MO, USA) and nitric acid (ACS grade) was obtained from VWR International Inc. (Mississauga, ON, Canada).

## 2.2 Sampling sites and sample preparation

A total of ten sites were used for sampling: five each in Sarnia, including the Aamjiwnaang First Nation in southern Sarnia (S\_AFN), and Hamilton. Nine of these sites were part of an earlier study by our team, which identified SVOCs in a non-targeted approach.<sup>32</sup> The coordinates are summarized in Table 1.

Polyurethane foam passive air samplers (PUF-PAS) were deployed at each site, mounted at a height of 1–4 meters above the ground. They comprised of two stainless steel covers, sandwiching a PUF disc that has been shown to efficiently adsorb SVOCs.<sup>19,33</sup> The steel covers protect the foam from external disturbances and direct deposition of pollutants, allowing passive sampling to occur by diffusion. PUF discs (15 cm × 1.5 cm) with a density of 0.030 g cm<sup>-3</sup>, were obtained from Tisch Environmental (Cleveland, Ohio, USA). The discs were cleaned with acetone and hexane using an ASE 350 Accelerated Solvent Extraction system (Thermo Fisher Scientific Inc., Wilmington, DE, USA), as previously described.<sup>33</sup> At each sampling location, a second PUF-PAS sampler was deployed for metal sampling. In addition to ASE, PUF discs designated for metal sampling were also cleaned using deionized water and dilute nitric acid, as previously described.<sup>35</sup> Afterwards, they were dried on aluminum foil in a fume hood before being stored in pre-cleaned glass jars. Two PUF-PAS were deployed at each sampling site (one for organics and the other for metals) and exchanged at 90 day intervals between November 2021 and December 2022. Sampling was completed in a total of four deployment periods for organics, within each season of the year: winter (November 2021–February 2022), spring (March 2022–June 2022), summer (June 2022–September 2022), and fall (September 2022–December 2022). Metals were sampled only in the 3rd and 4th deployment periods. The average temperature during each sampling period was −1.6 °C, 10.0 °C, 19.9 °C, and 5.4 °C, respectively.<sup>36</sup>

After each sampling event, the PUF discs intended for organics were divided into quarters, and a quarter of each PUF

disc was extracted through ASE for targeted screening (GC-MS), non-targeted screening,<sup>32</sup> and CALUX assay, respectively, to a total of three quarters. Afterwards, the extracts were dried in a vacuum evaporator and reconstituted in 0.5 mL of hexane prior to instrumental analysis. The conditions of the ASE extraction are as follows: the cell volume was set to 100 mL, rinse volume was 60%, temperature was set to 100 °C, heating time and static time were both 5 minutes each, and the purge time was 200 seconds. PUF extract concentration was done under nitrogen gas (99.99%). Separate PUF discs deployed for metal sampling were divided into 100 mg fractions. Each 100 mg fraction was prepared for metal analysis by ALS Laboratory Group (Burlington, ON, Canada), following USEPA method 3052 microwave digestion procedure.<sup>37</sup> The present study assumes a homogeneous distribution of metals and organic contaminants in PUF discs, due to long-term sampling (90 days per PUF). This has been reported in previous PUF-PAS studies.<sup>35,38</sup>

## 2.3 Instrumental analysis

Briefly, quarter PUF discs intended for targeted screening were fortified with isotopically labelled standards (surrogates) including 10 ng each of <sup>13</sup>C<sub>12</sub>-PCBs (-28, -52, -101, 118, -153, -138, and -180) and 20 ng each of <sup>13</sup>C<sub>10</sub>-chlordane, <sup>13</sup>C<sub>12</sub>-DDE, <sup>13</sup>C<sub>9</sub>-endosulfan, <sup>13</sup>C<sub>12</sub>-PBDEs (-47 and -99), D<sub>12</sub>-B[a]P, D<sub>12</sub>-perylene and D<sub>10</sub>-phenanthrene. Following ASE extraction and pre-concentration, PUF extracts were spiked with 10 ng of D<sub>10</sub>-anthracene as an injection standard. Target analytes were quantified using surrogates, while surrogates and their recoveries were quantified using the injection standard, summarized in Table S1a. An Agilent 8890 gas chromatograph (GC) coupled with a Waters Cyclic IMS cyclic ion mobility mass spectrometer (Wilmslow, UK), and equipped with an atmospheric pressure chemical ionization (APCI) source, was employed in the separation and detection of analytes and surrogates in the PUF extracts.<sup>34</sup> GC separation was performed using a 20 m long BP-5 column, with a diameter of 0.18 mm and film thickness of 0.18 μm. The GC oven temperature was held at 90 °C for 1 minute, then increased to 325 °C at a rate of 8.1 °C min<sup>-1</sup>. The final



temperature was held for 6 minutes. 1  $\mu\text{L}$  of PUF extracts and standard solutions containing 20–40  $\text{pg } \mu\text{L}^{-1}$  of surrogates and injection standards, were introduced into a standard splitless injector. The injection port was heated to 280  $^{\circ}\text{C}$ , while helium served as the carrier gas at a flow rate of 1.4  $\text{mL min}^{-1}$ . The GC eluant was directed through the ion volume aided by a nitrogen makeup flow (with a purity of 99.99%) at 350  $\text{mL min}^{-1}$ . APCI was achieved by a corona discharge set at 3  $\mu\text{A}$  in the positive ion mode. The ion source temperature was held at 150  $^{\circ}\text{C}$ , the sampling cone voltage was set to 40 V, extraction cone at 10 V, cone gas flow at 175  $\text{L h}^{-1}$ , and auxiliary gas flow at 100  $\text{L h}^{-1}$ . Mass spectra were obtained across an  $m/z$  range of 50–1200, following GC separation and ionization. The mass-to-charge ( $m/z$ ) measurements were calibrated using a column bleed ( $\text{C}_9\text{H}_{27}\text{O}_5\text{Si}_5^+$  with an  $m/z$  of 355.0705).

## 2.4 Metals analysis

Metals were analyzed by ALS Laboratory Group (Burlington, ON, Canada). Following U.S. EPA method 6020B, 100 mg PUF disc digests were characterized for the presence of metals (aluminum, barium, calcium, chromium, cobalt, copper, iron, lead, nickel, potassium, silver, and zinc) using inductively coupled plasma-mass spectrometry (ICP-MS).<sup>39</sup>

## 2.5 Uptake rate and air concentration

The uptake rate of organic contaminants at each sampling site was determined using the online model of Herkert *et al.*<sup>40</sup> This validated model uses a combination of meteorological data from NASA's Modern-Era Retrospective Analysis for Research and Applications (MERRA) and the target compounds' physico-chemical properties (molecular weight, octanol-air partition coefficient, and internal energy of octanol-air transfer) to generate hourly uptake rate data at specific locations. PUF-PAS model parameters were set as follows: sampling height was set to default (2 meters), sampling coordinates were inputted from Table 1, and deployment periods were set to 90 days. The final air concentration of each pollutant was estimated by dividing their PUF disc concentration with the product of their modelled uptake rate and the 90 day sampling period. PUF disc concentration of most pollutants was determined using internal standards as a reference. In one sample (H\_West summer 2022), the internal standards were not detectable and consequently, the data was excluded from our analysis.

