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Assessment and Characterization of Alkylated PAHs in Selected Sites across Canada

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Abstract: Alkylated polycyclic aromatic hydrocarbons (alkyl-PAHs), dibenzothiophenes (DBTs), and unsubstituted polycyclic aromatic hydrocarbons (PAHs) are naturally present in fossil fuels. Thus, they can be considered as candidates for markers of pollution from petrogenic emissions such as those from traffic. Consequently, ambient air concentrations of alkyl-PAHs, DBTs, and PAHs at selected ambient air monitoring sites of various types (residential, near-road, urban-industrial, agricultural) in Montréal, Toronto, Hamilton, Edmonton, and Simcoe, were evaluated from 2015 to 2016 to study their profiles, trends, and assess potential primary emission source types. Alkyl-PAHs were the prevailing species at all sites and were most elevated at the high-traffic impacted near-road site in Toronto which was also accompanied by the highest unsubstituted PAH concentrations. Comparison of relative abundance ratios of alkyl-PAH and PAH groupings suggests that the profile differences amongst sites were small. Source attribution with cluster grouping suggested similar emission sources of alkyl-PAH and PAH at all sites, with the exception of Hamilton which was particularly impacted by additional emission sources of PAHs. The Principal Component Analysis further indicated distinct PAC profiles at HWY401 and HMT that have the same variability of "heavy PACs" but differ in "medium mass PAHs" sources. Seasonality affected the bulk species trends (alkylated naphthalenes, fluorenes, and phenanthrenes/anthracenes), especially at sites with lower concentrations of these species. This study findings confirm a notable contribution of traffic emissions to alkyl-PAH levels in urban ambient air at the studied Canadian sites, and show that enhanced speciation of alkyl-PAHs provides more data on ambient air quality and additional health risks, and can also help distinguish petrogenic-influenced sources from other sources.

Keywords: alkylated-PAHs; DBTs; traffic; urban pollution; air quality

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1. Introduction

Polycyclic aromatic compounds (PACs) are hydrocarbons composed of fused benzene rings (unsubstituted PAHs) that may have alkyl sidechains (alkyl-PAHs) or ring carbon atoms replaced by heteroatoms (S, O, N). As they are toxic and ubiquitous in nature, they are considered prevalent atmospheric pollutants [1]. PAHs have already been well characterized in the environment and included in many monitoring programs around the globe for compliance with air quality regulations and objectives [2–5]. These compounds are known to be persistent in the environment, toxic, and carcinogenic to human health [6–10], thus indicating that long-term exposure poses a risk to living organisms. Unsubstituted PAHs have numerous origins usually associated with thermal decomposition of organic matter, such as from vehicular emissions and coal/wood/biomass burning [11,12], and often have common emission sources with alkyl-PAHs related to petrogenic materials whereof they may be released into the environment through fugitive emissions and incomplete combustion [13,14]. Given common sources/origins, a strong relationship has been observed between unsubstituted PAHs and alkyl-PAHs in petrogenic-related emissions, and described as a characteristic fingerprint of their emission sources [15–17].

Alkyl-PAHs are currently not included in routine monitoring programs, and the lack of available data on their fate and characterization raises concerns regarding their cumulative impacts on human and ecological health [13,18] as well as their combined effects with priority pollutants already monitored and regulated. Alkyl-PAHs are naturally present in bitumen deposits, petroleum, coal, and volcanic eruptions. They can also be released as pollutants into the environment by anthropogenic activities through the combustion of fossil fuels related to transportation, power generation and heating, and through numerous industrial processes like organic chemical, mining, and refining/processing [19–21]. Given the multitude of potential emission sources, increasing urbanization/traffic, and consumption of fossil fuels, alkyl-PAHs have become ubiquitous emerging pollutants, and the effects of these pollutants more relevant in the environment. Their pervasive presence raises concerns as toxicological studies suggest that many alkyl-PAHs have higher toxic and mutagenic potency than corresponding unsubstituted PAHs [22–26]. It has been thought that the toxicity effects (reactivity and degradation) of alkyl-PAHs are largely dependent on the positioning of the alkyl substituents on the fused aromatic rings [27]. Alkyl-PAHs may induce oxidative stress, reactive oxygen species (ROS) production and toxicity [28–30], organ damage [31], early life stage inhibition, and DNA damage [32–35] in biological systems including humans. These aromatic compounds are also known to condense into airborne particular matter (PM) and black carbon affecting air quality and radiative transfer which has climate change impacts. Recent findings on the fate of alkyl-PAHs in ambient air in Canada indicate their concentrations at industrial and urban sites that are impacted by petrogenic emissions are considerably elevated relative to their corresponding unsubstituted PAHs that many are regulated [15,36–39]. These studies determined that the most elevated alkyl-PAH levels were observed near industrial-petrogenic activities and in high-volume traffic urban areas. This may suggest that their petrogenic origins can make them convenient markers for tracing and quantifying the contribution of diesel- and gasoline-powered engine exhaust (traffic, transport, industrial equipment) to the atmosphere in urban areas.

Another important group of PAC pollutants often present in the environment in relation to petrogenic emissions are dibenzothiophenes (DBTs), both unsubstituted and alkylated. DBTs, similar to alkyl-PAHs, are enriched in bitumen and therefore are markers of fossil fuels in traffic and petroleum-related emissions [13,40]. These sulfur-containing alkyl-PAHs are more soluble than their corresponding hydrocarbon counterparts and therefore pose a higher risk of pollution through enhanced mobility and bioavailability [41]. Published toxicological studies identify DBTs as toxic and potentially carcinogenic pollutants to human and environmental health [42–45].

Since recent findings in Canada confirm that petrogenic-related emissions from traffic account for a large proportion of air pollutant emissions in large human agglomerations [20,46,47], this raises concerns about the contribution of petrogenic related PACs to traffic and urban related emissions and the need for revealing potential health risks associated with exposure to this pollutant group in urban air. Consequently, measurements of the individual and grouped alkyl-PAHs, DBTs, and unsubstituted PAHs were carried in a one-year (2015–2016) pilot study at five sites of various classification types in Canada. The ambient air quality at those sites was affected to a different degree by traffic and petrogenic emissions. Hence, the objectives of the current study were to assess and characterize the presence of these PAC groups in ambient air collected at different sites across Canada and to identify potential sources of PACs at those sites. Differences between PACs characteristics at these sites were compared with observations in the Athabasca Oil Sands Region (Canada), influenced by bitumen exploitation and petroleum processing emissions. This is the first study to characterize and compare alkyl-PAH, DBT, and PAH profiles across different cities in Canada and in relation to impacts from traffic and petrogenic emissions. These findings will assist in estimating contributions of alkylated species (including DBTs) to traffic and urban related emissions with a higher degree of specificity of identified sources. Ultimately, this will lead to better understanding and quantifying the contribution of emissions from the transportation sector in Canada and to justifying the potential inclusion of alkyl-PAHs monitoring in the National Air Pollution Surveillance (NAPS) monitoring program. Expanding PAH speciation to toxic alkylated species will provide better evidence of the cumulative impacts of pollution leading to improved health risk assessment.

2. Experimental

2.1. Study Sites

Time-integrated PAC samples were collected at five National Air Pollution Surveillance (NAPS) monitoring sites located in Montréal (MTL), Toronto (HWY401), Hamilton (HMT), Simcoe (SIM), and Edmonton (EDM) as shown in Figure 1. The sampling site located in the Athabasca oil sands area (57°01′36.7″ N; 111°30′03.0″ W; AMS11) was chosen for comparison; this industrial site is influenced by bitumen mining and petroleum processing emissions [16].

Figure 1. Location of the monitoring sites with reference to the map of Canada.

According to the NAPS classification framework, the sampling sites in MTL, HWY401, HMT, and EDM are classified as large urban areas, while SIM is a non-urban site (Table 1). In terms of local land use, the MTL, HMT, and EDM sites are considered residential, HWY401 as a commercial site and SIM as an agricultural site. The near-road site in Toronto is influenced primarily by transportation. It is located in a suburban Toronto area, south of the eastbound lanes of Highway 401 (hereafter referred to as HWY401), one of the busiest highway sections in North America. The residential sites in HMT and EDM are influenced by industrial emission point sources. The HMT site is influenced by nearby steel making industry and heavy machinery and transportation which supports this industry. The EDM site is located in a residential area potentially influenced by residential heating, within a few kilometers of a freeway and near petrochemical refineries. The MTL site is located in a suburban borough at the eastern end of the Island of Montréal. It is considered a general population exposure site, and like EDM is potentially influenced by residential heating activities during colder periods and by local traffic. The regional background site in SIM is situated near agricultural-based areas.

