PAPER

Urban sources of synthetic musk compounds to the environment†

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The occurrence and potential sources of synthetic musk compounds (SMCs) in the urban and surrounding environment were investigated. We analyzed air, soils and surface waters from a wide array of land-use types and urban densities including air from wastewater treatment plants (WWTPs), indoor, urban, rural, and remote Arctic sites; surface waters from urban and rural tributaries; and effluents of three WWTPs. In air, the median sum concentration of six selected polycyclic musks (Σ_6PCMs) (*i.e.*, galaxolide, tonalide, cashmeran, celestolide, phantolide, traseolide) were the highest from WWTP on-site > indoor > urban > WWTP off-site > rural. SMCs were not found in remote Arctic air indicating low potential for long-range atmospheric transport. SMCs were not found in soils, likely because of their high volatility and fast biodegradation rate. Galaxolide (HHCB) and tonalide (AHTN) were the two most abundant SMCs in air, tributaries and WWTP effluents. Σ_6PCM concentrations in air taken along urban–rural transects and in tributary water were positively correlated with population density. In WWTP on-site air, trace levels of the toxic nitro-musks, namely musk xylene and musk ketone were detected and macrocyclic musks accounted for ~10% of the total SMCs measured. In WWTP effluents, the concentrations of Σ_6PCMs were proportional to the population served. We conclude that sources of SMCs to the outdoor urban environment and hence the surrounding region, originate from releases from indoor air, and temperature-dependent volatilization from WWTPs during treatment.

Environmental significance

Synthetic musk compounds (SMCs) are high production volume substances that are widely used in everyday consumer products. Some have similar physical–chemical properties to persistent organic pollutants. Little is known about the major sources, occurrence, fate and transport of SMCs in the environment. We found that SMCs in ambient air and tributary surface water were positively correlated with population density. Their levels in the environment were influenced by local emissions from indoor air and release from wastewater treatment plants. Most SMCs have short half-lives, and thus were not found in soils and Arctic air, and are unlikely to undergo long-range atmospheric transport. However, the continuous release of SMCs in high volumes from the urban environment, notably wastewater treatment plants, could pose a chronic toxicological threat to biota in receiving waters.

Introduction

Synthetic musk compounds (SMCs) are semi-volatile cyclic organic chemicals that are used as fragrance materials. These compounds are widely used in many personal care products, including soaps, shampoo, detergents, and deodorants, as well as other scented products such as air fresheners and scented candles. Four main groups of SMCs are marketed in categories according to their chemical structures, namely nitro-musks (NMs), polycyclic musks (PCMs), macrocyclic musks (MCMs), and alicyclic musks (ACMs).

NMs have similar physical–chemical properties to persistent organic pollutants such as organochlorine pesticides and polychlorinated biphenyls (Table 1). For example, the octanol–water partition coefficients (log K_{OW}) of musk ketone (MK) and musk xylene (MX) are 4.3 and 4.9, respectively,[1,2] and octanol–air partition coefficient (log K_{OA}) is 12 for both MK and MX.[3] NMs, particularly MK and MX, have been found to be weakly estrogenic and may increase the genotoxicity of other chemicals in a species-specific fashion.[4,5] NMs are known to cause toxic effects at low concentrations in aquatic and terrestrial

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74 | *Environ. Sci.: Processes Impacts*, 2019, **21**, 74–88

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Table 1 Physical–chemical properties of synthetic musk compounds (refer to Table S1 for chemical name, structure, solubility and half-life in air)

Compound (abbrev.)	CAS number	MW (g mol⁻¹)	log K_{OW}	log K_{OA}	P_L (Pa)	HLC (Pa m³ mol⁻¹)
Nitro-musks						
Musk tibetene (MT)	145-39-1	266	5.2[a] 8.3[c]	10.1[b]	0.0074[a] 0.0068[b] 0.018[c]	100.8[a] 0.0295[b]
Musk ambrette (MA)	83-66-9	268	4.3[a]	10.4[b]	0.081[a] 0.0066[b]	25.6[a] 0.0014[b]
Musk moskene (MM)	116-66-5	278	5.8[a]	10.5[b] 7.8[c]	0.011[a] 0.0040[b] 0.11[c]	257.6[a] 0.0208[b]
Musk ketone (MK)	81-14-1	29 4	4.3[a]	12[b]	0.011[a] 0.00101[b] 0.00004[d]	5.8[a] 4.87[b] 0.0061[d] 0.336[f]
Musk xylene (MX)	81-15-2	297	3.8[a] 4.5[b] 4.9[d]	12[b]	0.035[a] 0.00058[b] 0.00003[d]	41.2[a] 0.000105[b] 0.018[d] 3.11[f]
Polycyclic musks						
1-Methyl-alpha-ionone	7779-30-8	206	4.8[b]	6.9[b]	1.6[b]	24.3[b]
Cashmeran (DPMI)	33704-61-9	206	4.9[a] 4.5[b]	6.7[b]	0.012[a] 1.5[b]	11.6[a] 14.4[b]
Iso E super (OTNE)	54464-57-2	234	5.2[b]	6.9[b]	0.56[b]	47.6[b]
Celestolide (ADBI)	13171-00-1	244	6.6[a] 5.9[b]	8.8[b]	0.15[a] 0.094[b]	2066[a] 3.22[b]
Phantolide (AHMI)	15323-35-0	244	6.7[a] 5.9[b]	8.7[b] 7.5[c]	0.096[a] 0.102[b] 0.16[c]	786[a] 3.22[b]
Traseolide (ATII)	68140-48-7	258	8.1[a] 6.3[b]	9.07[b] 7.7[c]	0.039[a] 0.053[b] 0.079[c]	113[a] 4.28[b]
Galaxolide (HHCB)	1222-05-5	258	7.3[a] 6.3[b] 5.9[e]	8.2[b] 7.8[c]	0.038[a] 0.068[b] 0.056[c] 0.073[e]	51.8[a] 13.4[b] 11.3[e]
Tonalide (AHTN)	21145-77-7	258	7.3[a] 6.3[b] 5.7[e]	8.0[b]	0.034[a] 0.047[b] 0.068[e]	1210[a] 4.28[b] 12.5[e]
Macrocyclic musks						
Exaltone	502-72-7	224	5.6[b]	7.1[b] 6.6[c]	0.13[b] 1.4[c]	66[b]
Muskone	541-91-3	238	5.9[b]	7.4[b]	0.109[b]	88[b]
Exaltolide	106-02-5	240	6.2[b]	7.2[b]	0.0080[b]	235[b]
Ambrettolide	7779-50-2	252	5.4[b]	6.3[b] 7.4[c]	0.0036[b] 0.33[c]	274[b]
16-Hexadecanolide	109-29-5	254	6.7[b]	7.6[b] 7.4[c]	0.0040[b] 0.22[c]	312[b]
Musk MC-4	54982-83-1	256	4.2[b]	8.2[b] 7.8[c]	0.00033[b] 0.11[c]	0.24[b]
Cervolide	6707-60-4	256	4.9[b]	8.0[b] 7.7[c]	0.0033[b] 0.14[c]	2.07[b]
Ethylene brassylate	105-95-3	270	4.7[b]	8.6[b]	0.00016[b]	0.32[b]