Air concentrations of metals were estimated using experimental uptake rates reported by Gaga *et al.*<sup>35</sup> For metals without experimental uptake rate information, a default value of 4  $\text{m}^3 \text{day}^{-1}$  was used. This was the average uptake rate for metals using PUF-PAS reported by Gaga *et al.*<sup>35</sup> who acknowledged that this value was associated with an uncertainty of  $\pm 2 \text{ m}^3 \text{day}^{-1}$ . Although the Herkert model accurately predicts the uptake of gas-phase organics by PUF-PAS, its application to particulate-phase contaminants is limited by several uncertainties<sup>40–42</sup> and for this reason, we have decided to employ the experimental uptake rates reported by Gaga *et al.*<sup>35</sup>

## 2.6 CALUX assay

Estrogenicity and anti-androgenicity activity were determined by BioDetection Systems (Amsterdam, Netherlands) through ER $\alpha$  and anti-TR $\beta$  CALUX assays, respectively. The PUF samplers extracts were supplied to BioDetection Systems, whereupon they were reconstituted in dimethyl sulfoxide (DMSO) and serially diluted 1000-fold to 0.1% DMSO in cell culture medium, as previously described.<sup>43,44</sup> In summary, U2OS human cell lines with luciferase genes incorporated (CALUX cells) were used to determine CALUX activities by incubating the cells for 24 hours in the presence of dilute sample extracts. Luminescence (response) was recorded using a Berthold luminometer. Reference ER $\alpha$  and anti-TR $\beta$  response were also measured from CALUX cells that were incubated with EC50 concentration of 17 $\beta$ -estradiol and deoxynivalenol, respectively. The CALUX cell culturing was done with 5% carbon dioxide in a dulbecco's modified eagle medium/nutrient mixture F-12 (DMEM-F12) with 7.5% fetal calf serum (FCS).

## 2.7 Quality assurance and quality control (QA/QC)

Field blanks were obtained by exposing a clean PUF disc to air for  $\sim 30$  seconds before placing it in a pre-cleaned jar on-site. One field blank was collected per city (Hamilton and Sarnia) during each sampling period. All utensils, such as tongs, were preheated to 500  $^{\circ}\text{C}$  to remove any carbon deposition. Both blank and sample PUF discs underwent the same pre- and post-sampling preparation steps, including being cut into quarters. Each quarter was spiked with isotopically labelled standards (surrogates) prior to extraction. The only exceptions were quarter discs intended for CALUX, which were extracted without spiking with surrogates to avoid interference with CALUX response. Average surrogate recoveries ranged from 47–103% for  $^{13}\text{C}_{12}$ -PCBs (-28, -52, -101, 118, -153, -138, and -180), 82–150% for OCPs ( $^{13}\text{C}_{10}$ -chlordane,  $^{13}\text{C}_{12}$ -DDE,  $^{13}\text{C}_9$ -endosulfan), 127–140% for  $^{13}\text{C}_{12}$ -PBDEs(-47 and -99) and 80–126% for PAHs ( $\text{D}_{12}$ -B[a]P,  $\text{D}_{12}$ -perylene and  $\text{D}_{10}$ -phenanthrene), summarized in Table S1a. A total of 6 laboratory blanks were extracted and levels of analytes quantified. Target analytes found in field blanks were <23% of those in the PUF samples. The method detection limit (MDL) of each compound was defined as the sum of the average peak abundance observed in blanks ( $\bar{x}$ ) and the product of the  $t$ -statistic (at 98% confidence) and standard deviation ( $\sigma$ ).

The method's performance is summarized in Tables S1a and b. Calibration curves were developed using authentic standards with a concentration range of 0.32–200  $\text{pg } \mu\text{L}^{-1}$  for most compounds and surrogates between 20–40  $\text{pg } \mu\text{L}^{-1}$ . Only compounds whose correlation coefficients were above 0.94 were considered for quantitative analysis. Method quality was evaluated through native spike recovery experiments summarized in Table S1b. PBDE-209, a current-use PBDE listed in 2017 under the Stockholm Convention, is still frequently detected in environmental samples from legacy and limited current sources.<sup>4,45–47</sup> However, it was not analyzed in the present study due to constraints related to GC column film thickness and





uncertainties in estimating its particulate-phase uptake rate in PUF-PAS.<sup>40,41</sup>

### 3. Results and discussion

#### 3.1 Spatial and temporal distribution of halogenated pollutants

The annual spatial distribution of halogenated pollutants in Sarnia and Hamilton is summarized in Fig. 1a and b, respectively. The results revealed that halogenated pollutants were present at all sites, with the most polluted being the urban and industrial sites of H\_North, H\_East, and S\_Central.

**3.1.1 Polychlorinated biphenyls (PCBs).** PCBs are carcinogenic chlorine-containing aromatic compounds, which were popular in the 1900s for their thermal and insulating properties. It wasn't until the 1970s before their production was discontinued due to their health risks.<sup>48</sup> In the present study,  $\sum_7$  PCBs were characterized including PCB-28, -52, -101, -118, -153, -138, and -180. These  $\sum_7$  PCBs represent the most abundant indicators of legacy PCB contamination.<sup>18</sup> In Sarnia, the concentration of  $\sum_7$  PCBs ranged between 8–118 pg m<sup>-3</sup>, while in Hamilton they ranged between 38–601 pg m<sup>-3</sup>. PCBs contributed a tetrachlorodibenzo-*p*-dioxin (TCDD) toxic equivalent (TEQ) concentration between 0.0001–0.003 pg m<sup>-3</sup> in

Sarnia, and 0.0009–0.006 pg m<sup>-3</sup> in Hamilton, which lie well below the regulatory criterion of 0.1 pg m<sup>-3</sup>.<sup>49,50</sup> The concentrations of PCBs recorded in the present study (8–118 pg m<sup>-3</sup> in Sarnia, and 38–601 pg m<sup>-3</sup> in Hamilton) were comparable with previously reported concentrations in urbanized and industrialized locations. In Concepcion, Chile, these  $\sum_7$  PCBs (excluding PCB-118) ranged from 33–117 pg m<sup>-3</sup>; in Chicago, USA they averaged 73 pg m<sup>-3</sup>; in Eastern China,  $\sum_7$  PCBs ranged from 50–270 pg m<sup>-3</sup> near an industrial area and waste incineration facility.<sup>47,51,52</sup> Schuster *et al.*<sup>53</sup> recorded a 3 year concentration range of  $\sum_7$  PCBs between 1–320 pg m<sup>-3</sup> across 17 urban locations worldwide, including Vancouver, Canada. Around two of the Great Lakes (Lake Erie and Lake Ontario), Liu *et al.*<sup>54</sup> recorded  $\sum_7$  PCBs ranging from 5.2–306 pg m<sup>-3</sup>, with higher concentrations corresponding to urbanized areas. In a recent study, Zhan *et al.*<sup>55</sup> reported  $\sum_7$  PCBs between 1–275 pg m<sup>-3</sup> across 93 urban and industrial locations in Canada. Despite declining trends in PCB levels,  $\sum_7$  PCBs were the most abundant halogenated pollutants in the present study.<sup>53</sup> This is consistent with the findings in a recent GAPS study<sup>53</sup> and Zhan *et al.*<sup>55</sup> that highlighted PCBs among the most abundant halogenated contaminants alongside current-use halogenated chemicals.

