FATE OF SYNTHETIC MUSK COMPOUNDS IN WASTEWATER TREATMENT PLANTS

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Introduction

Synthetic musk compounds (SMCs) are fragrant chemicals that are used widely in personal care and household products, e.g. lotions, soaps, perfumes, shampoos, detergents and deodorants etc. SMCs are ubiquitous in the environment due to their extensive use. They are semi-volatile and are generally categorized into three main groups based on 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 musk tibetene are prohibited, and the use of musk ketone is limited[1]. NMs have physical-chemical properties similar to many persistent organic pollutants (POPs) such as organochlorine pesticides and polychlorinated biphenyls[2,3]. NMs are considered to be very persistent and very bioaccumulative. Due to the restrictions and regulations on NMs, PCMs dominate the market. MCMs are more difficult to manufacture and production volumes are low. Also, they tend to degrade faster than the other SMCs. Therefore, MCMs are not frequently detected in environmental samples. However, the MCMs are becoming more available due to advances in synthesis methods. The lowered cost of manufacturing MCMs and their environmentally friendly properties will favour the replacement of the PCMs by the MCMs in the market in the future. ACMs are the fourth generation of odorant musks, but their use in personal care products is still very limited. In this study, the levels of SMCs in air, wastewater influent and effluent and biosolids at four WWTPs were measured and a fugacity-based mass balance model is used to better understand their fate in the wastewater treatment process.

Materials and methods

Air samples were collected at four WWTPs located in Ontario during the 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 are not disclosed. They are referred to as Plants J, K, P and W. 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 trap 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), first using acetone/hexane (1:4) two times, followed by hexane. The PUFs were dried under a 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 and d_3-tonalide were spiked into each sample to monitor recoveries. The GFFs and PUF sandwiches were separately extracted by the 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 isooctane 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 SMCs 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 biosolids samples were also collected at the same WWTPs. 24-hour composite samples of raw influent and treated effluent from WWTPs were collected using Sigma/Hach 900 refrigerated autosamplers (Loveland CO, USA) with Teflon-lined tubing and stainless steel containers at a frequency of 200 mL every 15

minutes. Subsamples were transferred into pre-cleaned 1L Amber glass bottles with Teflon-lined lids (Systems Plus, Baden ON). Grab samples of biosolids were collected using stainless steel containers. Samples were transported to the lab the same day as collection and were stored 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. Biosolids samples were freeze-dried (-80 °C) and extracted 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.

A Level 3 fugacity-based multi-media environmental model was used to elucidate the fate of musk compounds in WWTPs. Concentrations C (mol/m^3) can be expressed as a function of fugacity f (Pa):

$$C = Zf \qquad (1)$$

where Z is the proportionality constant (termed the fugacity capacity) has units of (mol/m^3·Pa) and is specific to temperature, the compound, and the phase in which the compound resides. Three phases are considered in a WWTP system, namely air (A), water (W) and solids/sludge (S) are considered. For compounds in air,

$$Z_A = 1/RT \qquad (2)$$

where R is the gas constant (8.314 Pa·m^3/mol·K) and T is absolute temperature (K).
For compounds in water,

$$Z_W = 1/H \qquad (3)$$

where H is the Henry's law constant (Pa·m^3/mol).
For compounds in solids,

$$Z_S = C_S \times Z_W /C_W \qquad (4)$$

where C_S and C_W are concentrations measured in biomass and the aqueous phase that are assumed to have reached equilibrium. An important step of calculation is to derive D values, which are transport or transformation parameters with units of mol/Pa·h. When multiplied by a fugacity, they give rates of transport or transformation. Magnitude of D values is a measure of the relative importance of that transport or transformation process to input or output to and from a specific medium. Three types of D values were calculated. For advective processes such as inflow and outflow of air, water, aerosol particles present in air, and particles and biota present in water, the fugacity rate constant is calculated as,

$$D = G \times Z \qquad (5)$$

where G is the flow rate of the phase with the unit of m^3/h.
For degrading reactions, the fugacity rate constant is expressed as,

$$D = k \times V \times Z \qquad (6)$$

where V is the volume of the phase (m^3), k is the first-order rate constant (h^{-1}), and.
For volatilization, the D value is calculated as,

$$D = K_V \times A \times Z \qquad (7)$$

where K_V is the overall mass transfer coefficient (m/h), A is the interfacial area of air and water. K_V is related to the water side (K_W), air side mass transfer coefficients (K_A), and the dimensionless Henry's law constant (H'),

$$1/K_V = 1/K_W +1/K_A H' \qquad (8)$$

Using the mass balance approach, input flux (I) should be equal to output flux (O) in each compartment,