Table 1. Description of the NAPS sampling locations.

Site (NAPS ID)	Abbreviation	Location	Source Sector
Montréal, QC (050129)	MTL	45°39′06.6″ N 73°34′25.1″ W	PE, LU, R, P6
Toronto, ON (060438)	HWY401	43°42′39.9″ N 79°32′36.0″ W	T, LU, C, P6
Hamilton, ON (060512)	HMT	43°15′28.0″ N 79°51′42.0″ W	PS, LU, R, P6
Simcoe, ON (062601)	SIM	42°51′24.7″ N 80°16′10.7″ W	RB, SU, A, P2
Edmonton, AB (090132)	EDM	53°29′09.6″ N 113°27′52.6″ W	PE, LU, R, P6

Site type (T: transportation influenced; PS: point-source influenced; PE: general population exposure; RB: regional background); Urbanization (LU: large urban area; SU: small urban; NU: non-urban); Local land use classification (A: agricultural; C: commercial; R: residential; I: industrial); Population (P1: <500; P2: 500–9999; P3: 10,000–49,999; P4: 50,000–99,999; P5: 100,000–149,999; P6: ≥150,000).

2.2. Sampling and Chemical Analysis

All ambient air samples were collected using high volume air samplers from September 2015 to September 2016. The samplers were operated using a one-in-six-day schedule with a 24 h sampling time (midnight–midnight) according to the procedure used in the NAPS program.

Details regarding PAC sampling and analysis are described in the Supplementary Information [48] and elsewhere [16]. Briefly, PM_{30}-bound and gaseous PACs were collected on a Teflon-coated borosilicate glass fiber filters and two polyurethane foams (PUF, placed downstream from the filter), respectively. After sampling, both media were wrapped separately, shipped back to the laboratory, and stored at −10 °C until analysis. The filter and PUFs were Soxhlet-extracted together according to the USEPA method TO-13A [49]. The extracts were consequently cleaned up and column-fractionated using benzene as the eluent to collect the analytes of interest. PACs were analyzed by gas chromatography coupled to mass spectrometry (GC-MS), and quantified by the internal standard method using selected ion monitoring (SIM). Samples were accompanied by field blanks that were collected once every four months at each of the monitoring stations. Field blanks consisted of setting up the sampler the same way as for a regular sample (and the same sampling time duration), but with the sampler pump not running [49].

2.3. Quality Assurance/Quality Control

For quality control, field blanks, control samples, and laboratory blanks were collected and subjected to the same extraction and fractionation procedures as ambient air samples. All samples were field blank-corrected. The analytical method detection limits (MDL) were calculated from data derived from seven replicate analyses of clean PUF/filter pairs spiked with PAC standards at 0.02 μg/μL. MDL based on nominal air volume of 720 m^3 ranged from 2 to 51 pg/m^3, and surrogate recoveries spiked into ambient air samples prior to the extraction ranged from 64% to 108% (Table S3 of the Supplementary Information (SI)).

2.4. Description and Grouping of Studied Compounds

In this study, polycyclic aromatic compounds (PACs) comprising 24 unsubstituted polycyclic aromatic hydrocarbons (PAHs), 72 alkylated polycyclic aromatic hydrocarbons (alkyl-PAHs), dibenzothiophene (DBT), and 14 alkylated DBTs were determined. The PACs include individually determined compounds and those determined as analyte groups C1 to C4 alkylated PAHs and DBTs (see Section S1 in SI for more details). Chemical names and details about the monitored chemicals are listed in Table S1. Only analytes with molecular weights above 140 g/mol were examined due to the low collection efficiency for naphthalene sampled on PUFs using high-volume TSP samplers [50]. The fate of PACs varies depending on their volatility. Therefore, in order to explore differences in their variability, the PAHs, alkyl-PAHs, and DBTs were separated into six groups: VOL-PAHs, SVOL-PAHs, and PM-PAHs; and G1 (VOL-alkyl-PAHs), G2 (SVOL-alkyl-PAHs), and G3 (PM-alkyl-PAHs) (description in Table S2 in SI).

2.5. Data Analysis and Processing

For the calculation of summary statistics, values below MDL were replaced by 1/2 MDL; for other statistical calculations, such as Non-parametric Kruskal–Wallis one-way Analysis of Variance (ANOVA), Grubb's test ($p < 0.05$) was used for the identification and removal of outliers, and all missing data values were excluded from the analysis. Factor Analysis (FA) and Principle Component Analysis (PCA) were performed using STATISTICA ver. 9.1 (StatSoft Inc., Tulsa, OK, USA). The multivariate analyses were used to group variables with similar temporal variabilities in order to identify potential emission source categories. Normalized varimax was applied for factor rotation in PCA. Only analytes at concentrations above MDLs for at least 50% of measurements were used for the multivariate analysis. Consequently, 19 individual PACs and six alkyl-PAHs and DBTs groups were retained for further analysis (PAC description in Section S1 in SI).

3. Results and Discussion

3.1. General Characteristics of Ambient PACs in Ambient Air

Figure 2A,B show the spatial median concentrations of alkyl-PAHs and unsubstituted PAHs at all sites; summary statistics for PAC (gaseous + particulate) compositions (PAHs, alkyl-PAHs, DBTs) are summarized in Tables S4–S9 (Supplementary Information). Amongst the NAPS sites, the highest median concentration (65 ng/m^3) of alkyl-PAHs was observed at the HWY401 site located close to the major highway 401. As previously reported [16,17] and shown in Figure 2A, elevated concentrations of alkyl-PAHs in the Oil Sand Region (AMS11) represent the influence of regional petrogenic sources associated with exploitation/mining and processing of fossil fuels. Thus, the observed elevated concentrations of alkyl-PAHs at the HWY401 site may indicate the contribution of traffic emissions associated with combusted fossil fuels. At other NAPS sites, alkyl-PAH levels were considerably lower with median concentrations ranging from 12 to 30 ng/m^3. As shown in Figure 2B, the most elevated levels of unsubstituted PAHs were also observed at the HWY401 (median = 24 ng/m^3) followed by Hamilton (median = 20 ng/m^3). The higher levels of PAHs in Hamilton, as compared to urban sites in Montréal and Edmonton, suggest impacts from additional sources other than traffic, such as PAH emissions originating from nearby steel industries [51–53].

Dibenzothiophenes (DBTs), another class of PACs enriched in fossil fuels, exhibited a similar spatial distribution pattern as alkyl-PAHs (Figure 2C). DBTs are sulfur containing alkyl-PAHs that are partially removed from raw petrogenic materials during desulfurization and other cleaning and refining processes for the purpose of oil upgrading [54]. According to the Environment Canada report, sulfur content in motor gasoline in Canada during 2015–2016 ranged from 16 to 18 mg/kg, in low-sulfur diesel fuel from 416 to 739 mg/kg, and in high-sulfur diesel fuel from 1048 to 1472 mg/kg [54]. Therefore, elevated levels of DBTs observed at the HWY401 (median = 1.9 ng/m^3) and HMT (median = 1.3 ng/m^3) sites suggest eminent use of less refined fuels, such as diesel, at those sites as compared to other studied sites (Figure 2C). However, the distribution of DBTs relative to alkyl-PAHs differs amongst the sites (Figure 3B). These data indicate that HMT emissions are impacted to a higher degree by less refined petrogenic materials (likely higher-sulfur diesel industrial machineries and engines). The data from EDM and MTL show a lower influence from diesel emissions. As seen for AMS11 (Figure 3B), fugitive emissions from raw and unrefined fossil materials are characterized by the most elevated DBT content.