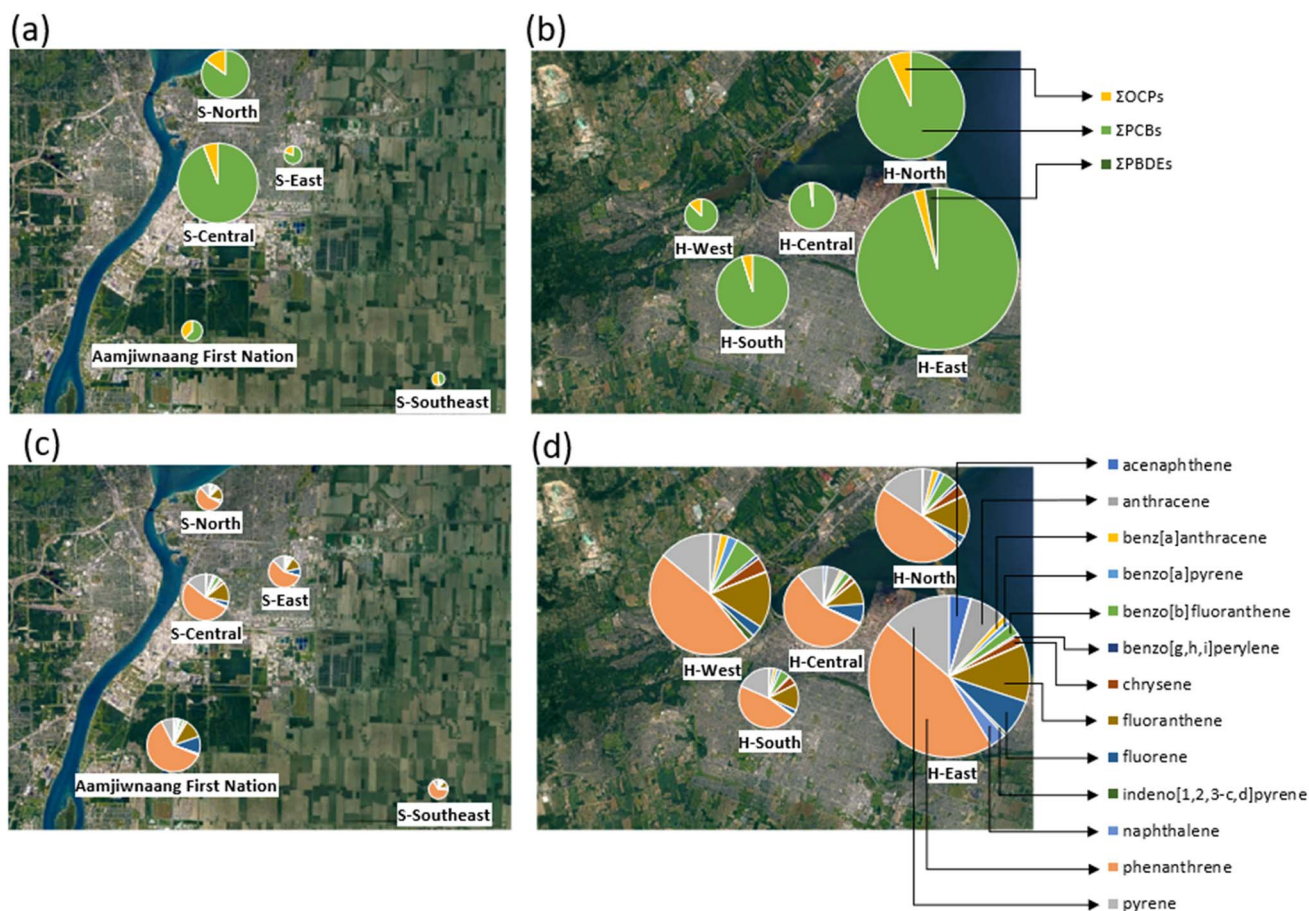


Fig. 1 Annual average spatial distribution of halogenated pollutants (a and b) and PAHs (c and d) in Sarnia (left: a and c) and Hamilton (right: b and d). The size of the pie charts corresponds with the relative abundance of the characterized compounds. The satellite image of study sites was obtained from Google [©2024 Google, Airbus, NOAA, Imagery © 2024 TerraMetrics, Map data © 2024].



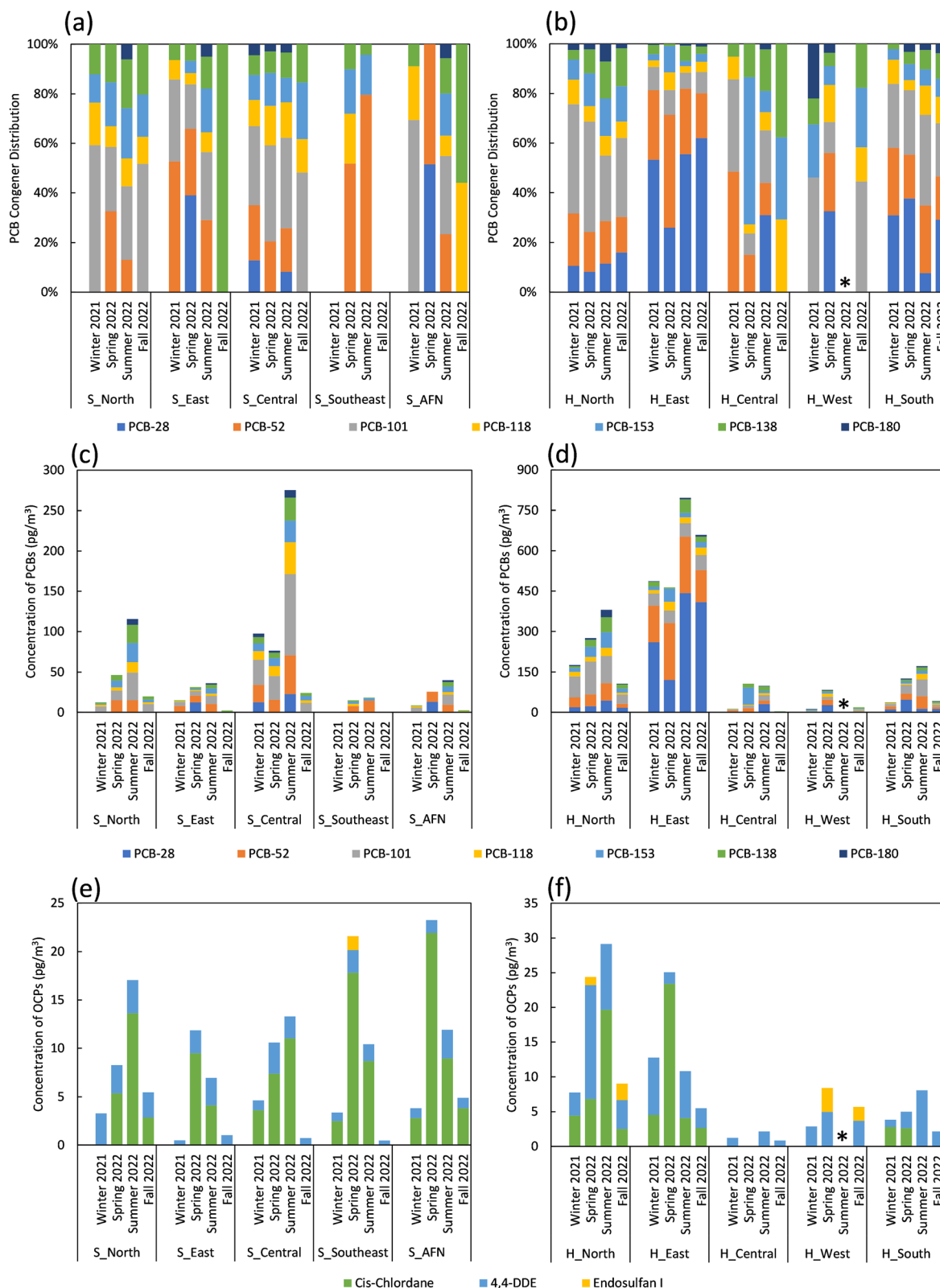


Fig. 2 Seasonal distribution of PCB congeners (a and b) and seasonal variation in air concentration ( $\text{pg}/\text{m}^3$ ) of PCB congeners (c and d) and OCPs (e and f) in Sarnia (left: a, c, & e) and Hamilton (right: b, d, & f). \*H\_West Summer data excluded.