[a] Paasivirta et al., 2002.[78] [b] US EPA., 2018. 3 EPI Suite™ version 4.11. Specific methods used: (i) solubility – WSKOW v1.42, based on EPI Suite estimated log K_{OW}; (ii) HLC – HENRYWIN v3.20 based on bond method; (iii) log K_{OW}: KOWWIN v1.68; (iv) sub-cooled liquid VP – MPBPWIN v1.43, based on mod-grain method; log K_{OA}; (v) log K_{OA}: KOAWIN. [c] Wong et al., 2017.[79] [d] Tas et al., 1997.[2] [e] Balk et al., 1999.[80] [f] Lee et al., 2012.[81]

organisms.[6,7] A recent exposure-based prioritization study indicated MX is a highly waterborne persistent contaminant that may pose potential planetary boundary threats.[8] MX has been banned in the European Union and Japan as it has been identified as very persistent and bioaccumulative chemical.[9,10] It is prohibited for use as fragrance by the International Fragrance Association (IFRA), a self-regulatory representative body of the worldwide fragrance industry. MK is not regulated by any

government agency but it is listed on the third Priority Substances List under the superseded Existing Substances Regulation (ESR) of REACH.[11] MK is prohibited by IFRA if it contains more than 0.1% of MX as an impurity.[12] Other NMs, including musk ambrette (MA), musk tibetene (MT) and musk moskene (MM) are prohibited by IFRA. In Canada, use of MA and MT is prohibited for use in cosmetic products.[13] Canada has also placed a Significant New Activity (SNAc) order on MM based on its potential toxicity, whereby ministerial approval is required for use in volumes greater than 100 kg per year.[14]

In the U.S., the national production volume of galaxolide (HHCB), the most widely used PCM worldwide, increased from approximately one million kg per year in 2011 to up to four million kg per year during 2012–2015.[15] Such an increase may be due to increased market demand for the chemical and the shift from NM to PCMs in the U. S.[16] Similar phenomenon is also observed in the European market as a result of the strict international regulation of NMs.[17]

Although the toxicity of PCMs is believed to be low, some evidence suggests that they may cause endocrine disruption through anti-estrogenic activity.[4,18,19] PCMs can also act as hormonal agonists and antagonists in humans and wild-life.[20,21] Recent studies have found that PCMs could have harmful health effect.[22,23] For example, Fang *et al.*[22] reported that tonalide (AHTN) can act as a photosensitizer to increase photo-induced oxidative damage to natural amino acid on skin surfaces. Gao *et al.*[24] reported that indirect photochemical transformation products of AHTN in water could have up to 8 times higher bioconcentration factor than parent AHTN. Quantitative Structure Activity Relationships (QSAR)-based risk assessment indicated that HHCB could pose a risk to biota exposed through sediment, soil, water and in some cases air by Homem *et al.*[25]

These potential effects of PCMs, when combined with their propensity to bioaccumulate due to their high lipophilicity (log $K_{OW} \sim 4.5$–7.0, Table 1), have led to concern about their long-term human and environmental health effects.[25–28] As such, IFRA has restricted the use of phantolide in "leave-on" products to no more than 2%.[12] Otherwise, there are no regulations in the use of other PCMs.

MCMs are more easily degraded than NMs and PCMs.[29] The production volume of MCMs is less than PCMs, but they are becoming more available because of advances in synthesis technology. Hence, increased use of MCMs is expected. ACMs are the fourth generation of odorant musks, but their current use in personal care products is very limited.

Most studies on SMCs have focused on NMs and PCMs with fewer conducted on MCMs.[1,30,31] NMs and PCMs have been reported in indoor dust,[1,32–34] indoor air,[32,35,36] outdoor air,[37–42] biota;[43–48] surface waters;[37,41,49–51] sea water,[37] sediments,[52] wastewater treatment plants (WWTPs);[53–55] drinking water,[56] human adipose tissue,[45,57,58] breast milk,[31,59–61] and serum.[59,62]

The potential for SMCs to undergo long-range transport is debatable. Villa *et al.*[63] reported that AHTN and HHCB were chemicals with high persistence and low long-range transport potential based on their overall persistence of 245–250 days, a characteristic travel distance of 150 km and a very low transfer

efficiency. Given the short half-lives of most SMCs (*e.g.* PCMs and MCMs) on the order of hours due to photodegradation, long-range transport is not anticipated.[64] HHCB and AHTN were not found in polar bears in Alaska[45] but HHCB, cashmeran (DPMI), traseolide (ATII), and MT were detected in polar bears in Greenland.[65]

Melymuk *et al.*[42] estimated that the main loadings of PCMs (*i.e.* sum of HHCB and AHTN) to Lake Ontario were from waste water treatment plant (WWTP) effluent which accounted for 83% of total loadings, with minor contributions from atmospheric deposition (10%) and tributary discharge into the lake (7%). McDonough *et al.*[41] reported that in Lake Ontario and Lake Erie, HHCB underwent net volatilization from water to air but the flux was variable for AHTN. The authors suggested that volatilization could be responsible for the loss of 64 to 213 kg PCMs per year from the lakes.

Harrad and Diamond[66] proposed a conceptual model for source-to-receptor transport of chemicals contained within a stock or inventory of materials and products (Fig. S1†). For chemicals used in everyday commodities, this inventory is held mainly indoors, which is the first environment into which the chemicals migrate. From indoors, chemicals migrate outdoors into the urban environment. Persistent chemicals will be exported from the urban area mainly by atmospheric movement and a smaller, but significant fraction will find its way to urban soils and surface waters. Very persistent chemicals will be transferred through terrestrial and aquatic food webs from which the chemicals may return to the urban area in foods that we eat. Although most SMCs are not persistent due to their ability to degrade *via* photolysis, their continual use and release has rendered them "pseudo-persistent" in densely populated locations.

Our main goal is to use the conceptual framework of Harrad and Diamond[66] to interpret measured concentrations of SMCs from potential urban sources, to receptor regions in rural or remote areas. This analysis includes data from air (i) indoors in offices and homes, (ii) outdoors along urban-rural transects, (iii) outdoors at an urban site in downtown Toronto, (iv) immediately adjacent to and at a distance from WWTPs, (v) outdoors at a rural site on the shore of Lake Ontario, and (vi) outdoors at a remote site in the Canadian High Arctic. We also consider SMCs in soils, final effluents from wastewater treatment plants (WWTPs), and surface waters of tributaries in Ontario, Canada. Our secondary goal was to establish baseline environmental concentrations of SMCs in different media in Canada.

Methods

Air and soil samples

Sampling Strategy. Fig. 1 shows a map of our sampling locations. Air samples were collected using a combination of active and passive air sampling techniques. Here we give a brief description of the sampling locations and analytical method. Details can be found in the references cited and in ESI.†

(i) Indoor air from homes and offices was sampled using polyurethane foam (PUF) disk-type passive samplers (PUF-PASs) ($n = 20$). Samplers were deployed for 30 days from August to
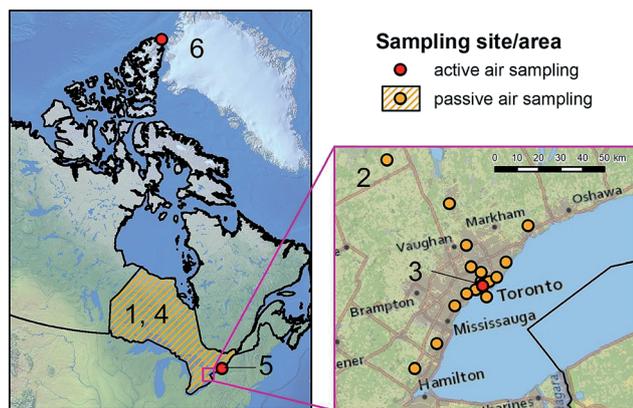
76 | *Environ. Sci.: Processes Impacts*, 2019, **21**, 74–88

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Fig. 1 Map of air sampling sites. (1) Indoor passive air sampling in 20 homes and offices in Ontario; (2) passive air sampling sites on 3 urban-rural transects in Ontario; (3) urban active air sampling in city of Toronto; (4) eight WWTP in Ontario by passive air sampling; (5) rural active air sampling on the shore of Lake Ontario; (6) remote active air sampling in the Canadian High Arctic, alert. Passive samplers are indicated by orange dots and active sampling sites by red dots.