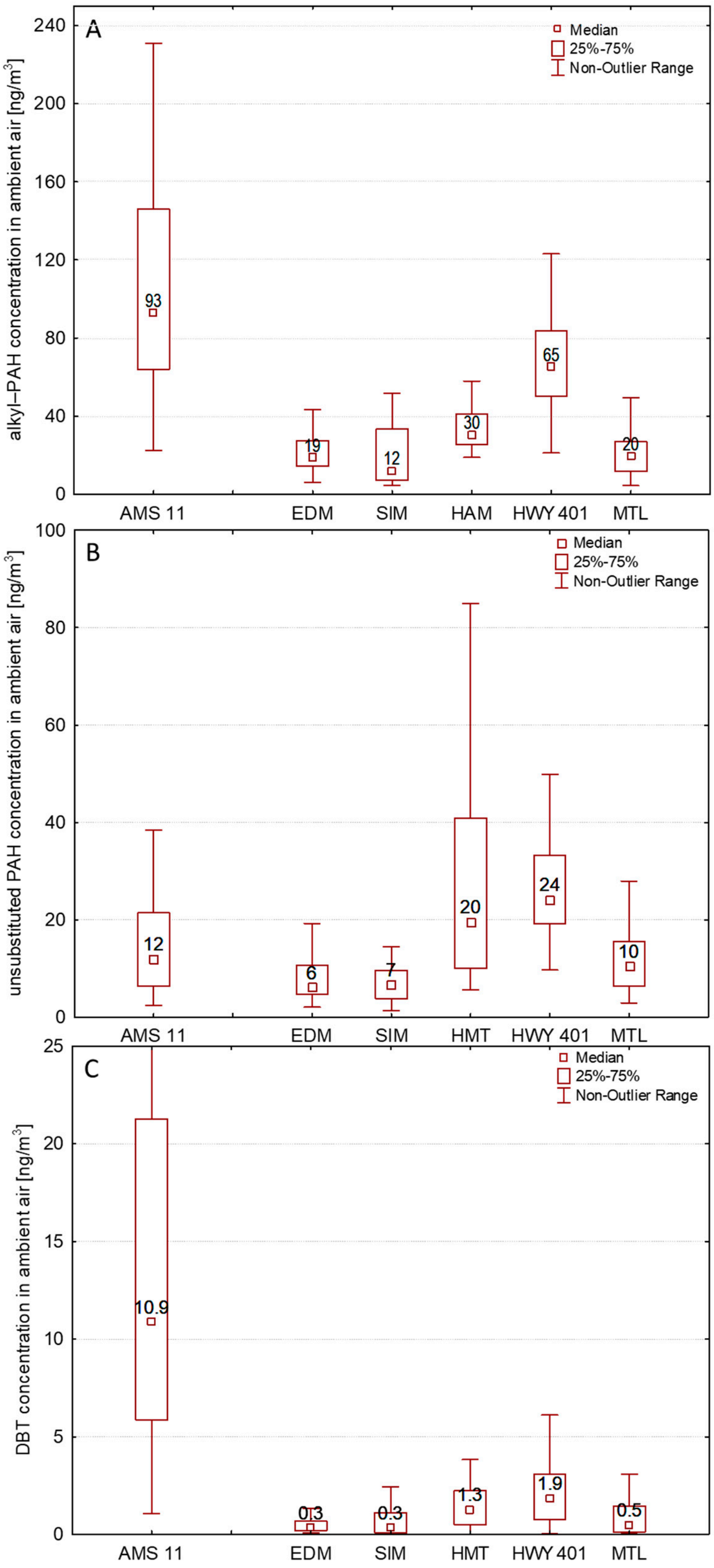

Figure 2. Median total concentrations of (**A**) alkyl-PAHs, (**B**) unsubstituted PAHs, and (**C**) DBTs (DBT + alkylated DBTs) in samples collected at the five NAPS sites. Note, median concentration of PACs collected in the Oil Sands Region (AMS11) is reported for comparison [16].

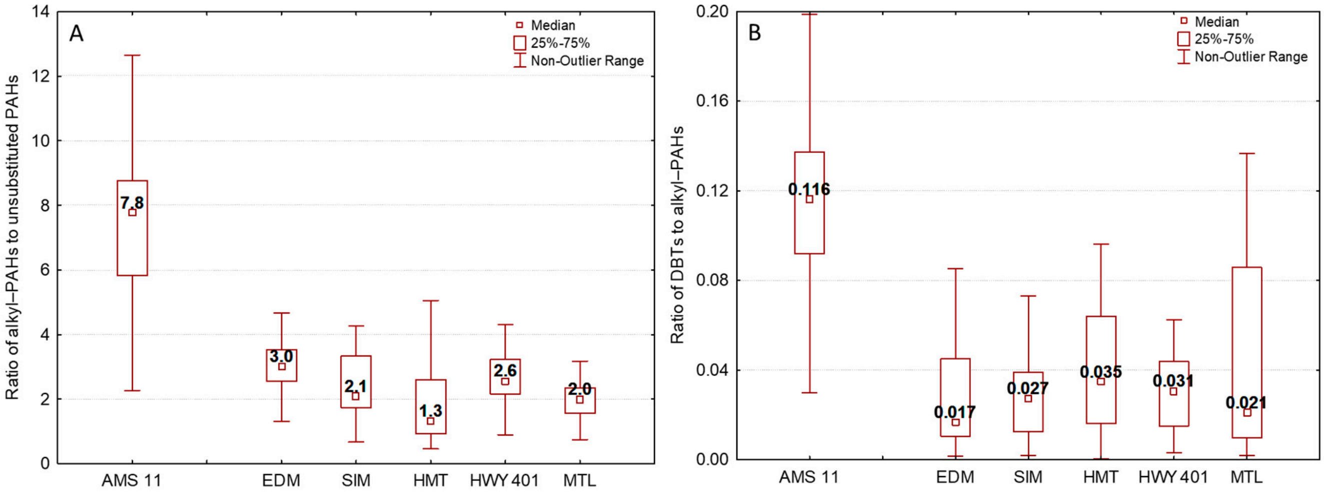

Figure 3. Ratios of (**A**) alkyl-PAHs/PAHs and (**B**) DBTs/alkyl-PAHs at the five NAPS sites and the industrial-petrogenic AMS11 site for comparison [16].

Seasonal Variations in PAC Levels

Seasonality (especially temperature) is an important factor to consider as it affects partitioning of semi-volatile (SVOL) species resulting in changes in their reactivity, deposition, bio-accessibility, and toxicity. Analysis of the PAC concentration trends in this study indicates that seasonal changes reflect the nature of sources, with an extent that varied from site to site. Seasonality effects were not statistically significant (t-test independent by variables, $p > 0.05$, $n = 54$) at HMT and HWY401 (Figure 4). These sites are characterized by the most elevated levels of alkylated and unsubstituted PAHs and reflect steady emission rates from industrial production (HMT) and traffic (HWY401) regardless of season. Significantly elevated concentrations of PACs ($p < 0.05$) in winter were observed at EDM and MTL, likely reflecting variability of local/specific source contributions, such as domestic heating. This phenomenon of elevated PAC levels has also been reported in other studies, and in addition to higher fuel consumption in winter can also be attributed to enhanced partitioning of semi-volatile PACs to the PM, decreased photolysis processes, lower air mixing heights, and less efficient combustion of fuels at cold temperatures [55–57].

The SIM agricultural/farming site, in contrast to other sites, shows uniquely significantly higher alkyl-PAH concentrations during the summer months (Figure 4). This may coincide with seasonal peak agricultural activities and the fact that farming machineries consume large quantities of fuel during this production season [58].

Although annual distribution of PAC groups (alkyl-PAHs > PAHs > DBTs) was similar across the sites (Tables S4–S9), cold and warm seasons affected individual PAC groups differently and the effects also varied from site to site (Figure S1). DBT concentrations were affected to a higher degree than PAHs or alkyl-PAHs during the cold season (October–March) compared to the warm season (April–September) at all NAPS sites. One of the explanations, for example at the SIM non-urban site, is less agricultural activity and less fuel consumption/combustion in winter. For all sites, it could result from a stronger association of DBTs with PM and higher deposition in winter that could result in lower ambient air levels. Observed increases in PAH and alkyl-PAH ambient levels during the heating season in large urban areas, MTL and to a higher degree in EDM, confirm again additional emissions from wood burning and heating oil combustion.

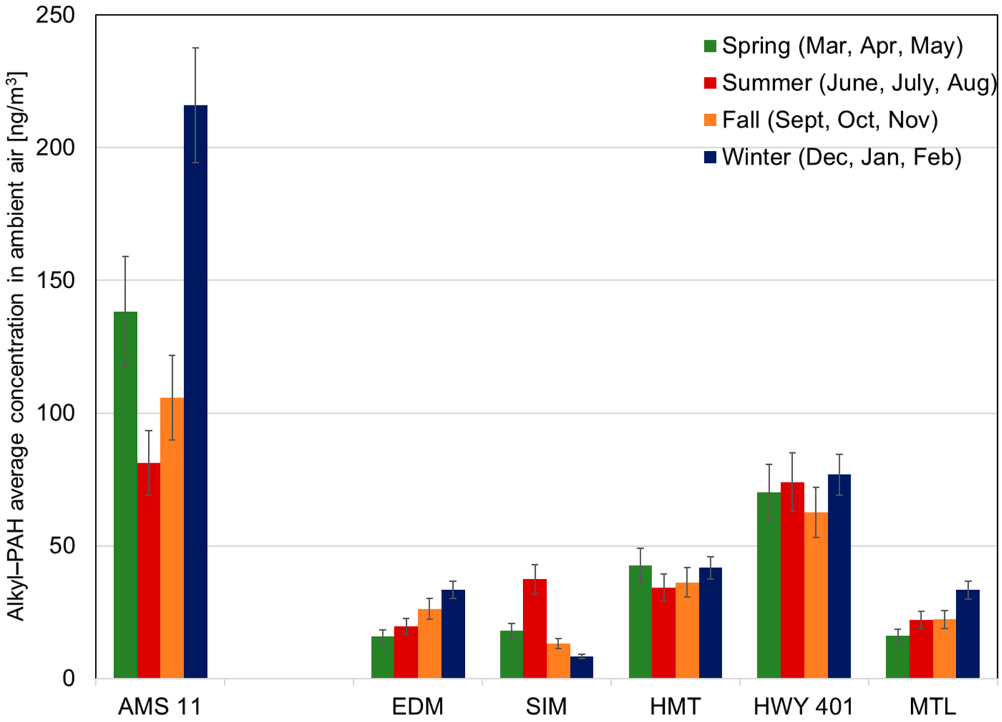

Figure 4. Seasonality effects of alkyl-PAH by site for 2015–2016 period; the data from the AMS11 site are reported for comparison [16].