The seasonal concentrations of PCBs are summarized in Fig. 2c and d. The concentration of PCBs fluctuated between seasons, with the highest concentrations observed during the

summer across all sites. This could be associated with increase in temperature, which cause PCBs to become more volatile and enter the gas phase: they could be volatilized from soil, old paints



and coatings.<sup>18,48</sup> They may also be emitted from old electrical equipment (produced before 1979) like transformers. However, this likely represents only a minor source of PCBs, since Canadian legislation eliminated all equipment containing >50 ppm of PCBs.<sup>56</sup> Alternative sources identified in recent years, termed “unintentional production” (UP) sources, include hazardous waste landfills, incineration, and metal production facilities.<sup>57</sup>

In the present study, PCB congener patterns varied between sites as highlighted in Fig. 2a and b: at most sites, the dominant congeners were the pentachlorinated biphenyls (PCB-101 and -118). In contrast, H\_East (an industrial site) was dominated by tri- and tetrachlorinated biphenyls (PCB-28 and -52). The variation in PCB congener distribution may be linked with the production and use of specific aroclors. Aroclors were mixtures of PCBs that used to be produced in North America prior to their ban in the 1970s. The elevated levels of pentachlorinated biphenyls in Sarnia and Hamilton sites could be associated with specific formulations like 1248, 1254 and 1260, which were viscous and among the most popular formulations at the time. The persistence of tri- and tetrachlorinated biphenyls in H\_East may be caused by dechlorination of higher chlorinated PCB congeners (penta- and higher), which break down over time in the environment.<sup>58</sup> However, it is more likely that the congeners in H\_East reflect the use of less viscous aroclor formulations as coatings and heat transfer oils. H\_North and H\_South displayed congener patterns dominated by PCB-101, PCB-28 and PCB-52 (Fig. 2b), which may result from wind-assisted fractionation of lighter congeners from H\_East. To determine whether there were any statistically significant differences among sampling sites, a Welch *t*-test was employed. Comparing the distribution of PCB congeners, H\_East (an industrial site), was characterized by congener pattern dominated by PCB-28 and -52 that averaged  $79 \pm 5\%$  of  $\sum_7$  PCBs, which is significantly higher than all other sites in Hamilton characterized by a combined average of  $30 \pm 21\%$  ( $p < 0.05$ ). This is consistent with the observations made by Li *et al.*,<sup>32</sup> who suggest that there are two distinct sources of PCB contamination in Hamilton, with one involving the use of historical aroclor (H\_East) and the other from non-aroclor sources which consist of “by-product” PCBs<sup>59</sup> used in paints and coatings in urban environments.<sup>59,60</sup> Zhan *et al.*<sup>55</sup> reported a similar trend in Quebec and British Columbia, Canada, highlighting unique PCB signatures arising from industrial and urban sources. While the present study did not characterize non-aroclor PCB congeners, the unique  $\sum_7$  PCB pattern in H\_East likely reflects emissions from UP sources.<sup>57</sup> Tri- and tetrachlorinated biphenyls (PCB-28 and -52) are commonly emitted alongside other PCBs from UP sources, increasing the fraction of PCB-28 and -52 up to 78% of  $\sum_7$  PCB congeners.<sup>57</sup> In the present study, PCB-28 and -52 averaged  $79 \pm 5\%$  of  $\sum_7$  PCBs in H\_East, and this suggests that the presence of the nearby metal recycling and production facilities could be potential sources of UP PCBs.

Fig. 2a reveals that PCB congener patterns also varied in Sarnia. S\_Central (an industrial site) dominated by pentachlorinated biphenyls (PCB-101 and -118) was significantly different from S\_East and S\_Southeast ( $p < 0.05$ ). PCB-101 and -118 made up  $52 \pm 8\%$  of  $\sum_7$  PCBs at S\_Central, while S\_East and S\_Southeast had a combined average of  $15 \pm 17\%$ . While

most sites (S\_AFN, S\_East, and S\_Southeast) were not statistically different from each other, the visual similarities between S\_North and S\_Central were likely influenced by their down-wind proximities. The data from Fig. 2c and d shows that S\_Southeast (a rural site) was the least polluted across all seasons. This agrees with previous studies that recorded lower PCB levels in rural locations compared to urban and industrial locations.<sup>18,53</sup>

**3.1.2 Polybrominated diphenyl ethers (PBDEs) and organic flame retardants.** PBDEs were employed in fireproofing a wide range of materials throughout the 20th century. In the present study, PBDE-28, -47, -99, and -153 were monitored, and found to be below detection limits in all sites across all seasons, except H\_East. PBDEs detected in H\_East include PBDE-47 and -99, which ranged between  $6\text{--}38 \text{ pg m}^{-3}$  respectively, with an annual average concentration of  $16 \text{ pg m}^{-3}$ . This is lower than the maximum reported PBDE (-47 and -99) concentration of  $28 \text{ pg m}^{-3}$  in Toronto.<sup>61</sup> This is consistent with previous findings that report PBDEs below  $30 \text{ pg m}^{-3}$  across rural and urban locations.<sup>18,51,53,61</sup> In downtown Chicago, USA, PBDE-47 and -99 averaged between  $14$  and  $27 \text{ pg m}^{-3}$ .<sup>62</sup> In recent years, PBDEs have been declining in the atmosphere.<sup>45,63</sup> Liu *et al.*<sup>45</sup> reported this trend near the Great Lakes, with average air concentrations ranging from  $3\text{--}21 \text{ pg m}^{-3}$  for the combined concentrations of PBDE-47 and -99. Higher concentrations corresponded to urbanized locations. They also showed the most significant decreasing trends with halving times between 5–11 years for both congeners. PBDEs were detected only in winter and fall in H\_East. Both congeners (-47 and -99) are likely associated with pentaPBDE formulation, which was one of the three most popular formulations from the 1970s to the early 2000s.<sup>64</sup> The occurrence of PBDE-47 and -99 in cold seasons is linked with their low tendency to volatilize and high particle-phase affinity at low temperatures.<sup>63</sup> Because PUF-PAS can trap both gases and particulate matter in the air, the concentration of particulate-bound PBDEs would be higher in the winter and fall. It is also possible that PBDE-47 and -99 undergo photodebromination during warmer seasons. Other studies have recorded similar trends in PBDEs concentrations in colder seasons compared with warmer ones.<sup>18,63</sup> Although PBDE-209 was not measured in the present study, its continued presence in some plastics, textiles, and imported products, and potential to degrade into more toxic congeners, has led to its increased detection in urban and industrial areas.<sup>46,63</sup>

Sources of PBDE-47 and -99 in the atmosphere range from electronics and computer hardware emissions to incineration and recycling processes of plastics and electronics. They could also be arising from the debromination of other brominated analogues (hexa- and higher) in the atmosphere.<sup>18,46,63,64</sup> We note that the sampler located at H\_East is only 500 m away from an automobile wrecking yard that could be a potential source of flame retardants.

TDCPP, a non-PBDE flame retardant, was also characterized in the present study, and it was only detected in H\_North in the fall at a concentration of  $14.2 \text{ ng m}^{-3}$ . Shoeib *et al.*<sup>65</sup> previously characterized this flame retardant in Toronto, ranging from below detection limit to  $1.2 \text{ ng m}^{-3}$  in the atmosphere. Other





studies have reported air concentration below  $0.07 \text{ ng m}^{-3}$  around the Great Lakes in Ontario, Labrador sea, Beaufort Sea, Hudson bay, Resolute Bay and around the Canadian Arctic Archipelago.<sup>66,67</sup> The high concentration of TDCPP in our study may be associated with a point source emission, considering the proximity of the PUF-PAS to a marina in H\_North. TDCPP has been increasingly utilized in plastics, furniture, and polyurethane foams in recent years, making it more ubiquitous in the environment.<sup>68</sup> This is evidenced by its high detection limit ( $3.9 \text{ ng m}^{-3}$ ) arising from high blank concentrations.