September 2006. Approximately 25 m^3 of air were collected for each sample, assuming a sampling rate of 0.7 m^3 per day. Further details about each sampling site and methods are described in Zhang *et al.*[67] (ii) Outdoor air and soils along three urban-rural transects that extended east, west, and north from downtown Greater Toronto Area (GTA). Air samples were collected using PUF-PAS deployed at 19 sites exposed for 3 months each, for over four seasonal periods during 2007–2008. Each sample represented ∼250 m^3 of air, assuming a sampling rate of 2.69 m^3 per day. The sampling rate was determined based on a 125 day calibration study specifically designed for SMCs.[68] Details about the passive sampling sites are reported by Melymuk *et al.*[69] Surface soils ($n = 19$) were collected at each passive air sampling site concurrent with initial deployment of sampler (October 2007). (iii) Outdoor air from an urban site, city of Toronto ($n = 32$) was obtained using a high volume active air sampler (HV-AAS). Glass fibre filter (GFF) and PUF plug samples were collected for particle- and gas-phases, respectively, every 12 days during 2007–2008. Each sample represented ∼450 m^3 of air.[70]

Archived air extracts provided by Environment and Climate Change Canada (ECCC) were also analyzed: (iv) WWTPs ($n = 32$), where air samples were obtained from 8 plants during the summer (August to November 2013) and winter (January to March 2014). Sorbent-impregnated polyurethane foam (SIP) disk-type PAS were deployed "on-site" (*i.e.* above the aeration tank or adjacent to the lagoon) and "off-site" (*i.e.* ∼100–150 m away from the active area on the premises of the WWTP). Details of the sampling sites and methods are presented by Shoeib *et al.*[71] A sampling rate of 4 m^3 per day derived for poly- and perfluroalkyl substances (PFASs) and organophosphate esters by SIP-PAS was used.[71–73] On average each sample represented ∼ 280 m^3 of air. (v) A rural site located at the nearshore of Lake Ontario ($n = 32$). The air samples were collected in 2010 using an HV-AAS, with GFF and PUF plug as sorbents. About ∼340 m^3 of air were collected for each sample.[74] (vi) A remote site in the

Canadian High Arctic ($n = 21$), where the air samples were obtained at Alert, Nunavut, Canada, during 2009–2010 using an HV-AAS with GFF, and PUF/XAD/PUF sandwich as sorbents. Each sample represented 2000 m^3 of air. Description of sampling method is given in Wong *et al.*[75]

Extraction and clean-up. Air samples from (i) indoor and (ii) urban-rural transects, and (iii) the urban sites, and soil samples were analyzed at the University of Toronto (UT). Details of the extraction and clean-up methods have been previously reported.[68] In brief, PUFs and filters were extracted by a Dionex ASE350 (Accelerated Solvent Extraction System) with dichloromethane (DCM). All samples were spiked 50 ng of d_{10}-fluoranthene prior to extraction. Samples were cleaned using a 1 g silica solid-phase extraction (SPE) cartridge (Varian, Canada) with 25 ml of 50 : 50 DCM/hexane.

Each soil sample (∼25 g) was combined with anhydrous sodium sulphate, then placed in a pre-cleaned cellulose thimble, and extracted for 18 hours in DCM in a Soxhlet apparatus. d_{10}-Fluoranthene (50 ng) was added to the thimble prior to extraction, and 2 g of activated copper was added to the solvent collection flask for sulfur removal. The soils underwent the same clean-up and analytical procedure as the air samples described above.

The air samples from the (iv) WWTPs (SIP-PAS), (v) rural (Lake Ontario) and (vi) remote (Arctic) site were analysed at ECCC. The WWTP air samples were extracted by a Dionex ASE350 using petroleum ether/acetone (83/17, v/v). The extracts did not undergo clean-up procedures. Details of the analytical procedure have been reported.[71] The rural air samples were extracted using a Soxhlet apparatus with hexane, dried with anhydrous sodium sulfate, and cleaned-up using a florisil column. The analytical procedure has been previously published.[74] The remote air samples from the Canadian Arctic were extracted by Dionex ASE350 with hexane. The extracts did not undergo clean-up procedures.[75]

Tributary surface waters and wastewater treatment plant effluent

Sampling strategy. Tributary surface water samples were collected in 2008 from 10 sites across the GTA that reflected a range of urban densities and land use types, and encompassed the 6 major watersheds in the area (Fig. 2). We sampled during 7 events of which 5 and 2 were taken under high and base flow conditions, respectively. At each sampling event, one 19 L sample was taken using a remotely triggered ISCO 6712 pump into pre-cleaned stainless steel canisters, after which it was stored at 4 °C until analysis.

Effluents of three WWTPs in the GTA were collected in 2008. The samples were obtained after the final treatment stage at each plant, immediately prior to being released into the receiving waters. Each 8 L sample was collected over the course of 24 h from each site using a remotely triggered ISCO 6712 pump into pre-cleaned amber glass bottles, which were immediately retrieved and stored at 4 °C until analysis. Ten samples were collected from each site over the same time period as the
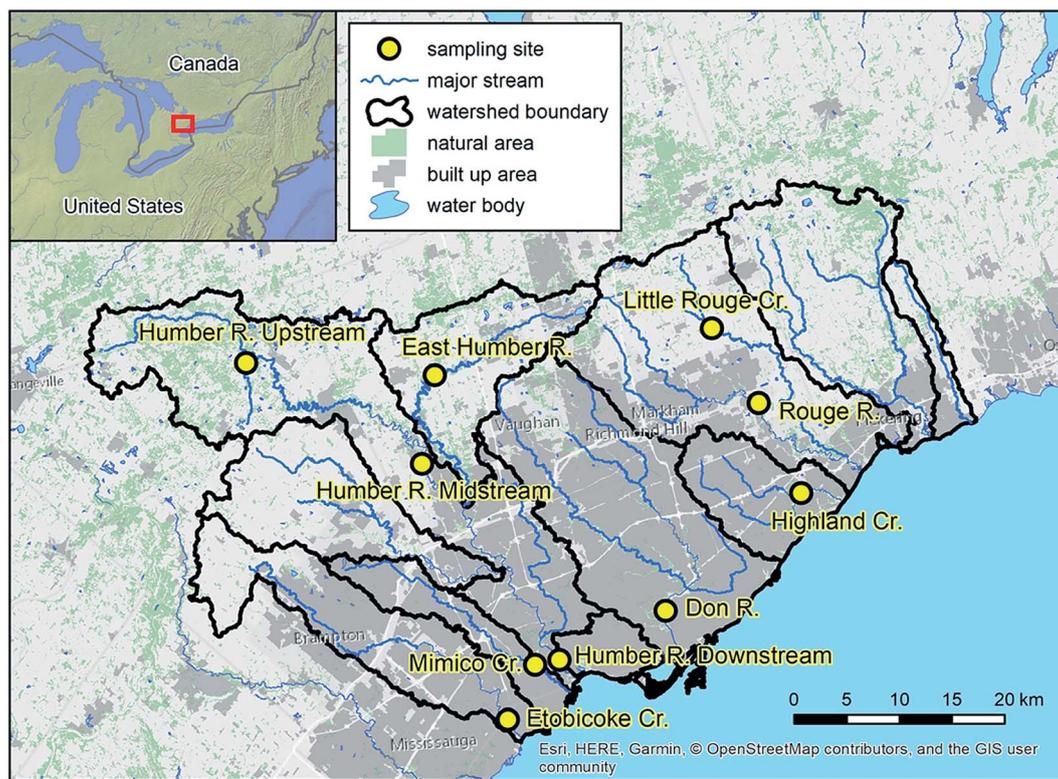
Fig. 2   Map of tributary surface water sampling locations.