3.2. Impact of Petrogenic Emissions

Different types of fossil fuel combustion processes can generate different distributions of PAC isomers; hence, the characteristic ratio of PAC classes can be used to characterize or identify potential source categories. According to previous studies [16,17] and as shown in Figure 3A, the high ratio (close to 8) of alkyl-PAHs to unsubstituted PAHs (alkyl-PAHs/PAHs) was indicative of oil sands exploration in the Athabasca region impacted by petrogenic emissions. Therefore, the value of the alkyl-PAHs/PAHs diagnostic ratio could indicate the magnitude of the impact of petrogenic and traffic related emissions in the urban atmosphere. Overall, the median alkyl-PAH/PAH ratios derived in this study were consistent through most of the NAPS sites but were much lower than the ratio at the petrogenic-industrial comparison site (AMS11) (Figure 3A). Amongst the NAPS sites, HWY401 and EDM show the highest impact of alkyl-PAHs relative to unsubstituted PAHs. EDM elevated ratio may reflect local traffic emissions arising from the Whitemud HWY located within 3 km but also due to additional impacts from nearby refineries emissions. HWY401 ratio may be proportional to the traffic volume and vehicular emission contributions that are higher for this near-road traffic-influenced site than other typical urban sites. The data for HWY401 from this study align with concentration ratios (alkyl-PAH/PAH = 2.5) for the same site reported by Jariyasopit [37]. Low alkyl-PAH/PAH ratio at HMT (1.3) does not necessarily indicate inconsiderable concentrations of alkyl-PAHs at this site (Figure 2A). The ratio at this site seems to be reduced relative to other NAPS sites by the contribution of unsubstituted PAHs from local emissions in addition to those from traffic. Consequently, due to additional and often notable sources of unsubstituted PAHs in urban ambient air other than just petrogenic, deployment of the alkyl-PAH/PAH ratio should not be considered as an unequivocal indicator of petrogenic and therefore traffic related contributions in urban environments.

DBTs on the other hand, similar to alkyl-PAHs are established markers of emissions from petrogenic sources [17,40] and therefore have a greater potential to serve as an indicator of traffic emission impacts in urban environments. As shown in Figure 3B, a particularly elevated DBTs to alkyl-PAHs ratio is observed at the industrial-petrogenic AMS11 site, which confirms a high content of DBTs in raw and less processed fossil fuels.

However, cleaning, fractionating, refining, and processing of petrogenic raw material result in final petrogenic products with lower concentrations of sulfur species. This may be observed in EDM, which is affected by emissions from nearby refineries and highly refined petroleum products. Therefore, it is expected to see lower DBTs to alkyl-PAHs ratios at sites with a predominant contribution from motor gasoline, and higher ratios at sites with combustion of diesel fuels or mixed petrogenic materials since diesel fuels contain on average higher sulfur content than gasoline [54]. Consequently, observed lower DBT/alkyl-PAH ratio at the MTL residential site suggests higher contribution of emissions from gasoline powered passenger vehicles. On the other hand, observed higher ratios at the industrialized site in HMT, near-road HWY401, or agricultural/farming machineries at SIM are indicative of elevated contributions of diesel vehicle and machinery emissions.

3.3. PACs Sources Identification

3.3.1. Fingerprint of Alkylated Classes

The combination of individual alkyl-PAH in group classes instead of total PACs (as often reported by other researchers) can add an additional dimension to better identifying PAC emission sources. If the distribution of individual alkylated classes at HWY401 is considered as a typical fingerprint of traffic emissions (Figure 5), then all NAPS sites show similar traffic related alkyl-PAH distribution profiles, made up of 93% on average by lighter species: naphthalenes, fluorenes, phenanthrenes, and anthracenes. On the other hand, alkylated series at AMS11 are additionally enriched in DBTs, and other heavier alkylated fractions—defining a typical fingerprint of petrogenic exploration and less refined fossil fuel emissions. Since similar alkyl-PAH and DBT distributions are observed across all NAPS sampling sites and alkylated hydrocarbons are most abundant amongst PACs (Figures 2, S1 and S2A), this may suggest that traffic emissions are the major contributor of PACs to the atmosphere at those sites. However, when daily alkyl-PAH, DBTs, and PAH concentrations (variable sets) from all six sites were compared statistically for similarities (paired t test), only MTL, SIM, and EDM concentration data showed no significant difference ($p < 0.05$), indicating that HMT, HWY401, and AMS11 concentrations are different.

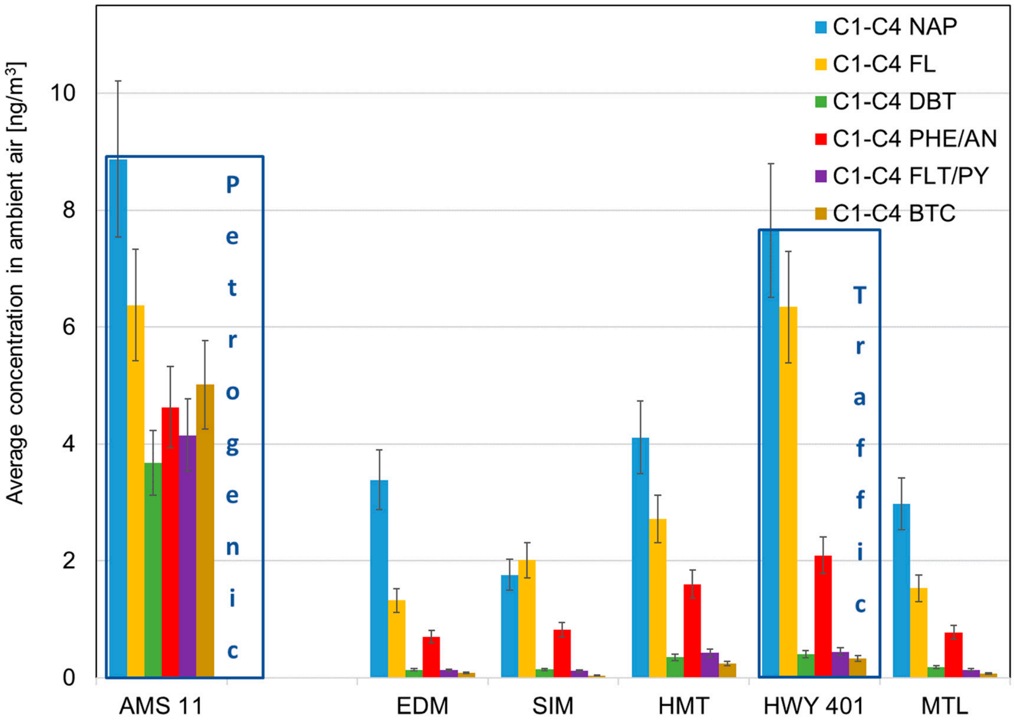

Figure 5. Characteristic profiles of individual alkyl-PAH classes by site.

3.3.2. Ternary Plots for Cluster Groupings

Ternary plots are graphical tools that permit the use of phase diagram properties to assess the dependence/relationship of the three variables/coordinates (X, Y, Z). Plotting in a ternary plot the coordinates of the annual median concentrations of VOL (X), SVOL (Y), and PM (Z) unsubstituted and alkylated PAHs for each site (Tables S4–S9) provides an additional tool for analyzing PAC groupings and detecting relationships leading to information about potential emission sources. We hypothesize here that similar volatility clustering amongst the sites would reflect similar emission composition and therefore, similar emission sources. To that effect, the annual median PAC concentrations were plotted as coordinates, separately for unsubstituted PAHs and for alkylated PAHs (Figure 6).