**3.1.3 Organochlorine pesticides (OCPs).** The OCPs identified in the present study are components and/or transformation products of the most popular pesticides in Canada from the 1940s, which have long since been regulated. The most abundant OCP at most sites was *cis*-chlordane, which was primarily employed in termite control.<sup>69</sup> It was used in farms, construction sites (for preserving stored materials and preparing building foundations), and private lawns. 4,4'-DDE (a degradation product of DDT (dichlorodiphenyltrichloroethane) and endosulfan I a component of endosulfan pesticide) were common insecticides used around the same period, with endosulfan being the last, among the three pesticides, to be restricted in Canada.<sup>70</sup> It was only detected during the spring and fall at concentrations below  $4 \text{ pg m}^{-3}$ . This may be because of its relatively short half-life compared to other OCPs.<sup>61</sup>

The other OCPs, *cis*-chlordane and 4,4'-DDE, were detected at all sites. Their combined concentrations, ranging from  $5\text{--}12 \text{ pg m}^{-3}$  in Sarnia and  $1\text{--}18 \text{ pg m}^{-3}$  in Hamilton, were within the lower range of OCP concentrations that have been previously reported in different parts of the world, which varied between  $0.1 \text{ pg m}^{-3}$  to  $19\,000 \text{ pg m}^{-3}$ .<sup>53,71,72</sup> OCPs, like other legacy POPs, show a declining trend in North America. Salamova *et al.*<sup>73</sup> recorded this decline around the Great Lakes, with halving times ranging from 9–13 years for chlordane and DDT, and <7 years for endosulfan. The most abundant OCP was *cis*-chlordane, which was predominantly detected at rural (S\_Southeast) and industrially influenced locations (H\_East, H\_North, and S\_AFN), but not urban (H\_Central) or suburban (H\_South and H\_West) locations. Contrasting trends in spatial distributions of OCPs was also reported in a GAPS study.<sup>18,53</sup> The elevated *cis*-chlordane concentration at S\_Southeast may reflect its historical use as an agricultural chemical. On the other hand, elevated concentrations of *cis*-chlordane at industrially influenced locations (H\_East, H\_North, and S\_AFN) may point to its use in construction and preservation. The seasonal distribution of OCPs in Sarnia and Hamilton (Fig. 2e and f respectively) is consistent with OCP behaviour, which is temperature dependent with a high gas-phase affinity.<sup>71,73</sup> Their elevated concentration in spring and summer is likely associated with volatilization of soil-bound OCPs under warmer temperatures.<sup>72</sup>

### 3.2 Spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAH) are emitted through combustion processes and are associated with increased cancer

risk.<sup>20,74</sup> The spatial distribution of priority<sup>74</sup> PAHs ( $\Sigma_{15}$  PAHs) in Sarnia and Hamilton is summarized in Fig. 1c and d, respectively. The data reveals that PAHs phenanthrene, pyrene, and fluoranthene were the dominant PAHs across all sites, with phenanthrene accounting for 45–65% of the targeted PAHs. This observation is consistent with reports by Peverly *et al.*<sup>62</sup> and Melymuk *et al.*<sup>75</sup> that recorded these three among the dominant PAHs in Chicago, USA and Toronto, Canada. These PAHs were also identified by Li *et al.*<sup>76</sup> near the Great Lakes, with phenanthrene accounting for 38–48% of priority PAHs. Peverly *et al.*<sup>62</sup> highlighted that Phenanthrene made up 48% of PAHs detected in Chicago, USA. In Canada, Zhan *et al.*<sup>55</sup> reported a similar profile, dominated by naphthalene and phenanthrene at most urban and industrial locations in British Columbia, Ontario, and Quebec, Canada. In the present study, naphthalene was below detection limit at most sites, likely due to its high volatility and poor retention on PUF-PAS samplers.<sup>33,77</sup>

The annual average concentration of  $\Sigma_{15}$  PAHs ranged from  $2.4\text{--}5.6 \text{ ng m}^{-3}$  in Sarnia, and  $7.4\text{--}42 \text{ ng m}^{-3}$  in Hamilton. These concentrations are comparable to previously reported concentrations in other urbanized and industrialized cities.<sup>17,20,51,53,78</sup> For example, Jariyasopit *et al.*<sup>20</sup> recorded  $5.0\text{--}33 \text{ ng m}^{-3}$  in neighboring Toronto. In a recent study, Zhan *et al.*<sup>55</sup> recorded  $\Sigma_{15}$  PAHs ranging from  $2.4\text{--}155 \text{ ng m}^{-3}$  ( $0.7\text{--}52 \text{ ng m}^{-3}$ , excluding naphthalene) across rural and industrial locations in Canada. Near the Great Lakes, Li *et al.*<sup>76</sup> recorded a declining trend in  $\Sigma_{15}$  PAHs, with concentrations ranging from  $0.05$  to  $19 \text{ ng m}^{-3}$  over a 20 year period. Higher levels of PAHs were detected in Hamilton compared to Sarnia because: (i) PAHs are associated with vehicular emissions, and the difference in PAH concentration between both cities may be caused by the population difference in Hamilton (over 500 000) compared to Sarnia (under 80 000);<sup>3,20</sup> Tevlin *et al.*<sup>79</sup> recorded a similar trend across Canada, with consistently higher concentrations of PAHs in densely populated and industrialized areas. (ii) PAHs also arise from steel production.<sup>3</sup> Hamilton, popularly known as “steel city”, is home to two major steel facilities and one carbon black production facility that contribute to PAH emissions. In contrast, Sarnia is dominated by petrochemical plants (three oil refineries and one carbon black production facility) among 60 other chemical facilities.<sup>23</sup>

Fig. 3 shows the seasonality of priority PAHs in Sarnia and Hamilton. The data reveal that the highest concentrations of PAHs were observed mostly in the spring (March 2022–June 2022) with average temperatures of  $10^\circ\text{C}$ . This observation agrees with Melymuk *et al.*<sup>75</sup> that recorded a similar trend in Toronto. This is possibly because cold air closer to the ground traps primary pollutants, leading to a build-up in ambient ground-level concentrations (deployment had an average of 2 meters from the ground). It is also likely that gas-phase partitioning of relatively abundant PAHs like Phenanthrene is responsible, which would be particulate-bound at sub-zero temperatures of winter, affecting its uptake by PUF-PAS.<sup>40,41,75,80</sup> Additionally, temperature inversion prevents these pollutants from reaching higher atmospheric altitudes (above ground level). In winter, elevated concentrations of PAHs may be linked to the same temperature driven processes like





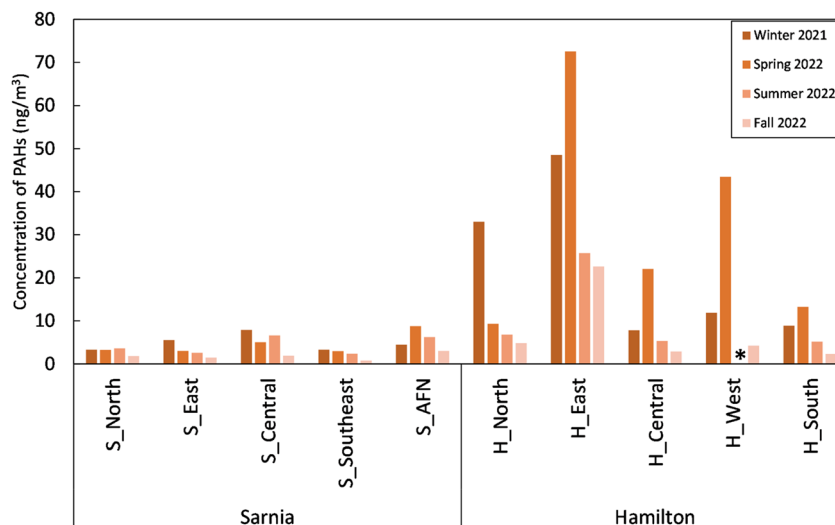


Fig. 3 Seasonal variation in air concentration ( $\text{ng m}^{-3}$ ) of  $\Sigma_{15}$  priority PAHs in Sarnia and Hamilton. \*H\_West Summer data excluded.

