Wastewater Treatment Plants as a Source of Synthetic Musks in the Great Lakes Region

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Introduction

Synthetic musk compounds (SMCs) are semi-volatile cyclic organic chemicals that are used as fragrance materials. These compounds are used widely as additives in personal care and household products such as perfumes, soaps, lotions, cosmetics, shampoos, air fresheners, detergents and deodorants. Synthetic musks are categorized into three main groups according to their chemical structures: i) nitro musks (NM), ii) polycyclic musks (PCM), iii) macrocyclic musks (MCM) and alicyclic-musks (ACM). NMs are known to be toxic and have been phased out in Europe and Japan. In Europe, the use of several NMs, i.e., musk xylene, musk ambrette, musk moskene and tibetene is prohibited, and the use of musk ketone is limited[1]. NMs have vapour pressures (musk xylene and musk ketone of 3×10^{-5} Pa and 4×10^{-5} Pa, respectively) and octanol-water partition coefficients (K_{OW}) (log K_{OW} of musk xylene and musk ketone of 4.9 and 4.3, respectively) similar to hydrophobic chemicals such as organochlorine pesticides and polychlorinated biphenyls[2,3]. NMs are considered to be very persistent and very bioaccumulative, although the US and Canada do not have restrictions on these chemicals. As a result of the regulations and restrictions of NMs in Europe and Japan, PCMs dominate the market. MCMs are not frequently detected in the environment due to their low production volume, and are quick to degrade as their chemical structures resemble the natural musks. However, the MCMs are becoming more available because of the advances made in synthesis methods over the last few years. It is expected that the decrease in the synthesis price of the MCMs and their environmentally friendly properties will favour the replacement of the PCMs by the MCMs in the market in the coming years. ACMs are the fourth generation of odorant musks, but their use in personal care products is still very limited. SMCs are ubiquitous in the environment due to their extensive use. Melymuk et al.[4] calculated annual loadings of PCMs to Lake Ontario from Toronto to be mainly via waste water treatment plant (WWTP) effluent (~83% of total loadings) with gas absorption from the atmosphere at ~10 % and tributaries contributed ~7 %. In this study, the levels of SMCs in air, wastewater influent and effluent and biosolids at four WWTPs are assessed to determine how their usage and releases have changed over the last decade. This information is essential for the evaluation of how these compounds are released to the Great Lakes Basin (GLB) from WWTPs, how they change over time and their cycling in the GLB environment.

Materials and methods

Air samples were collected at four WWTPs located in Ontario during winter (February 28 to March 9) and summer (August 15 to 31) of 2017. The WWTP facilities participated in this study on the condition of anonymity; therefore names and locations will not be disclosed. They will be referred to as Plants K, W, P and J. At each WWTP, 3 on-site and 1 off-site air samples were obtained. The on-site samples were collected above the aeration tank or adjacent to the lagoon, while the off-site samples were collected ~100 to 150 m upwind of the on-site sampling location. Air samples were collected using high-volume active samplers (Hivol),The sampling train consisted of one glass fiber filter (GFF) (10cm Pall Corporation, Millipore Sigma), followed by a PUF/XAD-2 (pre-cleaned, Millipore Sigma, 15 g)/PUF sandwich (hereafter referred as PUF sandwich). Each sample represented ~540 m^3 of air, taken over 24 hours with flow rate of ~25 m^3/hour. Before deployment, the GFFs were baked at 400 °C for 24 hours, and the PUFs were extracted by an accelerated solvent extraction system, Dionex ASE350, twice using acetone/hexane (1:4), followed by a final extraction with hexane. The PUFs were dried under gentle stream of nitrogen for 70 minutes at ~60°C. All samples were stored at 4°C until