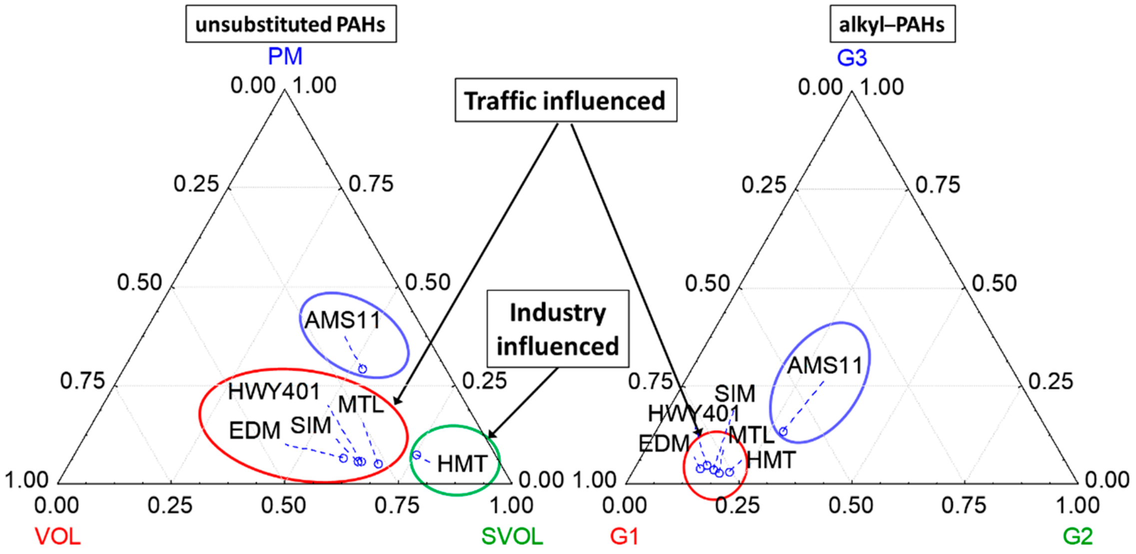

Figure 6. Unsubstituted PAH and alkylated PAH grouping clusters at the five NAPS sites and the industrial-petrogenic AMS11 site [16]. Circled grouped sites indicate similar relationship of volatility groupings amongst the sites (see Table S2 for grouping description).

As shown in Figure 6, unsubstituted PAH concentration coordinates are clustered into three groupings: HWY401, SIM, EDM, and MTL (Transportation-influenced), HMT (Industry influenced); AMS11 (Oil sands petrogenic influenced). Similar annual composition of unsubstituted PAHs at MTL, HWY401, SIM, and EDM sites suggests that vehicle/transportation emissions were a major contributor to PAHs in ambient air. In addition to transportation, the PAH distribution shows the influence of other local sources, such as nearby refineries for EDM and, to a lesser degree, diesel emissions from local traffic for the residential area in MTL. Amongst all the sites, unsubstituted PAH composition in HMT shows the highest levels of SVOL and lowest levels of VOL PAHs, indicating a distinct profile due to the addition of another emission source likely from nearby steel industry in addition to those from transportation. On the other extreme, PM PAH levels at AMS11 were on average five times more elevated than those at the NAPS sites, highlighting the difference in PAH composition unique to combination of mining and refining emissions. Noteworthy is the fact that all six sites are dominated by SVOL PAHs (FLT, PY, B[a]A, CHRY) in the range of 50 to 75%, suggesting a prevailing impact of petrogenic emissions on air quality at those Canadian sites (discussed in next section). This study's findings provide a direct link between petrogenic influenced pollution and air pollution health risks.

In contrast, the alkyl-PAH concentration groupings are all clustered very closely for all NAPS sites (Figure 6), indicating similar composition and therefore suggesting similar emission sources of alkyl-PAHs. Furthermore, HMT does not show a distinct composition for alkyl-PAHs like for unsubstituted PAHs, indicating that additional emissions at the HMT site are enriched in industry-influenced unsubstituted PAHs but not in alkyl-PAHs.

Concentration cluster groupings show that NAPS sites are dominated by G1-VOL alkyl-PAH fraction (C1–C4 NAP, C1–C4 FL, DBT) at 75–80% and have lower content of G3-PM alkyl-PAH (C1–C4 FLT/PY, C1–C4 BTC) compared to typical oil sands concentration clustering at AMS11.

3.3.3. Potential Source Attribution by Factor Analysis

One of the principal drivers for this study was the identification of contributing source types and to estimate the contributions of traffic and petrogenic related emissions on unsubstituted and alkylated PAH levels at sites of various classification. For that purpose, multivariate modeling, such as factor analysis (FA), was applied to the PAC concentration data. Grouped variables (concentrations) with similar temporal variability were used to derive specific factors providing an additional look into/perspective on potential emission source contributions. Each specific factor may link grouped variables to a common emission source(s). Although ambient PACs are due to emissions, no emission profile data were used in the FA but only observed air levels of PACs. All of the PAC datasets from the monitoring sites were combined into a single matrix to group variables with similar temporal variabilities to identify potential emission source categories. Consequently, four potential sources of PACs were identified by FA explaining 87% of the PAC variability (Table 2).

Table 2. Factor Analysis of PAC concentrations for monitored sites *.

Factor 1—"Heavy Mass" PACs	**Factor 2—"Medium Mass" PAHs**	**Factor 3—"Medium Mass" alkyl-PAHs**	**Factor 4—"Volatile" PACs**
C1-C4 FLT/PY (**0.88**)	PHE (**0.84**)	C1-C4 FL (**0.90**)	C1-C4 NAP (**0.79**)
C1-C4 BTC (**0.89**)	AN (**0.74**)	C1-C4 DBT (**0.76**)	AL (**0.78**)
B[a]AN (**0.93**)	FLT (**0.95**)	C1-C4 PHE/AN (**0.85**)	AE (**0.78**)
CHRY (**0.72**)	PY (**0.89**)		FL (**0.72**)
B[b]FLT (**0.74**)			
B[k]FLT (**0.77**)			
B[a]P (**0.95**)			
B[e]P (**0.93**)			
IP (**0.73**)			
B[ghi]P (**0.89**)			
47%	**20%**	**13%**	**7%**
< - Total Variance - >			

* Only analytes with factor loadings values > 0.70 and factor score coefficients > 0.1 are presented. Factor score loadings are in brackets.

As shown in Table 2, Factor 1 explains 47% of the total variance with the highest component loading for the "heavy mass" alkylated and unsubstituted PAHs. Heavier PACs are usually associated with pyrogenic sources while lighter PAHs with more refined petrogenic sources [59]. Pyrogenic processes may be an indication of incomplete combustion of motor fuels in cars and trucks, with the consequence that observed concentrations of pyrogenic PAHs are higher in urban areas and may serve as an indication of petrogenic related emissions [60]. This aligns with data in Figure 6 showing that the PAC clustering at the AMS11 site stands out due to the heavier series of PACs that are markers of petrogenic materials. Factor 2, explaining 20% of the total variance, showed high loadings for "medium mass" PAHs, often reported as traffic related PAHs [61,62] and characteristic of petrogenic origins [15,16]. Factor 3, which explains 13% of the total variance, is characterized by high loadings for "medium mass" alkyl-PAHs including DBTs, which are often associated with the raw and less treated fossil products and suggests contributions from high-sulfur fuels, such as diesel and residential heating oil. Accounting for 7% of the total variance, Factor 4 comprises mainly the most volatile alkylated and unsubstituted PAHs. The association of this factor with low molecular weight compounds may suggest a higher contribution of PACs originating from the lighter fractions of fossil fuels and unburned petroleum-based fuels, but also soil, dust, and long-range transport impacts. The four factors resulting from multivariate analysis seem to indicate petrogenic and traffic related source contributions that likely differ in the combustion process (diesel and gasoline vehicular motors, industrial and agricultural heavy engines, unburnt fuel/oil components, re-suspended road dust, etc.) and therefore in the concentration and composition of measured PACs.

3.3.4. PCA: Projection of Cases on Factor-Plane

The Principal Component Analysis plot presented in Figure 7 incorporates all sites and target analysis from FA in a projection of cases on factor-plane. The five NAPS sites are grouped together under Factor 1 "heavy mass" PACs; however, two subgroups can be distinguished in the upper portion of the plot. Factor-plane PCA shows that although MTL, SIM, and EDM are clustered together through two factors—Factor 1 ("heavy mass" PACs) and Factor 2 ("medium mass" PAHs)—these sites do not demonstrate distinct PAC profile, indicating mixed influence of traffic and local PAC sources. Subgroup HWY401 and HMT has the same *X*-axis value, which suggests that these two sites show the same variability of "heavy mass" PACs, most probably a similar source such as transportation. However, here most of the variability between these two sites is on the *Y*-axis ("medium mass" PAHs) which suggests different sources of these compounds, as already demonstrated on the Ternary Plot (Figure 6). It is the Factor 2 PAHs that make HMT different due to the potential impacts from the steel industry emissions. PCA indicates that the AMS11 site was influenced by a different profile of PACs than that of the NAPS sites, reflecting raw petrogenic materials and processing emissions.