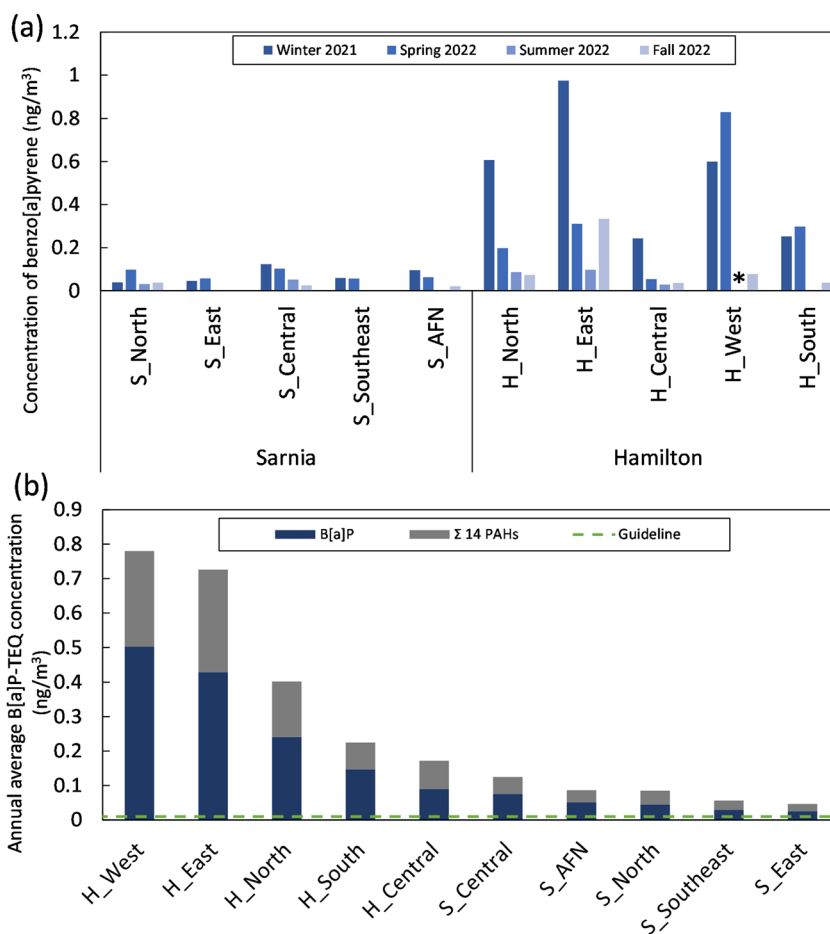


Fig. 4 Seasonal variation in air concentration ( $\text{ng m}^{-3}$ ) of B[a]P in Sarnia and Hamilton (top: a). The annual average B[a]P toxic equivalent concentration ( $\text{ng m}^{-3}$ ) of B[a]P and other  $\Sigma_{14}$  priority PAHs in Sarnia and Hamilton, in descending order (bottom: b). The dashed line in green represents the Ontario Ambient Air Quality criterion for annual B[a]P concentration ( $\text{ng m}^{-3}$ ). \*H\_West Summer data excluded.

temperature inversion, as well as limited sunlight, which is necessary for breaking down atmospheric PAHs through photooxidation.<sup>20,25,81</sup> Household heating, particularly with

wood-burning stoves, represents an additional source of PAHs in the winter. However, retene (a characteristic PAH of wood burning) was not quantified in the present study.<sup>82</sup>



Among the priority PAHs, benzo[a]pyrene (B[a]P) is one of the most carcinogenic. For this reason, B[a]P concentration is the most accepted and regulated determinant of population health risk from PAHs.<sup>74,81</sup> Fig. 4a shows the seasonal fluctuation in B[a]P concentration, which, conversely to Fig. 3, shows that it is highest mainly in the winter. This suggests that more abundant PAHs drive levels of  $\Sigma_{15}$  PAHs in the spring compared to winter, including phenanthrene and fluoranthene. Both PAHs (phenanthrene and fluoranthene) are significantly more volatile than B[a]P.

The annual average distribution of B[a]P, as summarized in Fig. 4b, reveals that all sites in Sarnia and Hamilton exceeded the Ontario Ambient Air Quality criterion of  $0.01 \text{ ng m}^{-3}$ .<sup>50</sup> Tevlin *et al.*<sup>79</sup> reported similar across 62 locations (rural, urban, and industrial) in Canada, except in the arctic. Though the concentrations exceeded the Ontario guideline, the study highlights a decreasing trend in atmospheric PAHs, directly influenced by reduced emissions from metal manufacturing industries. In the present study, B[a]P ranged from  $0.03\text{--}0.08 \text{ ng m}^{-3}$  in Sarnia, and  $0.09\text{--}0.5 \text{ ng m}^{-3}$  in Hamilton, below previously recorded averages ranging from  $0.1$  to  $1.2 \text{ ng m}^{-3}$  in Hamilton.<sup>79</sup> This is equivalent to an increased inhalation cancer risk ranging between  $3 \times 10^{-6}\text{--}7 \times 10^{-6}$  in Sarnia, and  $8 \times 10^{-6}\text{--}40 \times 10^{-6}$  in Hamilton.<sup>20</sup> Despite exceeding the Ontario Ambient Air Quality criterion, B[a]P in this study was in the lower range of previously reported concentrations in other parts of the world. Bukowska *et al.*<sup>83</sup> compiled B[a]P concentrations across multiple locations and found that it ranged broadly between  $0.05\text{--}20 \text{ ng m}^{-3}$  in Europe and Asia. In Canada, Jariyasopit *et al.*<sup>20</sup> recorded B[a]P ranging from  $0.03\text{--}0.26 \text{ ng m}^{-3}$  in Toronto, while Tevlin *et al.*<sup>79</sup> reported concentrations  $<0.01 \text{ ng m}^{-3}$  in the Canadian arctic. In USA, Peverly *et al.*<sup>62</sup> reported B[a]P concentrations ranging from  $0.15\text{--}0.38 \text{ ng m}^{-3}$  in densely populated regions of Chicago.

Other PAHs also contribute to cancer risk. Nisbet and Lagoy<sup>74</sup> proposed a method for estimating the toxicity and carcinogenicity of other PAHs in reference to B[a]P. Estimating the B[a]P toxic equivalent concentration (B[a]P-TEQ) of the other 14 priority PAHs considered in the present study, raised the B[a]P equivalent concentration in each site by 53–94% of their initial B[a]P concentration. The annual average B[a]P toxic equivalent (TEQ) concentration contributed by all 15 PAHs (including B[a]P) is summarized in Fig. 4b. Total B[a]P-TEQ concentration ranged from  $0.05\text{--}0.13 \text{ ng m}^{-3}$  in Sarnia, and  $0.17\text{--}0.78 \text{ ng m}^{-3}$  in Hamilton. This is equivalent to an additional increase in PAH-associated inhalation cancer risk between  $2 \times 10^{-6}\text{--}4 \times 10^{-6}$  in Sarnia, and  $7 \times 10^{-6}\text{--}20 \times 10^{-6}$  in Hamilton.<sup>20</sup> However, the inhalation cancer risk associated with these 15 PAHs does not reflect the total risk of the population in both cities, which is a cumulative result of multiple carcinogen exposures. For example, Larsen *et al.*<sup>84</sup> estimated that cancer risk from 2 VOCs in the Aamjiwnaang First Nation exceeded regulatory guidelines and the provincial average. However, because data on other unidentified toxicants remains limited, the overall cumulative risk from industrial and vehicular emissions is still unclear.