analysis. Prior to extraction, 100 ng each of d_{15}-musk xylene, d_9-musk ketone, d_3-tonalide were spiked to each sample to monitor recoveries. The GFFs and PUF sandwiches were separately extracted by Dionex ASE350. The extraction was carried out using hexane (100%, 3 cycles) at 75 °C, 240 seconds purge, static time of 5 minutes, and rinse volume of 100%. All samples were concentrated using a Turbovap system at 38°C followed by gentle nitrogen blow down, solvent exchanged into iso-octane with a final volume of 1 mL. Prior to instrumental analysis, d_{10}-fluoranthene (200 ng) was added to each sample as the internal standard for sample volume adjustment. Air samples were analyzed by gas chromatography coupled to tandem mass spectrometry (GC/MS/MS), operated in multiple reaction mode (MRM) in electron ionization (EI) mode. Twenty one SMC compounds were analyzed including five NMs [Musk Tibetene (MT), Musk ambrette (MA), Musk moskene (MM), Musk ketone (MK), Musk xylene (MX)], eight PCMs [1-methyl-alpha-ionone, Cashmeran (DPMI), Amberonne (OTNE), Celestolide (ADBI), Phantolide (AHMI), Traseolide (ATII), Galaxolide (HHCB), Tonalide (AHTN)], and eight MCMs (exaltone, muscone, exaltolide, ambrettolide, 16-Hexadecanolide, MUSK M4, cervolide, ethylene brassylate).

Wastewater and biosolid samples were also collected at the same WWTPs. All 24-hour composite samples of raw influent and treated effluent from WWTPs were collected using Hach refrigerated autosamplers (Loveland CO, USA) with Teflon-lined tubing and stainless steel containers at a frequency of 200 mL every 15 minutes. All grab samples of biosolids were collected using stainless steel containers. Subsamples were transferred into pre-cleaned 1L Amber glass bottles with Teflon-lined lids (Systems Plus, Baden ON). All samples were stored in coolers with icepacks during transport. Upon arrival they were stored in a refrigerator at 4 °C until analysis. 500 mL of water or wastewater sample was spiked with internal standards (D_3-tonalide and D_{15}-Musk Xylene) and extracted three times with 50 mL of petroleum ether. Fractionation was accomplished using 2 g of 5% deactivated silica gel and eluted with 10 ml of 5 % acetone in hexane. Biosolid samples were oven dried (120 °C) overnight and extracted using by Accelerated Solvent Extraction (ASE) in acetone/hexane (1:1 v/v). The cleanup procedure was the same as used for wastewater. NMs were analyzed by GC/MS/MS operating in electron capture negative ion (ECNI) where the remaining SMCs were analyzed by GC/MS/MS in EI mode.

Results and discussion:

Concentrations of SMCs in WWTP on-site air The sum of SMCs on the GFF and PUF sandwich is reported, i.e. representing the total gas and particle phase chemicals. Thirteen musk compounds (MK, MX, 1-methyl-alpha-ionone, DPMI, OTNE, ADBI, AHMI, HHCB, AHTN, muscone, 16-Hexadecanolide, MUSK M4, ethylene brassylate) were detected in the WWTP on-site air samples. Overall, SMCs in the on-site air collected from plants K and W were similar with Σ21-SMCs = 830 and 800 ng/m^3, respectively. SMCs in the on-site air from these two sites were ~80 times higher than those from plants P (Σ21-SMCs = 10) and J (Σ21-SMCs = 6.6 ng/m^3). The higher air concentrations of SMCs at plants K and W may be due to the larger population served and/or greater influent flow rate of these facilities relative to plants P and J. Positive correlation between SMC air concentration and WWTP population served and influent flow rate has been seen in a previous study conducted in 2013/14 at 8 WWTPs[5].

At all WWTPs, the most abundant SMCs in the on-site air were the PCMs. At K and W, the highest concentration of PCMs were OTNE (430, 390 ng/m^3) >HHCB (510, 290 ng/m^3) >AHTN (8.1, 6.3 ng/m^3). At plants P and J, concentrations of OTNE (3.9, 2.8 ng/m^3) and HHCB (5.1, 3.0 ng/m^3) were similar. Air concentrations of these two musk compounds were about 10 times higher than AHTN (0.56, 0.37 ng/m^3).

Only two NMs (MK and MX) were detected in the on-site air samples and their concentrations were low. MK ranged from 0.022-0.088 ng/m^3, and MX ranged from non-detected to 0.18 ng/m^3.

WWTP On-site vs Off-site air In general, the Σ_5NMs and Σ_8PCMs in the on-site air were higher than the off-site air (Figure 1). The greatest difference was observed with the PCMs. It is interesting to note that the air concentrations of Σ_8MCMs were similar between the on-site and off-site air for P. Furthermore, Σ_8MCMs was

higher in the off-site air than the on-site air at plant J. This may indicate an additional source of MCMs (other than the WWTP) at this off-site sampling location.