tributary surface water samples. Further details are provided by Melymuk *et al.*[42]

Extraction and clean-up. SMCs were extracted from the water and wastewater samples by filtering them through a pre-cleaned GFF (142 mm diameter, 1.2 μm nominal pore size) followed by a XAD-4 sorbent resin column (30 mL bed volume). Both the XAD column and filter were then spiked with the internal standard (d_{10}-fluoranthene) and extracted on a Dionex ASE300 using acetone/hexane (1 : 1, v/v). The GFF and XAD extracts were then combined and dehydrated on a sodium sulfate column. Extracts were then purified as per the passive air samples that were taken at the urban-rural transects. Procedures are reported by Melymuk *et al.*[42]

Instrumental analysis

Table 1 lists the target SMCs along with their physical–chemical properties including partition coefficients of octanol–water (K_{OW}), octanol–air (K_{OA}), Henry's law constant (HLC), and sub-cooled liquid vapour pressure (P_L). The structures, chemical name, CAS no., supplier, % purity of standard used, solubility and half-live in air due to hydroxyl radical (OH) reaction are given in Table S1.† The indoor air, urban-rural transect air, urban air, soils, tributary surface waters and WWTP effluents were analysed at UT for 6 PCMs, namely cashmeran (DPMI), galaxolide (HHCB), tonalide (AHTN), phanolide (AHMI), celestolide (ADBI), traseolide (ATII). Analysis was achieved by gas chromatography-mass spectrometry analysis (GC/MS), using an Agilent 6890N gas chromatograph coupled to an Agilent 5975 Inert Mass Selective Detector (MSD) in electron impact (EI)

mode. GC/MS operation parameters are presented in S1.† The target SMCs were quantified against d_{10}-fluoranthene which was added prior to extraction. d_{10}-*p*-Terphenyl was added prior to instrumental analysis and it was used to quantify the recovery of d_{10}-fluoranthene.

The archived air samples from the WWTPs, rural and remote Arctic sites were analyzed at ECCC for 21 musks, including the 6 PCMs analyzed at UT. Samples were analyzed using an Agilent 7000C triple quadrupole MS connected to a 7890B GC, operated in multiple reaction mode (MRM) under EI conditions. The monitoring transitions for each target chemical are presented in Table S2.† Details about the operation parameters of the instrumental analysis are given in S1.† The SMCs were quantified against mirex, which was added prior to instrumental analysis.

Quality assurance and quality control

Each of the air sampling techniques that were used has been tested for many groups of persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), organochlorine pesticides and polybrominated diphenyl ethers (PBDEs).[76,77] Since PCMs have similar physical and chemical properties as POPs (*e.g.* log $K_{OA} \sim 8$), we believe that these collection techniques were suitable for PCMs.

The validity of the analytical method for SMCs in air, tributary surface water and WWTP effluents analyzed by UT was assessed through spikes of native musks to PUF-PAS ($n = 5$) and XAD resins used for tributary surface water samples ($n = 5$). These spiked samples underwent the same analytical

78 | *Environ. Sci.: Processes Impacts*, 2019, **21**, 74–88

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procedures as the air and water samples. Recoveries of native musks were 87% and 111%, respectively, for PUF-PAS and XAD. Mean recoveries for d_{10}-fluoranthene was ~80%. Further information about the QA/QC is given by Melymuk et al.[42]

The validity of the method for SMCs in air analyzed by ECCC was evaluated by external spike experiments to assess the recovery of 21 native SMCs on PUF-plugs ($n = 3$) and filters ($n = 3$). The spike samples were extracted by Dionex ASE350 with hexane and did not undergo clean-up. Recoveries of the 21 native SMCs ranged from 66–93% for the filters and 82–153% for the PUFs (Table S3†), which was considered satisfactory. The mean recoveries and standard deviations of individual native SMC spiked to each matrix is presented in Table S3.†

All sample and blank extracts were stored in amber GC vials, sealed with Teflon tape and stored in a freezer at $-10\ °C$. Calibration standards were stored in a separate freezer to prevent contamination of the sample extracts. Most samples were analyzed for SMCs within two years of sample collection. These included the indoor passive air samples, passive air and soil samples collected along the 3 urban-rural transects, urban active air samples, tributary surface water samples and waste-water treatment plant effluent samples. The archived air samples from the eight WWTPs in Ontario, rural site on the shore of Lake Ontario and remote site in the Canadian High Arctic were analyzed within 7 years of sample collection. To reduce blank contamination, all analysts were encouraged to reduce the use of any SMC-containing products. No SMC-containing products were allowed into the laboratories where the analyses were carried out. Trace amounts of SMCs were found in most blanks. The mean ± standard deviation (sd) of blank values for air and water are given in Table S5.† All data were blank corrected and non-detects were replaced with 2/3 instrumental detection limit (IDL) when performing statistical calculations. Values that were below 3 × sd of the mean blank were considered non-detect. IDL and blank values are given in Tables S4 and S5,† respectively. Statistical analysis was performed using Microsoft Excel 2010 and OriginPro 2017. We report total air concentrations as the sum of chemicals found in the filters and PUFs for samples which were collected by HV-AAS. We used medians and ranges to describe chemical concentrations in the discussion. As the air and water data were not normally distributed, Mann–Whitney test was used to assess the significant difference between datasets.

Readers are advised to interpret the data with caution in light of possible compromising factors including potential contamination and degradation of the less recalcitrant SMCs, such as the macrocyclic musk compounds. Particular care should be exercised in consideration of the archived air extracts from the eight WWTPs in Ontario, rural site on the shore of Lake Ontario and remote site in the Canadian High Arctic because of the extended extract storage time.

Results and discussion

Indoor air

Air concentrations of individual indoor sample were given in Table S6.† The sum of six polycyclic musks, (Σ_6PCMs), i.e.,

DPMI, ADBI, AHMI, ATII, HHCB, AHTN, in indoor air ($n = 20$) ranged from 0.42–200 ng m^{-3}, with a median concentration of 8.6 ng m^{-3}. AHMI was found in 80% of the samples and the other 5 PCMs were detected in 100% of the samples. Median concentrations of Σ_6PCMs in homes ($n = 10$, 12 ng m^{-3}) were 3 times greater than those in offices ($n = 10$, 3.8 ng m^{-3}) but not significantly different ($p > 0.05$). We found concentrations of DPMI in two homes (162 and 152 ng m^{-3}) and one office (79 ng m^{-3}) that were up to 5 orders of magnitude greater than those at other indoor locations (range 0.009–0.37 ng m^{-3}). PCMs in indoor air sorted in order of highest to lowest median concentration (ng m^{-3}) were: HHCB (4.5) > AHTN (2.1) > ADBI (0.15) > DPMI (0.090) > ATII (0.083) > AHMI (0.030). Excluding the three indoor environments that had high levels of DPMI, indoor air ($n = 17$) was dominated by HHCB (60%) and AHTN (29%) (Fig. S2†).

The overall range of HHCB and AHTN in our indoor air were respectively, 0.30–18 ng m^3, and 0.09–17 ng m^{-3}. These levels were much lower than those previously reported by Regueiro et al.[36] in homes from Spain, in which HHCB and AHTN, respectively, were in the range of 140–1130 ng m^{-3} and 21–77 ng m^{-3}; and those from Fromme et al.[32] in German kindergardens, in which HHCB and AHTN have mean concentrations of 120 ng m^{-3} and 47 ng m^{-3}, respectively. Sofuoglu et al. reported HHCB and AHTN range from 145–270 ng m^{-3} and 41–58 ng m^{-3}, respectively in classroom and sports center in Turkey. The wide-range in concentrations of SMCs in indoor air may be due to the diverse application and amount of SMC-containing consumer products, area of use, and type of building ventilation system.