### 3.3 Spatial and temporal distribution of metals

Metals represent a broad class of air contaminants, some of which have been linked to endocrine disruption activities and increased cancer risk.<sup>85</sup> Metals typically bind to soil particles, allowing them to persist in the atmosphere when (re)suspended by natural or anthropogenic activities.<sup>86</sup> Twelve metals were characterized in the summer and fall in Sarnia and Hamilton including aluminum, barium, calcium, chromium, cobalt, copper, iron, lead, nickel, potassium, silver, and zinc. Their sum concentrations decreased at all sites between summer and fall, except H\_East which increased by 21% in the fall (Fig. 5). The decrease in metals concentrations between both seasons is consistent with PM<sub>2.5</sub> behavior reported in Ontario.<sup>86</sup> In Sarnia, metals ranged between  $4\text{--}11 \text{ } \mu\text{g m}^{-3}$  in summer and  $0.4\text{--}5 \text{ } \mu\text{g m}^{-3}$  in fall. In Hamilton, they ranged from  $11\text{--}57 \text{ } \mu\text{g m}^{-3}$  in summer and  $3\text{--}72 \text{ } \mu\text{g m}^{-3}$  in fall. The concentration observed in Sarnia was below the previously reported concentration by Olawoyin *et al.*,<sup>24</sup> which ranged from  $37\text{--}94 \text{ } \mu\text{g m}^{-3}$ . This difference is likely due to the sampling techniques: Olawoyin *et al.*<sup>24</sup> employed active samplers with polycarbonate filters that collect PM<sub>2.5</sub>–PM<sub>10</sub>, as opposed to the present study which employed passive sampling with PUF filters that primarily collect PM<sub>2.5</sub>.<sup>35</sup> Metal concentration in the present study agrees with a recent GAPS study that highlighted they typically ranged between  $<10\text{--}100 \text{ } \mu\text{g m}^{-3}$  in most cities around the world (including Toronto, Canada), using PUF-PAS.<sup>19</sup> The only site that exceeded the  $100 \text{ } \mu\text{g m}^{-3}$  mark in this study was H\_South (a residential site), where metals were detected at  $1420 \text{ } \mu\text{g m}^{-3}$ . This concentration far exceeds even total ambient particulate matter (PM<sub>2.5</sub>–PM<sub>10</sub>) that have previously been reported in urban locations and is likely due to contamination.<sup>24,25,87</sup> Consequently, this data point (H\_South Summer 2022) was removed from the analysis.

Fig. 5 reveals a shift in dominant metal species between summer and fall. In summer, Sarnia's atmosphere was dominated primarily by calcium likely from construction activities and dust control, while iron dominated in Hamilton, a common emission from steel production.<sup>25,88</sup> The fall was characterized mainly by iron and aluminum across all sites, except H\_North and H\_East where zinc was also detected at concentrations of  $3.1 \text{ } \mu\text{g m}^{-3}$  and  $13 \text{ } \mu\text{g m}^{-3}$ , respectively. The presence of zinc at industrial and urban sites (H\_North and H\_East), aligns with previous reports on their elevated concentrations in urban locations.<sup>19</sup> Iron and aluminum are among the most abundant crustal metals and may be attributed to resuspension of dust. This agrees with Mastin *et al.*<sup>19</sup> that also detected both metals across GAPS monitoring locations. Most metals detected in the present study were below the Ontario Ambient Air Quality criterion, except iron and cobalt.<sup>50</sup> In the fall, iron was detected in H\_North, H\_East, and H\_Central at concentrations 1.5–14 times higher than the 24 hour threshold of  $4 \text{ } \mu\text{g m}^{-3}$ . While in the summer, cobalt (a potential carcinogen)<sup>89</sup> was also detected in S\_North, S\_East, and H\_West 1.9–46 times higher than the 24 hour threshold of  $0.1 \text{ } \mu\text{g m}^{-3}$ .<sup>50</sup>

However, it is important to note that metals were estimated using previously reported uptake rates, which range from 0.3–8



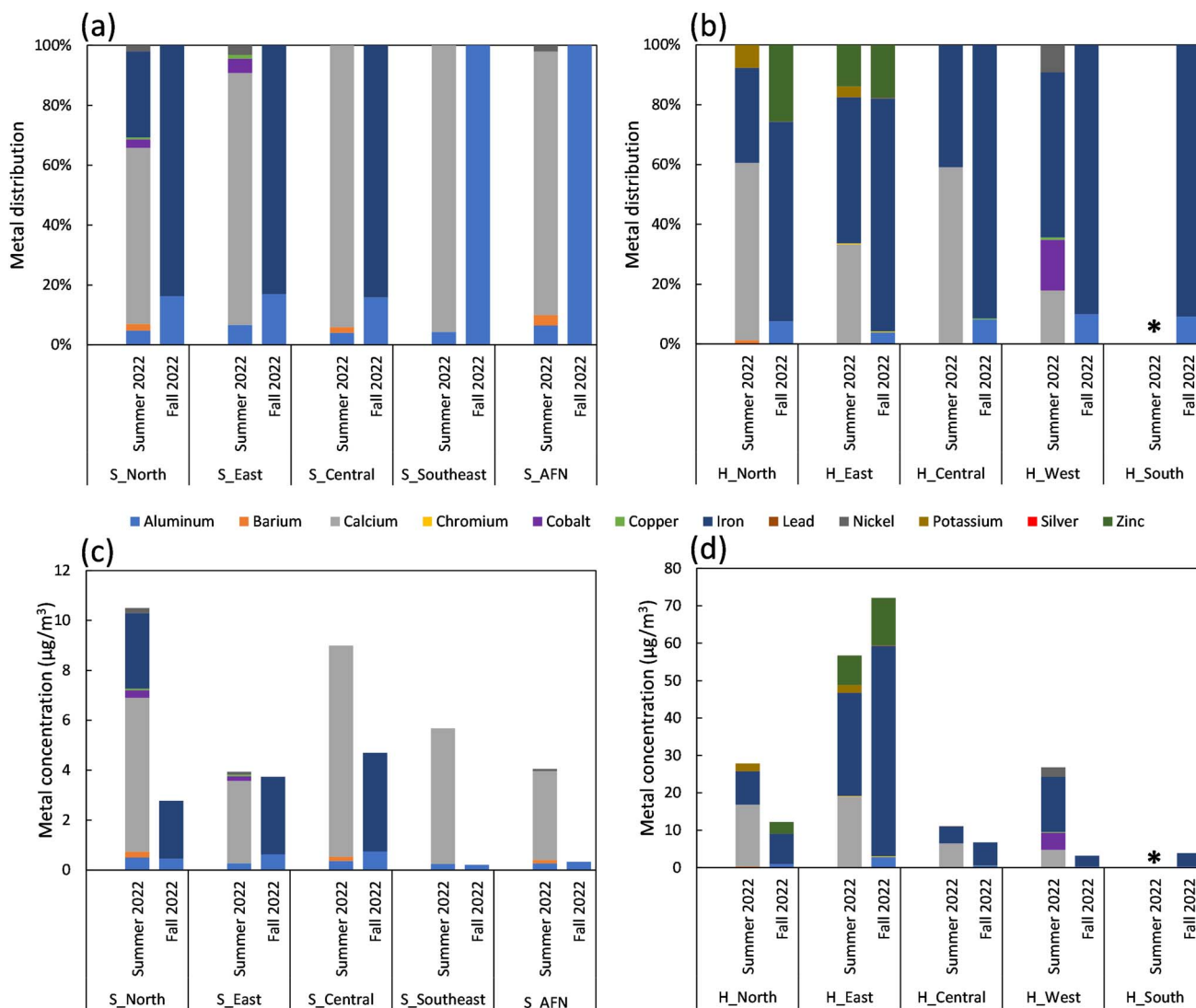


Fig. 5 Seasonal metal profile (a and b) and seasonal variation in air concentration ( $\mu\text{g m}^{-3}$ ) of metals (c and d) in Sarnia (left: a and c) and Hamilton (right: b and d). \*H\_South Summer data excluded.