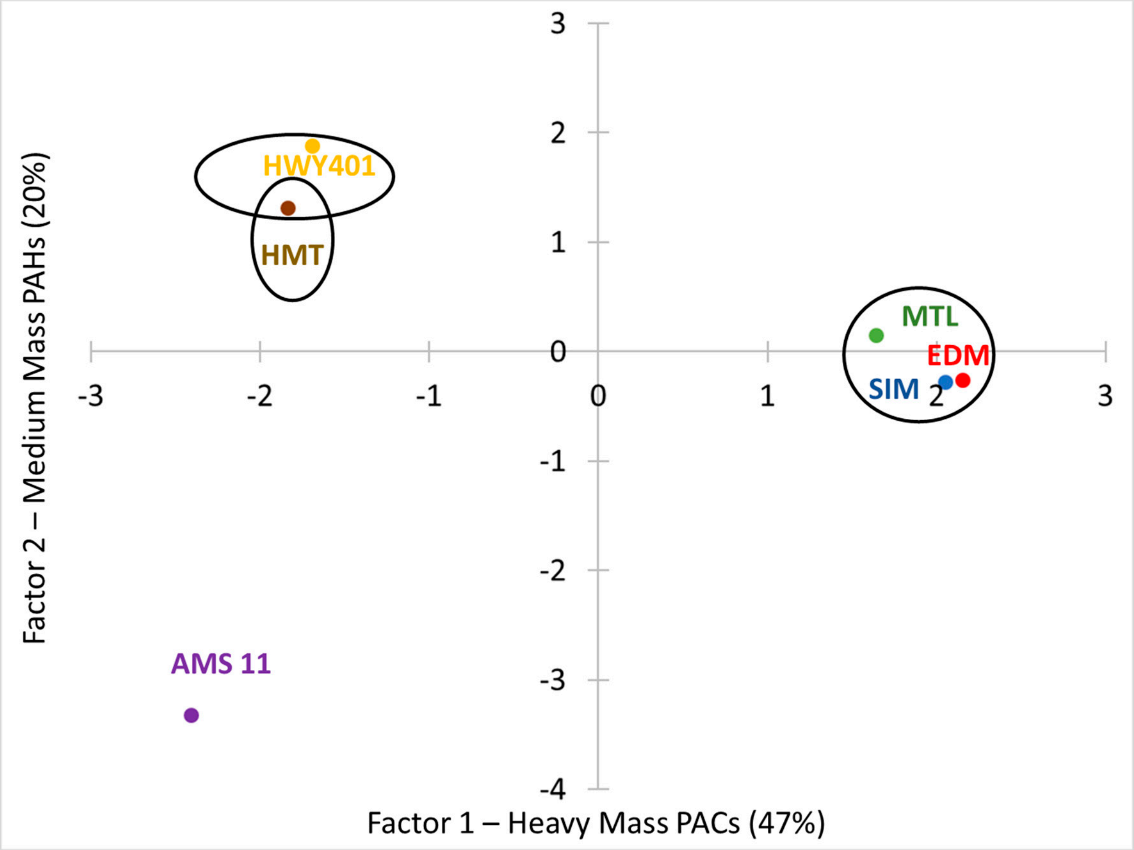

Figure 7. PCA projection of cases on the factor-plane for Factors 1 and 2 at the studied sites.

In this study, for data multivariate analysis the PCA was deployed as a screening and exploratory tool. However, it has to be highlighted that although PCA provides valuable information through a simplistic approach, it also has its limitations. The eigenvector-based methods suffer from the absence of data point weights and therefore may not provide the best estimates of the parameters of interest, in addition to apportioning the variance rather than the variation of the measured concentrations [63]. Consequently, many authors suggest deployment of modern data analysis methods, such as non-negative least squares, positive matrix factorization, and non-negative constrained alternating least squares for more comprehensive source apportionment [64–66].

4. Conclusions

In summary, this study compares the impact of petrogenic emissions on ambient air quality at sites of various classification types in Canada. Alkylated species represent the majority of the PACs in the air. Application of PCA supports observations that urban sites are influenced by mixed sources of PACs, with alkyl-PAHs originating mostly from petrogenic related emissions while unsubstituted PAHs, in addition to petrogenic sources, are also originating from industrial processes and activities. The presence of alkyl-PAHs is consistent with DBT contributions suggesting their possible use as universal markers of petrogenic/traffic pollution. This pilot study confirms that enhanced speciation of alkyl-PAHs provides important data on air quality, and can help to distinguish petrogenic influenced sources from other sources.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/atmos13081320/s1, Table S1: Properties and Characteristics of Studied Individual and Grouped PACs; Table S2: PACs grouping; Table S3: Method performance parameters; Table S4: Total (GP + PM) PAC concentrations (ng/m^3) measured at the Montréal site during the study period (2015–2016); Table S5: Total (GP + PM) PAC concentrations (ng/m^3) measured at the Toronto site during the study period (2015–2016); Table S6: Total (GP + PM) PAC concentrations (ng/m^3) measured at the Hamilton site during the study period (2015–2016); Table S7: Total (GP + PM) PAC concentrations (ng/m^3) measured at the Simcoe site during the study period (2015–2016); Table S8: Total (GP + PM) PAC concentrations (ng/m^3) measured at the Edmonton site during the study period (2015–2016); Table S9: Total (GP + PM) PAC concentrations (ng/m^3) measured at the AMS 11 site during the study period (2015–2016); Figure S1: Unsubstituted PAH, alkyl-PAH and DBT concentration changes at cold (October–March) versus warm (April–September) season by site for the 2015–2016 period. Note, the data for the AMS11 site are reported for comparison.

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References

1. Keyte, I.J.; Harrison, R.M.; Lammel, G. Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons—A review. *Chem. Soc. Rev.* **2013**, *42*, 9333–9391. [CrossRef] [PubMed]
2. Andersson, J.T.; Achten, C. Time to Say Goodbye to the 16 EPA PAHs? Toward an Up-to-Date Use of PACs for Environmental Purposes. *Polycycl. Aromat. Compd.* **2015**, *35*, 330–354. [CrossRef] [PubMed]