Outdoor air and soils

Urban-rural transects in Toronto. Air concentrations along the three transects (total 19 sites) are presented in Table S7.† Detection frequencies of ADBI, AHMI, ATII, HHCB, and AHTN ranged from 78–93%. DPMI was not found in any of the samples. The concentration of Σ_6PCMs (DPMI, ADBI, AHMI, ATII, HHCB, AHTN) along the North transect ranged from 0.002–4.6 ng m^{-3}, the west transect ranged from 0.014–3.8 ng m^{-3} and the east transect 0.31–0.46 ng m^{-3}. HHCB was the most abundant PCM detected with a median concentration, of 0.99 ng m^{-3}, followed by AHTN, with a median concentration of 0.22 ng m^{-3}. The median percent contribution of HHCB and AHTN to Σ_6PCMs was 77% and 19% respectively.

Air concentrations of Σ_6PCMs along the urban-rural transect were positively correlated with population density (Fig. 3).[69] In general, the median Σ_6PCMs was ~3 times higher at the 3 most urban sites, which were located at 0 km, 1 km, and 5 km from the city centre, than at the 3 most rural sites, which were located 40 km, 60 km and 80 km from the city centre. Our results are consistent with those of McDonough et al.[41] who found significant correlations between population density and Σ_5PCMs (ADBI, AHMI, ATII, HHCB, AHTN) in both air and water. We hypothesize that PCM sources supporting this gradient are the collective emissions from indoor air via building ventilation and from WWTPs during the treatment process. The gradient is also accentuated by the relatively short atmospheric half-lives of
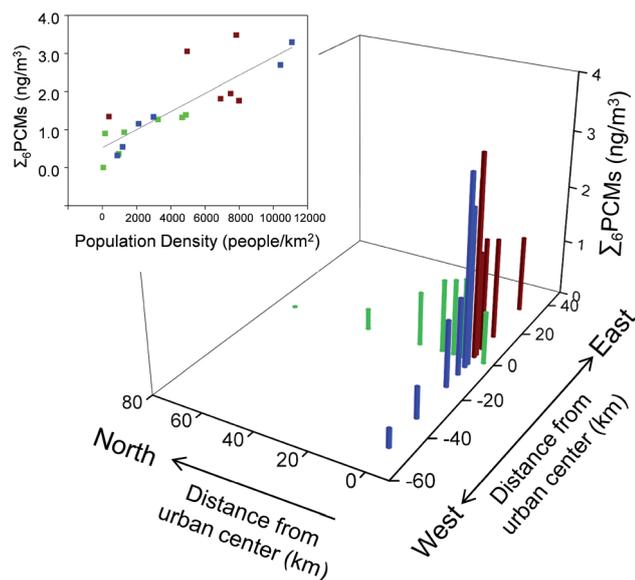
Fig. 3 Sum of 6 PCMs (Σ_6PCMs) along the urban-rural transects and correlation with population density. Urban centre is indicated as 0 km on the x and y scales. Red bar indicates the east transect, blue bar indicates the west transect and green bar indicates the north transect. Readers are referred to the web version of this article for interpretation of the references to colour.

the PCMs, which preclude significant atmospheric transport. Half-lives of these 6 PCMs in air ($t_{1/2,AIR}$) due to reaction with the hydroxyl radical range from 2.4 to 33 h (Table S1†).

In soils, none of the PCMs were found at detectable levels (*i.e.* in excess of the levels found in the laboratory blanks). The low levels of PCMs in soils were expected given the relatively high volatility (vapour pressure ranged from 0.034 to 1.6 Pa (ref. 3)) and fast biodegradation rate.[82,83] Therefore, despite high usage of PCMs in urban areas, urban soils are not considered to be a reservoir of PCMs in the environment.

Urban site at downtown Toronto. The total gas- and particle-phase concentrations of PCMs in Toronto urban air ($n = 32$) are given in Table S8.† The median concentration of Σ_6PCMs (DPMI, ADBI, AHMI, ATII, HHCB, AHTN) was 1.5 ng m^{-3}, ranging from 0.033–4.4 ng m^{-3} or within 2 orders of magnitude at the same site. DPMI was not found in any of the samples at this urban site. Median concentrations of HHCB and AHTN were 1.2 and 0.26 ng m^{-3} respectively. The median percent contribution of HHCB and AHTN to Σ_6PCMs was 80% and 16%, respectively (Fig. S2†).

Wastewater treatment plants in Ontario. Eleven SMCs (MX, MK, DPMI, ADBI, AHMI, HHCB, AHTN, 16-hexadecanolide, musk M4, cervolide, ethylene brassylate) were found in the air from 8 WWTPs in Ontario. Data are given in Table S9.† The median concentration of Σ_{11}SMCs in on-site air (WWTP-On) (mean of winter and summer) was 25 ng m^{-3} (range 0.36–166 ng m^{-3}), and off-site air (WWTP-Off) was 0.38 ng m^{-3} (range 0.19–35 ng m^{-3}). Thus, concentrations dropped by ∼100 times within 100–150 m of the source. It is also interesting to note that the WWTP-On concentrations were similar to those measured indoors, as discussed below.

Again, HHCB and AHTN were the dominant musks in all samples at both on-and off-site locations and seasons (Fig. S2†). In the WWTP-On air, HHCB ranged from 0.22–115 ng m^{-3} and AHTN ranged from 0.11–45 ng m^{-3}. In the WWTP-Off air, HHCB ranged from 0.091–22 ng m^{-3} and AHTN ranged from 0.049–11 ng m^{-3}. Nitro-musks (MK, MX) were found in WWTP-On air with concentration ranges of MK of <0.0017–0.23 ng m^{-3} and MX of <0.0028–0.21 ng m^{-3}. MK and MX were mostly non-detectable in WWTP-Off air (MK < 0.0017–0.104 ng m^{-3}; MX 0.0028–0.095 ng m^{-3}). Several MCMs (*i.e.* 16-hexadecanolide, musk MC-4, cervolide and ethylene brassylate) were found in the WWTP air at low concentrations. The sum of these four MCMs ranged from 0.052–20 ng m^{-3} for WWTP-On air and 0.053–1.9 ng m^{-3} for the WWTP-Off air. Fig. S2† shows the composition of SMCs in the WWTP-On air. HHCB, AHTN and cervolide accounted for 60%, 23% and 5.3% of the sum of SMCs. It is noted that overall PCMs and MCMs respectively accounted for 92% and 7% of the Σ_{11}SMCs found in the WWTP-On air. Our results agree with those of Upadhyay *et al.*[55] who reported that air from aeration basins of WWTPs in Arizona, U. S. was dominated by HHCB and AHTN. Our data support their contention that direct emissions of PCM from aeration tanks contributes to the environmental occurrence of SMCs.

We analyzed the correlation between the Σ_{11}SMCs from the WWTP-On air and selected operational parameters of the specific WWTP[71] (Fig. 4). Σ_{11}SMCs in WWTP-On air were positively correlated with population served ($p < 0.001$, $r = 0.77$) and influent water flow rate ($p < 0.001$, $r = 0.80$, but were negatively correlated with retention time ($p < 0.001$, $r = -0.91$) which may reflect greater removal of musks in the wastewater with extended time allowed for microbial activity in the aeration tank/lagoon.