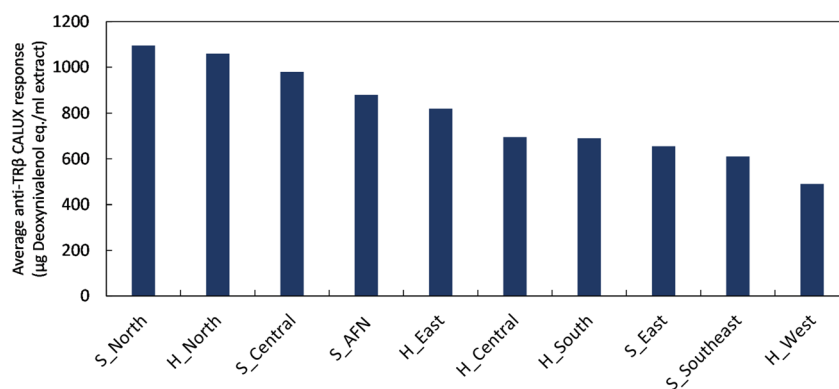


Fig. 6 Average anti-androgenicity activity determined by anti-TRP CALUX response ( $\mu\text{g Deoxynivalenol eq. per ml extract}$ ) from PUF extracts collected in winter 2021 and summer 2022, in descending order.

$\text{m}^3 \text{ day}^{-1}$  (aluminum, iron, and zinc).<sup>35</sup> Metals with unknown uptake rates were estimated using a default value of  $4 \text{ m}^3 \text{ day}^{-1}$ , which is the average rate reported using PUF-PAS.<sup>35</sup> This increases the uncertainty in estimating the concentrations of metals in the present study. However, it still provides a semi-quantitative estimate of metals in the atmosphere, which is essential for understanding their distribution.

### 3.4 Screening for biological activity (CALUX assays)

Endocrine disruption, which refers to mimicry or interference of normal hormone function, can be measured through *in vitro* assays such as CALUX.<sup>26,29</sup> We analyzed winter and summer passive air sample extracts from all sites in Sarnia and Hamilton for ER and AR disruption using ER $\alpha$  and anti-TR $\beta$  CALUX assays. The results revealed that estrogenicity activity was below the detection limit at all sites in both seasons, whereas anti-androgenicity activity was elevated at all sampling sites. Average anti-TR $\beta$  response ranged from 490–1100  $\mu\text{g}$  Deoxynivalenol eq. per ml extract in both cities (Fig. 6). The present study agrees with Kennedy *et al.*<sup>90</sup> that reported no estrogenicity activity in outdoor air in Brisbane, Australia. In contrast, elevated estrogenicity activity has been reported in Toronto, Canada and Flanders, Belgium likely due to variations in both sampling techniques and chemical composition.<sup>27,91</sup> Anti-androgenicity is the ability of a chemical to block male hormones (androgens) from binding.<sup>31</sup> This has been linked with abnormalities in male fetal development in animal studies and an increased risk of preterm birth of male fetuses during human pregnancy.<sup>30,31,92</sup> Until now, atmospheric anti-androgenicity activity was unknown in Canada, however, anti-androgenic pesticides and pharmaceuticals have previously been identified in surface water 57 km away from Hamilton.<sup>93</sup> In general, its elevated activity was related to both urban and industrial sampling locations in both cities, except S\_North and S\_AFN which are residential locations.

To determine if there were any correlations between the measured contaminants and the measured anti-androgenicity activity, a Pearson correlation analysis was performed with the results summarized in Table S15. The analysis revealed a statistically significant correlation ( $p$ -value < 0.05) between anti-androgenicity activity and PCB-101, -118, and -153. These  $\Sigma_3$  PCBs were the most abundant PCB congeners at most sites, contributing to up to 80% of the combined concentrations of the targeted PCBs. Despite the statistically significant correlation between these PCBs (-101, -118, and -153) and anti-androgenicity activity, there is still a mismatch between their concentrations and the endocrine disruption activity at some locations (S\_North and S\_AFN). S\_North, a residential location that recorded the highest level of anti-androgenicity activity, is less than 350 m from a golf course and 250 m from a major highway that is often congested with long lines of heavy-duty diesel trucks waiting to cross into the United States. It is possible that pesticides from the golf course and traffic emissions may be more relevant than typical industrial contaminants when assessing endocrine disruption and related impacts to human health.<sup>93,94</sup> Contrary to studies that have previously

reported PAHs as major contributors to anti-androgenicity activity, there were no correlations between them in the present study.<sup>26</sup> Since PAHs are major components of traffic emissions, it is more likely that pesticides are responsible for the anti-androgenicity activity observed at S\_North. On the other hand, S\_AFN is less than 7 km away from 6 petrochemical facilities and within 25 km of 54 others,<sup>23</sup> which suggests that (unknown) industrial SVOCs emissions contribute significantly to the observed anti-androgenicity. While the puzzlingly high CALUX activities observed at S\_North and S\_AFN could not be explained by the compounds targeted in the present study, it may still be possible to identify unknown endocrine disrupting chemicals using non-targeted screening (NTS).<sup>32,95,96</sup> For example, our team has recently identified halogenated chemicals emitted in Hamilton and Sarnia,<sup>32</sup> and future work will investigate the potential correlation between their emission and CALUX response.”

## 4. Conclusion

In summary, this research provides a comprehensive characterization of the seasonal and annual levels of SVOCs and metals in two industrialized cities in Ontario, Canada (Sarnia and Hamilton). The results showed a consistent pattern of industrial sites characterized by higher concentrations of air pollutants compared to rural or urban locations. Halogenated pollutants, dominated by PCBs, were below regulatory limits, whereas PAH concentrations, including benzo[*a*]pyrene, exceeded the regulatory guideline at all sampling locations.<sup>50</sup> Metals were the most abundant pollutants, comprised primarily of crustal metals (aluminum, iron, and calcium) that are non-carcinogenic to humans under the IARC classification.<sup>89</sup> CALUX experiments revealed elevated levels of anti-androgenicity activity in both cities, especially at locations most impacted by industrial emissions. Correlation analysis suggests that the presence of regulated pollutants, such as PCBs-101, -118, and -153, could potentially explain this activity at some but not all locations. This raises the question of whether there are unregulated endocrine-disrupting chemicals, and underlines the need to expand the list of monitored pollutants in industrialized cities.

## Author contributions

Emmanuel C. Tolefe: data curation, formal analysis, methodology, writing – original draft. Robert Healy: conceptualization, writing – review & editing. Sonya Kleywegt: conceptualization, formal analysis, resources, writing – review & editing. Andre J. Simpson: conceptualization, writing – review & editing. Myrna J. Simpson: conceptualization, funding acquisition, writing – review & editing. Karl J. Jobst: conceptualization, methodology, funding acquisition, supervision, writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.





## Data availability

The data supporting this article have been included as part of the SI. Supplementary information is available. See DOI: <https://doi.org/10.1039/d5em00493d>.

## Acknowledgements

This study was funded by the Canada Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council (NSERC), the Newfoundland and Labrador Department of Industry, Energy and Technology, and the Government of Ontario (Canada-Ontario Agreement grant #2711). Such support does not indicate endorsement by the Government of Ontario of the contents or conclusions of this contribution. The authors are grateful to the Environment Committee of the Aamjiwnaang First Nation for their support and valuable discussions. Mahin Hashemihedeshi and Jake Breen are gratefully acknowledged for their assistance with sample collection and preparation. KJJ is grateful to Dr. Paul Helm for his assistance regarding passive sampling.

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