3. Galarneau, E. Editorial to "Polycyclic aromatic compounds (PACs) in the Canadian environment: Overview of results and knowledge gaps from the special issue". *Environ. Pollut.* **2021**, *285*, 117607. [CrossRef] [PubMed]
4. Xing, W.; Zou, T.H.; Lee, J.J.; Shih, T.T. Variations in traffic-related polycyclic aromatic hydrocarbons in PM2.5 in Kanazawa, Japan, after the implementation of a new vehicle emission regulation. *J. Environ. Sci.* **2022**, *121*, 38–47. [CrossRef] [PubMed]
5. Zhu, F.-J.; Ma, W.-L.; Hu, P.-T.; Zhang, Z.-F.; Li, Y.-F. Temporal trends of atmospheric PAHs: Implications for the influence of the clean air action. *J. Clean. Prod.* **2021**, *296*, 126494. [CrossRef]
6. Armstrong, B.; Hutchinson, E.; Unwin, J.; Fletcher, T. Lung cancer risk after exposure to polycyclic aromatic hydrocarbons: A review and meta-analysis. *Environ. Health Perspect.* **2004**, *112*, 970–978. [CrossRef]
7. IARC. Working Group on the Evaluation of Carcinogenic Risks to Humans. Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. *Int. Agency Res. Cancer* **2010**, *92*, 1–853.
8. IARC. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans—Chemical Agents and Related Occupations. *Int. Agency Res. Cancer* **2012**, *9*, 100F.
9. Kim, K.H.; Jahan, S.A.; Kabir, E.; Brown, R.J. A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. *Environ. Int.* **2013**, *60*, 71–80. [CrossRef]
10. Mallah, M.A.; Changxing, L.; Mallah, M.A.; Noreen, S.; Liu, Y.; Saeed, M.; Xi, H.; Ahmed, B.; Feng, F.; Mirjat, A.A.; et al. Polycyclic aromatic hydrocarbon and its effects on human health: An overview. *Chemosphere* **2022**, *296*, 133948. [CrossRef]
11. Du, W.; Yun, X.; Chen, Y.; Zhong, Q.; Wang, W.; Wang, L.; Qi, M.; Shen, G.; Tao, S. PAHs emissions from residential biomass burning in real-world cooking stoves in rural China. *Environ. Pollut.* **2020**, *267*, 115592. [CrossRef] [PubMed]
12. Liu, Y.; Wang, S.; Lohmann, R.; Yu, N.; Zhang, C.; Gao, Y.; Zhao, J.; Ma, L. Source apportionment of gaseous and particulate PAHs from traffic emission using tunnel measurements in Shanghai, China. *Atmos. Environ.* **2015**, *107*, 129–136. [CrossRef]
13. Harner, T.; Rauert, C.; Muir, D.; Schuster, J.; Hsu, Y.-M.; Zhang, L.; Marson, G.; Watson, J.G.; Ahad, J.; Cho, S.; et al. Air synthesis review: Polycyclic aromatic compounds in the oil sands region. *Environ. Rev.* **2018**, *26*, 430–468. [CrossRef]
14. Yunker, M.B.; Macdonald, R.W.; Vingarzan, R.; Mitchell, R.H.; Goyette, D.; Sylvestre, S. PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* **2002**, *33*, 489–515. [CrossRef]
15. Schuster, J.K.; Harner, T.; Su, K.; Eng, A.; Wnorowski, A.; Charland, J.P. Temporal and Spatial Trends of Polycyclic Aromatic Compounds in Air across the Athabasca Oil Sands Region Reflect Inputs from Open Pit Mining and Forest Fires. *Environ. Sci. Technol. Lett.* **2019**, *6*, 178–183. [CrossRef]
16. Wnorowski, A.; Aklilu, Y.A.; Harner, T.; Schuster, J.; Charland, J.P. Polycyclic aromatic compounds in ambient air in the surface minable area of Athabasca oil sands in Alberta (Canada). *Atmos. Environ.* **2021**, *244*, 117897. [CrossRef]
17. Schuster, J.K.; Harner, T.; Su, K.; Mihele, C.; Eng, A. First Results from the Oil Sands Passive Air Monitoring Network for Polycyclic Aromatic Compounds. *Environ. Sci. Technol.* **2015**, *49*, 2991–2998. [CrossRef]
18. Marvin, C.H.; Tomy, G.T.; Thomas, P.J.; Holloway, A.C.; Sandau, C.D.; Idowu, I.; Xia, Z. Considerations for Prioritization of Polycyclic Aromatic Compounds as Environmental Contaminants. *Environ. Sci. Technol.* **2020**, *54*, 14787–14789. [CrossRef]
19. Hawthorne, S.B.; Miller, D.J.; Kreitinger, J.P. Measurement of total polycyclic aromatic hydrocarbon concentrations in sediments and toxic units used for estimating risk to benthic invertebrates at manufactured gas plant sites. *Environ. Toxicol. Chem.* **2006**, *25*, 287–296. [CrossRef]
20. Berthiaume, A.; Galarneau, E.; Marson, G. Polycyclic aromatic compounds (PACs) in the Canadian environment: Sources and emissions. *Environ. Pollut.* **2021**, *269*, 116008. [CrossRef]
21. Pampanin, D.M.; Sydnes, M.O. Polycyclic Aromatic Hydrocarbons a Constituent of Petroleum: Presence and Influence in the Aquatic Environment. In *Hydrocarbon*; Kutcherov, V., Kolesnikov, A., Eds.; InTech: Rijeka, Croatia, 2013.
22. Ott, F.S.; Harris, R.P.; O'Hara, S.C.M. Acute and sublethal toxicity of naphthalene and three methylated derivatives to the estuarine copepod, Eurytemora affinis. *Mar. Environ. Res.* **1978**, *1*, 49–58. [CrossRef]
23. Marvanova, S.; Vondracek, J.; Penccikova, K.; Trilecova, L.; Krcmarr, P.; Topinka, J.; Novakova, Z.; Milcova, A.; Machala, M. Toxic effects of methylated benz[a]anthracenes in liver cells. *Chem. Res. Toxicol.* **2008**, *21*, 503–512. [CrossRef] [PubMed]
24. Turcotte, D.; Akhtar, P.; Bowerman, M.; Kiparissis, Y.; Brown, R.S.; Hodson, P.V. Measuring the toxicity of alkyl-phenanthrenes to early life stages of medaka (Oryzias latipes) using partition-controlled delivery. *Environ. Toxicol. Chem.* **2011**, *30*, 487–495. [CrossRef] [PubMed]
25. Jariyasopit, N.; Harner, T.; Wu, D.; Williams, A.; Halappanavar, S.; Su, K. Mapping Indicators of Toxicity for Polycyclic Aromatic Compounds in the Atmosphere of the Athabasca Oil Sands Region. *Environ. Sci. Technol.* **2016**, *50*, 11282–11291. [CrossRef]
26. Lam, M.M.; Bulow, R.; Engwall, M.; Giesy, J.P.; Larsson, M. Methylated PACs are more potent than their parent compounds: A study of aryl hydrocarbon receptor-mediated activity, degradability, and mixture interactions in the H4IIE-luc assay. *Environ. Toxicol. Chem.* **2018**, *37*, 1409–1419. [CrossRef]
27. Liu, Z.; Liu, J.; Zhu, Q.; Wu, W. The weathering of oil after the Deepwater Horizon oil spill: Insights from the chemical composition of the oil from the sea surface, salt marshes and sediments. *Environ. Res. Lett.* **2012**, *7*, 14. [CrossRef]
28. Custer, T.W.; Custer, C.M.; Dummer, P.M.; Bigorgne, E.; Oziolor, E.M.; Karouna-Renier, N.; Schultz, S.; Erickson, R.A.; Aagaard, K.; Matson, C. W EROD activity, chromosomal damage, and oxidative stress in response to contaminants exposure in tree swallow (*Tachycineta bicolor*) nestlings from Great Lakes Areas of Concern. *Ecotoxicology* **2017**, *26*, 1392–1407. [CrossRef]
29. Kang, H.J.; Lee, S.Y.; Kwon, J.H. Physico-chemical properties and toxicity of alkylated polycyclic aromatic hydrocarbons. *J. Hazard. Mater.* **2016**, *312*, 200–207. [CrossRef]