Seasonal variation in WWTP on-site air   In the WWTP on-site air, concentrations of most SMCs were higher in summer than winter. OTNE, HHCB, AHTN and 16-hexadecanolide showed a distinct difference between summer and winter time. This may due to greater volatilization of these chemicals with higher temperature. However, concentrations of the other two MCMs (i.e. MUSK M4 and ethylene brassylate) were similar in the summer and winter times and the reason is unclear.
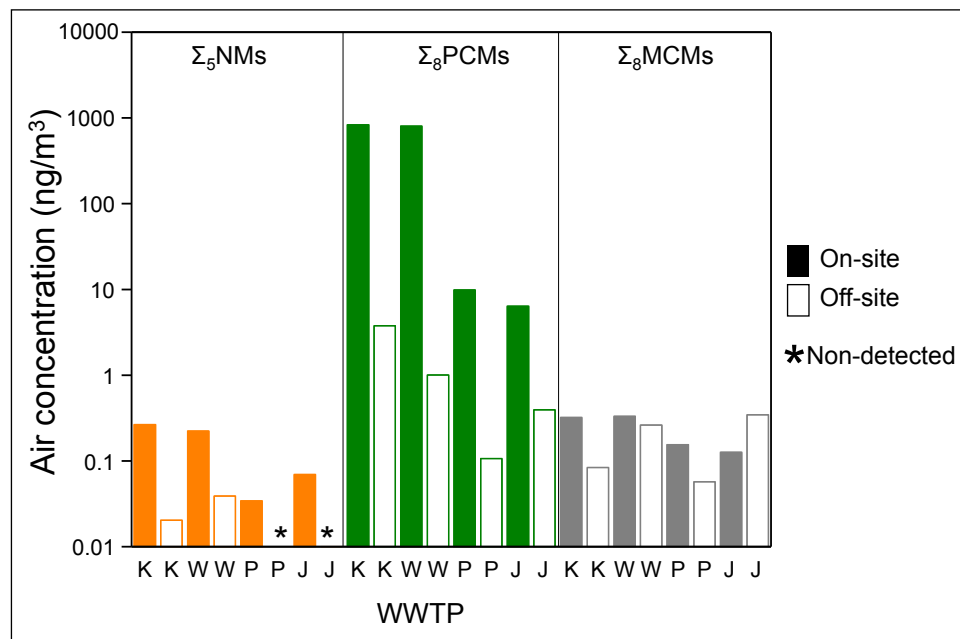

Figure 1. Sum of 5 NMs, 8 PCMs and 8 MCMs in WWTP on-site and off-site air. Mean concentrations (ng/m^3) of winter and summer data are presented.

Wastewater concentrations All MCMs with the exception of ethylene brassylate were below detection limit in the influent and effluent of all WWTPs. HHCB and OTNE had the highest concentration followed by AHTN. Similar results have been observed in air samples collected from the same sites. For one of the 4 WWTPs, Smyth et al.[6] collected wastewater samples between Aug 2003 and Apr 2005 and reported that HHCB had the highest concentration followed by AHTN, albeit they did not report on OTNE. The average concentrations for these two compounds increased by 67 % and 200 % for HHCB and AHTN, respectively, over the past 12 years.

For NMs, MK and MX have the highest concentrations and have been frequently reported in previous studies. A comparison of results from this study with results reported by Smyth et al.[6] from the same sampling site indicates a major reduction in levels of NMs. Levels of MK have dropped by a factor of 8, while levels of MX have dropped by a factor of 26 during cold sampling periods and 130 for samples collected during warm periods. This indicates that risk management measures put in place have been effective in reducing the use of these compounds.   In terms of removal efficiencies for PCMs and MCMs, overall removal efficiencies were above 60% except for DMPI in plant J and K.

Biosolid concentrations In general, NMs were detected at trace concentrations in biosolids from these sites**.** MA and MM were the most commonly detected NMs with typical concentrations in the 10 – 40 ng/g. However, the biosolids data for NMs do not indicate that biosolids constitute a significant sink, or vector for entry of these compounds into the environment. We were also unable to distinguish any apparent seasonal trends in NM

concentrations in biosolids. For the MCMs, HHCB was detected in all samples with a concentration range of 2.2 – 71 ng/g (average value of 32 ng/g); OTNE was also prevalent and detected in roughly half of the sample set.

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