Rural site in the Great Lakes Basin and remote site in the Arctic. Only HHCB and AHTN were detected in the gas-phase extracts from the rural site in the Great Lakes Basin ($n = 32$) (Table S10†). No SMCs were detected in the particle-phase. The median concentration (range) for HHCB was 0.031 (<0.00032–0.072) ng m^{-3} and for AHTN was 0.028 (<0.00024–0.038) ng m^{-3}. A similar proportion of HHCB (54%) and AHTN (46%) was found (Fig. S2†). At the remote site in the Arctic ($n = 21$), SMCs were not detected in any samples, except in one sample in which we found HHCB, musk M4 and ethylene brassylate. It is suspected that this sample had been contaminated during sample collection or analysis.

Overview of SMCs in air

Fig. 5 shows the Σ_6PCMs (DPMI, ADBI, AHMI, ATII, HHCB, AHTN) found in air from the WWTPs (on- and off-sites), Indoor, Urban and Rural sites (left panel) and the urban-rural transects (right panel). Median Σ_6PCMs of the 5 site types sorted in the order of highest to lowest concentrations were: WWTP-On > indoor > urban > WWTP-Off > rural. PCM concentrations in WWTP-On and indoor air were not significantly different, but both of them were significantly higher than all other sites, including the urban air, WWTP-Off and rural air. PCM concentration in rural air was significantly lower than all other sites. Σ_6PCMs in passive air samples from sites that were closer
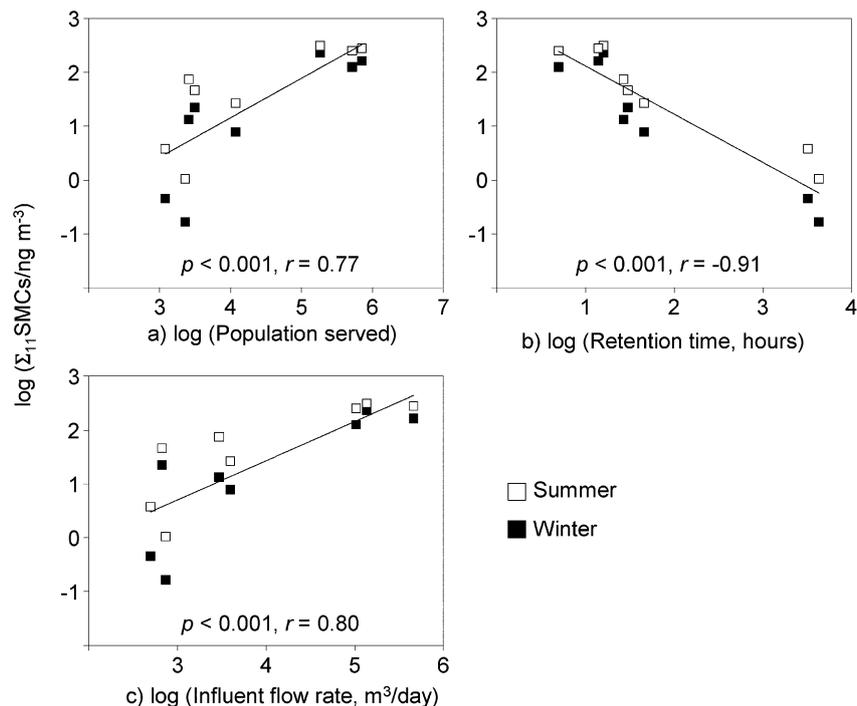
80 | *Environ. Sci.: Processes Impacts*, 2019, **21**, 74–88

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Fig. 4 Correlation between Σ_{11}SMCs in WWTP-On air (ng m^{-3}) and selected operational parameters, (a) population served, (b) hydraulic, retention time and (c) influent water flow rate.

to the urban center is within the range of those collected by active air sampling at the urban site of Toronto. Σ_6PCMs in passive air samples from sites that were further away from the urban center (>40 km) were similar to those obtained in rural site (Fig. 5, right panel). Our results imply that WWTPs and indoor environment are likely significant sources of SMCs to outdoor air, supporting the hypothesis of Harrad and Diamond (2006).[66]
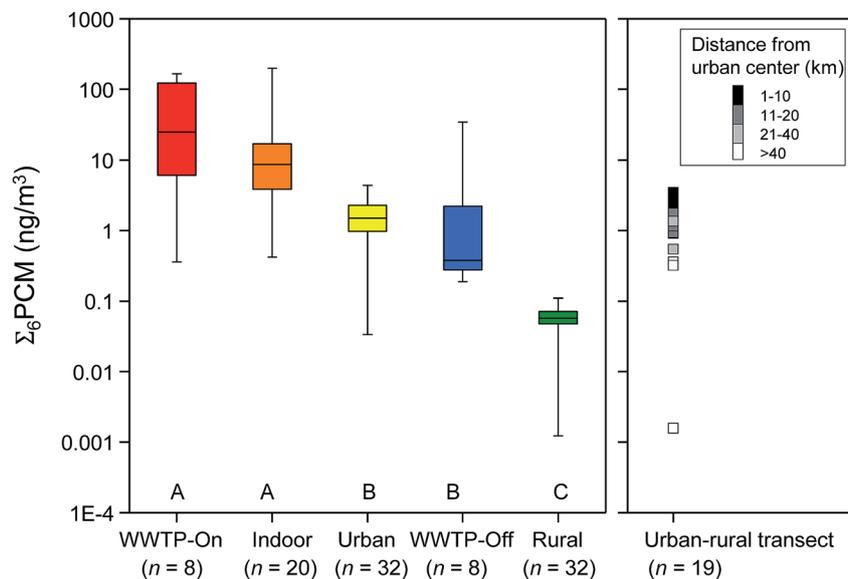

Fig. 5 The sum of 6 PCMs (Σ_6PCMs) found in air from: the on-site locations of the WWTPs (WWTP-On), indoor, urban, the off-site locations of the WWTPs (WWTP-Off) and rural site. n is the number of samples. The mid-line represents the median, whiskers are the maximum and minimum and the box represents 25th and 75th percentile of the data. WWTP-On refers to air taken above the aeration tank or adjacent to the lagoon. WWTP-Off refers to air ~100 m away from the premises of the WWTP. The mean of summer and winter data were used to summarize the levels in WWTP-On and WWTP-Off air. The urban and rural sites were represented by downtown Toronto and nearshore of Lake Ontario, respectively. Data for the urban-rural transect represent the mean of four sampling periods. Compounds sharing the same letter are not statistically different ($p > 0.05$).

We plotted literature concentrations of SMCs according to the nature of the sampling sites in Fig. 6 along with results from our study. The overall concentration gradients found for literature data were consistent with our results, with the highest SMC concentration found in indoor air, followed by urban, rural and remote air. The literature indoor air concentrations of the selected chemicals (HHCB, AHTN, ADBI, AHMI an MX) were higher than our WWTP-On and indoor air. In general, literature air concentrations of SMCs from the urban sites were in the same range as those in our urban air. The HHCB and AHTN levels in our rural site were in the lower range of those in the literature rural sites. Data about the nitro-musks in the literature were scarce and their levels were variable among the sampling sites.

Temperature dependence and seasonal trend of SMCs

The temperature dependence of selected SMCs was investigated in air from the urban and rural sites obtained by HV-AAS every 12 days (Fig. 7). We observed a negative correlation ($p < 0.05$) between the natural log gas-phase concentrations (ln C) of HHCB and AHTN and the inverse temperature at both these sites and ATII at the urban site. Air concentrations were generally higher during the warm season than the cold season, consistent with greater volatilization from sources (e.g., WWTP) and/or the effect of greater releases of indoor air during warm weather when ventilation increases. Peck and Hornbuckle[39] also found a strong negative relationship between HHCB and AHTN

in outdoor air in Iowa and inverse temperature. We observed that Σ_{11}SMCs in SIP-PAS-derived air concentrations from the WWTP-On and WWTP-Off site taken during the summer were greater than those in the winter which is consistent with greater temperature-dependent volatilization (Fig. S3†). At WWTP-On, the median concentration of Σ_{11}SMCs in summer was 41 vs. winter 7.1 ng m^{-3}, at WWTP-Off, the level of Σ_{11}SMCs in summer was 0.84 vs. winter was 0.20 ng m^{-3}. No significant correlation was observed between concentrations of ADBI and AHMI and temperature and the reason is unclear.