30. Wallace, S.J.; de Solla, S.R.; Head, J.A.; Hodson, P.V.; Parrott, J.L.; Thomas, P.J.; Berthiaume, A.; Langlois, V.S. Polycyclic aromatic compounds (PACs) in the Canadian environment: Exposure and effects on wildlife. *Environ. Pollut.* **2020**, *265*, 114863. [CrossRef]
31. Khan, R.A.; Ryan, P. Long term effects of crude oil on common murres (*Uria aalge*) following rehabilitation. *Bull. Environ. Contam. Toxicol.* **1991**, *46*, 216–222. [CrossRef]
32. Iakovides, M.; Iakovides, G.; Stephanou, E.G. Atmospheric particle-bound polycyclic aromatic hydrocarbons, n-alkanes, hopanes, steranes and trace metals: PM2.5 source identification, individual and cumulative multi-pathway lifetime cancer risk assessment in the urban environment. *Sci. Total Environ.* **2021**, *752*, 141834. [CrossRef]
33. Lewis, C.; Galloway, T. Genotoxic damage in polychaetes: A study of species and cell-type sensitivities. *Mutat. Res.* **2008**, *654*, 69–75. [CrossRef] [PubMed]
34. Page, D.S.; Boehm, P.D.; Stubblefield, W.A.; Parker, K.R.; Gilfillan, E.S.; Neff, J.M.; Maki, A.W. Hydrocarbon composition and toxicity of sediments following the Exxon Valdez oil spill in Prince William Sound, Alaska, USA. *Environ. Toxicol. Chem.* **2002**, *21*, 1438–1450. [CrossRef] [PubMed]
35. Phillips, D.H.; Grover, P.L.; Sims, P. A quantitative determination of the covalent binding of a series of polycyclic hydrocarbons to DNA in mouse skin. *Int. J. Cancer* **1979**, *23*, 201–208. [CrossRef] [PubMed]
36. Cheng, I.; Wen, D.; Zhang, L.; Wu, Z.; Qiu, X.; Yang, F.; Harner, T. Deposition Mapping of Polycyclic Aromatic Compounds in the Oil Sands Region of Alberta, Canada and Linkages to Ecosystem Impacts. *Environ. Sci. Technol.* **2018**, *52*, 12456–12464. [CrossRef]
37. 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. *Environ. Pollut.* **2019**, *252 Pt B*, 1882–1891. [CrossRef]
38. Moradi, M.; Hung, H.; Li, J.; Park, R.; Shin, C.; Alexandrou, N.; Iqbal, M.A.; Takhar, M.; Chan, A.; Brook, J.R. Assessment of Alkylated and Unsubstituted Polycyclic Aromatic Hydrocarbons in Air in Urban and Semi-Urban Areas in Toronto, Canada. *Environ. Sci. Technol.* **2022**, *56*, 2959–2967. [CrossRef]
39. Studabaker, W.B.; Puckett, K.J.; Percy, K.E.; Landis, M.S. Determination of polycyclic aromatic hydrocarbons, dibenzothiophene, and alkylated homologs in the lichen Hypogymnia physodes by gas chromatography using single quadrupole mass spectrometry and time-of-flight mass spectrometry. *J. Chromatogr. A* **2017**, *1492*, 106–116. [CrossRef]
40. Yang, C.; Wang, Z.; Yang, Z.; Hollebone, B.; Brown, C.E.; Landriault, M.; Fieldhouse, B. Chemical fingerprints of Alberta oil sands and related petroleum products. *Environ. Forensics* **2011**, *12*, 173–188. [CrossRef]
41. Larsson, M.; Lam, M.M.; van Hees, P.; Giesy, J.P.; Engwall, M. Occurrence and leachability of polycyclic aromatic compounds in contaminated soils: Chemical and bioanalytical characterization. *Sci. Total Environ.* **2018**, *622–623*, 1476–1484. [CrossRef]
42. Eisentraeger, A.; Brinkmann, C.; Hollert, H.; Sagner, A.; Tiehm, A.; Neuwoehner, J. Heterocyclic compounds: Toxic effects using algae, daphnids, and the Salmonella/microsome test taking methodical quantitative aspects into account. *Environ. Toxicol. Chem.* **2008**, *27*, 1590–1596. [CrossRef]
43. Kropp, K.G.; Fedorak, P.M. A review of the occurrence, toxicity, and biodegradation of condensed thiophenes found in petroleum. *Can J. Microbiol.* **1998**, *44*, 605–622. [CrossRef]
44. Eastmond, D.A.; Booth, G.M.; Lee, M.L. Toxicity, accumulation, and elimination of polycyclic aromatic sulfur heterocycles in Daphnia magna. *Arch. Environ. Contam. Toxicol.* **1984**, *13*, 105–111. [CrossRef]
45. Zhang, Y.; Song, Y.; Chen, Y.-J.; Chen, Y.; Lu, Y.; Li, R.; Dong, C.; Hu, D.; Cai, Z. Discovery of emerging sulfur-containing PAHs in PM2.5: Contamination profiles and potential health risks. *J. Hazard. Mater.* **2021**, *416*, 125795. [CrossRef]
46. Tian, X.; An, C.; Chen, Z.; Tian, Z. Assessing the impact of COVID-19 pandemic on urban transportation and air quality in Canada. *Sci. Total Environ.* **2021**, *765*, 144270. [CrossRef]
47. ECCC. Sources of Air Pollution-Canada. *Department of the Environment and Climate Change Canada.* 2017. Available online: https://www.canada.ca/en/environment-climate-change/services/air-pollution/sources/transportation/cars-trucks-vans-suvs.html (accessed on 11 March 2021).
48. Wnorowski, A.; Tardif, M.; Harnish, D.; Poole, G.; Chiu, C.H. Correction of analytical results for recovery: Determination of PAHs in ambient air, soil, and diesel emission control samples by isotope dilution gas chromatography-mass spectrometry. *Polycycl. Aromat. Compd.* **2006**, *26*, 313–329. [CrossRef]
49. USEPA. *Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MD), Compendium Method TO-13A*, 2nd ed.; USEPA: Cincinnati, OH, USA, 1999. Available online: https://www.epa.gov/sites/default/files/2019-11/documents/to-13arr.pdf (accessed on 11 March 2021).
50. Wnorowski, A. Characterization of the ambient air content of parent polycyclic aromatic hydrocarbons in the Fort McKay region (Canada). *Chemosphere* **2017**, *174*, 371–379. [CrossRef]
51. Wallace, S.J.; de Solla, S.R.; Thomas, P.J.; Harner, T.; Eng, A.; Langlois, V.S. Airborne polycyclic aromatic compounds contribute to the induction of the tumour-suppressing P53 pathway in wild double-crested cormorants. *Ecotoxicol. Environ. Saf.* **2018**, *150*, 176–189. [CrossRef]
52. Halappanavar, S.; Wu, D.; Boyadzhiev, A.; Solorio-Rodriguez, A.; Williams, A.; Jariyasopit, N.; Saini, A.; Harner, T. Toxicity screening of air extracts representing different source sectors in the Greater Toronto and Hamilton areas: In vitro oxidative stress, pro-inflammatory response, and toxicogenomic analysis. *Mutat. Res./Genet. Toxicol. Environ. Mutagenesis* **2021**, *872*, 503415. [CrossRef]

53. Poerschmann, J.; Parsi, Z.; Gorecki, T. Non-discriminating flash pyrolysis and thermochemolysis of heavily contaminated sediments from the Hamilton Harbor (Canada). *J. Chromatogr. A* **2008**, *1186*, 211–221. [CrossRef]
54. ECCC. 2003–2016 Fuel Volumes and Sulphur Mass Content National. In *Data Collected under the Fuels Information Regulations*; No. 1.; Department of the Environment and Climate Change Canada. 2017. Available online: http://data.ec.gc.ca/data/regulatee/submissions/data-collected-under-the-fuels-information-regulations-no.-1/2003-2016FuelVolumesAndSulphurMassAndContentNationalVolumesDeCarburantEtTeneurEtMasseDeSoufreNational.csv (accessed on 20 May 2021).
55. Pehnec, G.; Jakovljević, I.; Šišović, A.; Bešlić, I.; Vađić, V. Influence of ozone and meteorological parameters on levels of polycyclic aromatic hydrocarbons in the air. *Atmos. Environ.* **2016**, *131*, 263–268. [CrossRef]
56. Prevedouros, K.; Brorström-Lundén, E.; Halsall, C.J.; Jones, K.C.; Lee, R.G.M.; Sweetman, A.J. Seasonal and long-term trends in atmospheric PAH concentrations: Evidence and implications. *Environ. Pollut.* **2004**, *128*, 17–27. [CrossRef] [PubMed]
57. Soleimanian, E.; Taghvaee, S.; Sioutas, C. Characterization of organic compounds and oxidative potential of aqueous PM2.5 suspensions collected via an aerosol-into-liquid collector for use in toxicology studies. *Atmos. Environ.* **2020**, *241*, 117839.
58. Juostas, A.; Janulevičius, A. Evaluating working quality of tractors by their harmful impact on the environment. *J. Environ. Eng. Landsc. Manag.* **2009**, *17*, 106–113. [CrossRef]
59. Marris, C.R.; Kompella, S.N.; Miller, M.R.; Incardona, J.P.; Brette, F.; Hancox, J.C.; Sørhus, E.; Shiels, H.A. Polyaromatic hydrocarbons in pollution: A heart-breaking matter. *J. Physiol.* **2020**, *598*, 227–247. [CrossRef]
60. Abdel-Shafy, I.H.; Mansour, M.S.M. A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egypt. J. Pet.* **2016**, *25*, 107–123. [CrossRef]
61. Gunawardena, J.; Egodawatta, P.; Ayoko, G.A.; Goonetilleke, A. Role of traffic in atmospheric accumulation of heavy metals and polycyclic aromatic hydrocarbons. *Atmos. Environ.* **2012**, *54*, 502–510. [CrossRef]
62. Harrison, R.M.; Tilling, R.; Callén Romero, M.S.; Harrad, S.; Jarvis, K. A study of trace metals and polycyclic aromatic hydrocarbons in the roadside environment. *Atmos. Environ.* **2003**, *37*, 2391–2402. [CrossRef]
63. Hopke, K.P.; Jaffe, D.A. Letter to the Editor: Ending the Use of Obsolete Data Analysis Methods. *Aerosol Air Qual. Res.* **2020**, *20*, 688–689. [CrossRef]
64. Camp, C.H. PyMCR: A python library for multivariatecurve resolution analysis with alternating regression (MCR-AR). *J. Res. Natl. Inst. Stand. Technol.* **2019**, *1*, 124. [CrossRef]
65. Paatero, P.; Tapper, U. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics* **1994**, *5*, 111–126. [CrossRef]
66. Tauler, R.; Kowalski, B.; Fleming, S. Multivariate Curve Resolution Applied to Spectral Data from Multiple Runs of an Industrial Process. *Anal. Chem.* **1993**, *65*, 2040–2047. [CrossRef]