HHCB/AHTN ratio was calculated to investigate potential sources. Here, the ratio of HHCB/AHTN was calculated when both compounds were above the detection limit in the same sample. The ratio should decrease with distance from the source because HHCB ($t_{1/2,\text{AIR}} = 0.22$ d (ref. 64)) has a shorter atmospheric lifetime than AHTN (($t_{1/2,\text{AIR}} = 0.60$ d (ref. 3)). The median (range) of HHCB/AHTN ratios were as follows: WWTP-On: 2.6 (1.5–6.8); indoor: 2.3 (0.88–4.0); urban: 4.9 (0.98–7.8); WWTP-Off: 2.2 (0.71–7.0); and rural: 1.2 (0.82–1.9). The HHCB/AHTN ratio at the urban site agrees well with those reported in the nearshore air samples from Toronto by McDonough et al.[41] of 5 ± 1. However, it is odd that the ratio for indoor air, the presumed source of these compounds that are not influenced by atmospheric loss processes was lower than for urban air. HHCB/AHTN ratio of 0.9–1.7 in air in the North Sea and 0.1–0.4 in air in the Arctic was reported by Xie et al.[37] In a urban site in Germany, ratio of HHCB/AHTN was 3.5, which was similar to our HHCB/AHTN ratio at the urban site. We note that the ratio
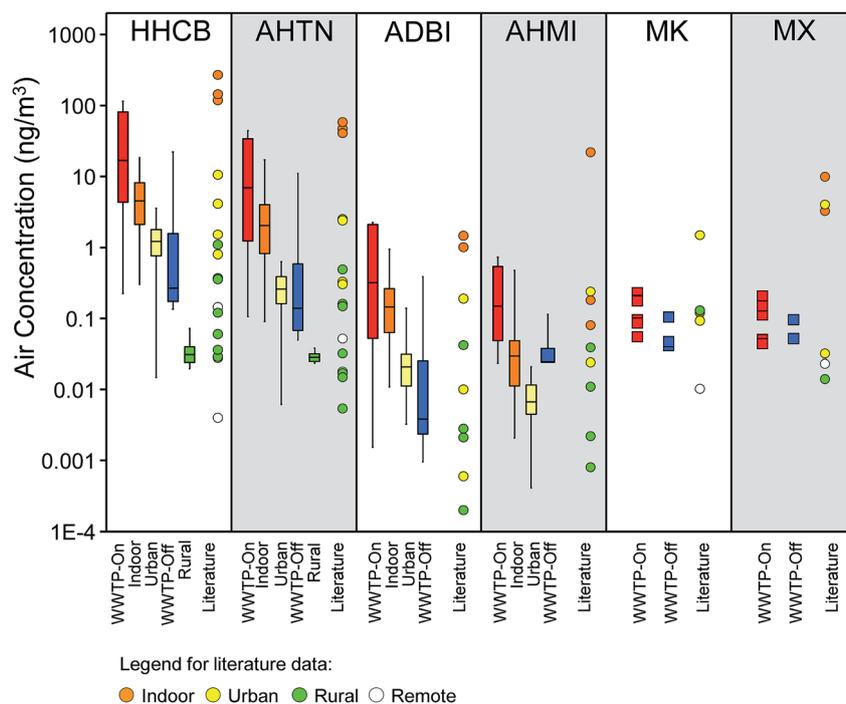
Fig. 6 Air concentrations of SMCs measured in this study and the literature. The literature data are given in Table S11.† Data from this study is shown as whisker–box plot. Refer to Fig. 5 for definitions of the whiskers and box. Data for MK and MX from this study are shown as individual data because only few data was available. Reference for the indoor air (orange dot) – Fromme et al.,[32] Sofuoglu et al.,[35] urban air (yellow dot) – Peck et al.,[38,39] Ramírez et al.,[84] McDonough et al.,[41] rural air (green dot) – Peck et al.,[38,39] Xie et al.[37] McDonough et al.;[41] remote air (white dot) – Xie et al.,[37] Kallenborn et al.[85]

82 | Environ. Sci.: Processes Impacts, 2019, 21, 74–88

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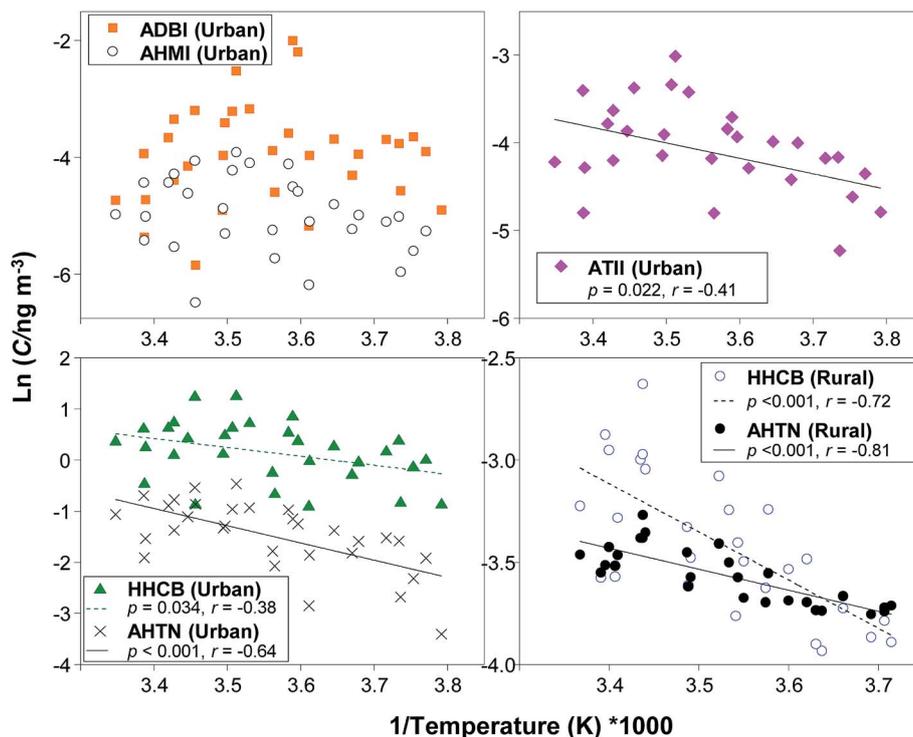**Fig. 7** Correlations between gas-phase air concentrations of selected PCMs (ln (C/ng m^{-3})) and inverse temperature (T, K^{-1}) at urban and rural sites. Linear regression statistics are shown for significant correlations. r represents the Pearson's correlation coefficient. Air concentrations were obtained from a HV-AAS.

of HHCB/AHTN is influenced by the difference in volatility of the two chemicals. However, the extreme uncertainty in the Henry's law constant of AHTN, which ranged from 4.28–1210 Pa m^3 mol^{-1}, makes the interpretation difficult (Table 1).

Our results suggested that the occurrence of PCMs in ambient air is due to local emissions from indoor air ventilation, as well as volatilization from WWTP during the treatment process. We did not observe any evidence of regional or long-range transport of the PCMs or other SMCs. This is likely because most SMCs are short-lived chemicals (Table S1†).

Surface waters of tributaries in GTA and wastewater plant effluents

Concentrations of PCMs in the tributary surface waters are given in Table S12,† and are summarized in Fig. 8 and S4.† A strong urban-rural trend was evident with tributary concentrations 1–4 orders of magnitude higher at the urban ($n = 5$) than at the rural sites ($n = 5$). Specifically, the median Σ_6PCM concentrations of the seven sampling events ranged from 0.016 ng L^{-1} at the rural site, Humber River Upstream, to 100 ng L^{-1} at the urban site, Don River. In general, median concentrations at the urban sites (Σ_6PCM range 3.9–100 ng L^{-1}) exceeded those at the rural sites (range 0.016–2.7 ng L^{-1}). These values were less than those reported elsewhere *e.g.* the Elbe River in Germany at 184 ng L^{-1} Σ_5PCM,[86] the Glatt River in Switzerland at 214 ng L^{-1} Σ_5PCM,[58] and the Ruhr River in Germany at 600 ng L^{-1} Σ_5PCM.[87]

HHCB and AHTN dominated SMCs in the tributary surface water, which respectively accounted for 74% (48–87%) and 19%

(9–27%) of Σ_6PCMs. Other PCMs contributed <2% of Σ_6PCMs. The median concentrations of PCMs in the urban sites ranged from 2.9–83 ng L^{-1} for HHCB and 0.99–15 ng L^{-1} for AHTN, which generally exceeded those in Lake Ontario and Lake Erie for HHCB and AHTN of non-detect to 1.6 ng L^{-1} and 0.014 to 0.16 ng L^{-1}, respectively.[41]

Several sources likely contribute to PCMs in urban surface waters: (1) entry *via* storm water, (2) direct discharge into tributaries due to illegal sanitary sewer cross connections, and (3) WWTP discharges. The first explanation (1) involves PCM scavenged from air by precipitation and wash-off of atmospherically deposited PCMs to films on impervious surfaces.[88] By far the highest concentration seen at one urban site (Don River) was likely due to releases from an upstream WWTP.

Concentrations of PCMs in WWTP effluent are given in Table S13.† The median Σ_6PCMs concentrations in WWTP effluents were one order of magnitude higher than those in the tributary surface water (Table 2). Within WWTPs, the highest Σ_6PCM concentration was in Plant 2 (median 3300 ng L^{-1}; 1600–11500 ng L^{-1}), which is the largest of the three WWTPs, serving a population of approximately 1,524,000 as well as numerous commercial and some industrial facilities. HHCB and AHTN were the most abundant SMCs found in WWTP effluents, as reported previously.[53]

Median concentrations of HHCB in the effluents of the three plants ranged from 1000–1800 ng L^{-1} and for AHTN ranged from 140–270 ng L^{-1}, which were comparable with effluents from other WWTPs in Canada[89,90] but much higher than one WWTP located in Peterborough, Canada.[82] These variations
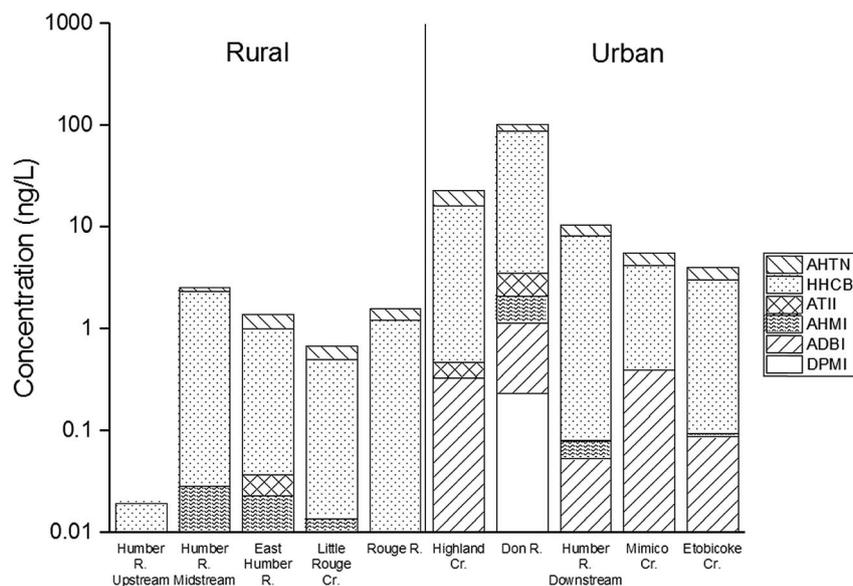
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Environ. Sci.: Processes Impacts, 2019, **21**, 74–88 | 83

Fig. 8 Median concentrations of PCMs (ng L^{-1}) in surface waters of tributaries in rural and urban sites of the Greater Toronto Area (GTA).

Table 2 Σ_6PCMs (*i.e.*, DPMI, ADBI, AHMI, ATII, HHCB, AHTN) in effluents of WWTPs

	Plant 1 ($n = 4$)	Plant 2 ($n = 6$)	Plant 3 ($n = 7$)
Population served	450 000	1 524 000	651 000
Σ_6PCMs (ng L^{-1})			
Median	2100	3300	1800
Standard deviation	430	3900	2500
Minimum	1700	1600	860
Maximum	2600	11 500	8200

were likely due to differences in inputs within the sewer-sheds, facility capacities, and retention times, in addition to differences in contributions from storm water to WWTP.

The half-life of HHCB in experimental lake water due to photolysis is about 25 times longer than for AHTN (109 *vs.* 4 h) and hence a higher HHCB/AHTN may indicate an aged source.[91] The HHCB/AHTN ratios in the urban tributary surface waters (2.6–5.9) were not significantly different from those at the rural sites (1.2–4), with one exception for Humber River Midstream that showed a high ratio of 23, consistent with aging. In the WWTP effluents, the HHCB/AHTN ranged from 7.2–8.3, which was higher than those in the tributary surface waters but similar to those reported in water from Lake Ontario, with ratio of 6–9 measured in 2005 (ref. 92) and 7–12 measured in 2012.[41] In water of the North Sea, the median (range) ratio of HHCB/AHTN of 2.0 (0.8–5.0) was reported,[37] which is much lower than the ratio in our WWTP effluents.

Conclusions

We investigated the occurrence and potential sources of SMCs in the urban environment in Canada. Highest concentrations of SMCs were found in indoor air, and WWTP On-site air, and the levels of which were not significantly different. SMCs in ambient air and tributary surface water were positively correlated with population density. These concentrations varied by ~3-fold and ~20-fold between urban and rural sites for air and water, respectively. Our results indicated that WWTP and indoor environment are likely main sources of SMCs to the environment. SMCs were not found in remote Arctic air indicating low potential for long-range atmospheric transport. SMCs were also not found in soils, consistent with their high rates of biodegradation and relatively high volatility. In all media, the PCMs particularly, AHTN and HHCB dominated the composition of SMCs. WWTP On-site air, trace levels of the toxic nitro-musk, namely MX and MK were detected despite having been phased out since the late 1990's. MCMs accounted for ~10% of the total SMCs measured. Although the long-range transport potential of these chemicals is low, the continuous release of SMCs in high volumes from the urban environment, notably wastewater treatment plants, could pose a chronic toxicological threat to biota in receiving waters. We noted that there are factors that may compromise the interpretation of our results. Such factors include the various sampling techniques, analytical approaches and sample extract storage and archiving conditions. However, our initial screening of SMCs in a wide-array of environmental media provided valuable baseline information for planning future research specifically built for these chemicals. Finally, we recognize that experimental physical–chemical properties of SMCs are scarce. Large discrepancies in the physical–chemical property values of SMCs were found in the literature (Tables 1 and S1†). Future studies focusing on the physical-chemical and toxicological properties of SMCs and their degradation products are recommended to improve our understanding of their environmental fate and risk to ecological and human health.

84 | *Environ. Sci.: Processes Impacts*, 2019, **21**, 74–88

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Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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