$$I = O = f (\Sigma D) \qquad (9)$$

where f is the fugacity of a compound in a compartment, ΣD is the sum of the D values for all the possible fates in that compartment. A schematic diagram of a WWTP is shown in Figure 1.
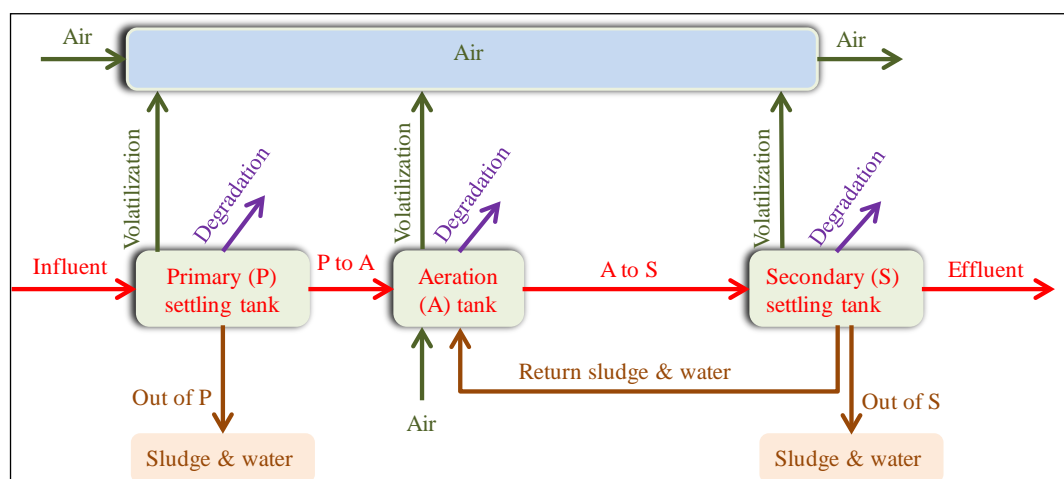
Figure 1 Schematic diagram of fugacity-based model

Results and discussion:

Measured Concentrations in Air, Wastewater and Biosolids
Details in the measured SMCs found in air, wastewater and biosolids were previously reported.[4] In brief, 13 musk compounds (MK, MX, 1-methyl-alpha-ionone, DPMI, OTNE, ADBI, AHMI, HHCB, AHTN, muscone, 16-Hexadecanolide, MUSK M4, and 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 but were ~80 times higher than those from plants P and S; this is probably due to the much smaller populations than the former 2 plants serve and, also, much smaller surface areas of the WWTP processing units. At all WWTPs, the most abundant SMCs in air and wastewater were the PCMs. Only two nitro musks (MK and MX) were detected in the on-site air samples and their concentrations were low. For the NMs, when comparing the 2017 wastewater measurement results with results reported by Smyth et al.[5] from the same sampling site indicates a major reduction in levels of NMs, indicating the effectiveness in the regulation of these compounds. MA and MM were the most commonly detected NMs in biosolids at trace amounts.

Mass Balance for SMCs
As a case study, SMCs measured in wastewater and air samples taken from plant K, Ontario in August, 2017 were selected for use in this mass balance analysis. Detailed results of HHCB are discussed here as an example because it is one of the most abundant target compound in the water and air samples from this study. The fugacity of HHCB in the primary settling (P) tank, aeration (A) tank, secondary settling (S) tank, and air were calculated as 2.5×10^{-4} Pa, 1.7×10^{-4} Pa, 1.7×10^{-4} Pa, and 1.3×10^{-6} Pa, respectively. Input flux from influent was calculated at 0.13 mol/h or 32 g/h, while the output flux to effluent was 0.0082 mol/h or 2.1 g/h, suggesting that most of HHCB was removed from wastewater treatment process. Output flux to air from P tank, A tank, S tank were calculated to be 0.077 g/h, 0.46 g/h and 0.054 g/h, respectively, suggesting that output to the air was mostly from A tank. Output flux to sludge from P tank (19 g/h) and S tank (4.0 g/h) accounts for the largest proportion of input flux from influent, suggesting that most of HHCB was removed via sorption to the sludge.

Fate of SMCs
Our results suggested that removal of the target compounds from the wastewater was governed by the combined effects of sorption, advection, volatilization and biotransformation. It is confirmed that musk compounds entering WWTPs are partially partitioned to biosolids, with the percentage ranging from 29% for musk MC-4 to 72% for traseolide, suggesting that the majority of target compounds were removed from the wastewater mainly through sorption to biosolids. Musk ketone had approximately 56% of its mass remaining in effluent water due to relatively low bio-transformation (4.5%) and volatilization (2.7%) rates. Final removal rate of SMCs ranged from 44 % for MK to 98% for 16-hexadecanolide, indicating that target compounds are not completely removed from the effluent. Musk MC-4 had the highest proportion of removal via biotransformation (38%) whereas MK had the lowest (4.5%). For all musk compounds, volatilization to the air represented a small loss mechanism, ranging from 0.01% for musk MC-4 to 11% for celestolide.

Comparison of Modeled and Measurement Results
For effluent, the predicted concentrations of target compounds were generally lower than that of measured concentrations within one order of magnitude, except for 1-methyl-alpha-ionone, which shows higher predicted concentration than measured. However, predicted effluent concentrations and measured values were significantly correlated with each other (r = 0.79, p < 0.05), implying the good fit between measured and estimated effluent concentrations of target compounds. For air, according to the prediction, the proportion of musk compounds emitted to the air were 0.01-11.08%, which could result in considerable amounts of musk compounds being emitted to the air because wastewater influent concentrations were very high. Predicted air concentrations of musk compounds ranged from 27 to 4.5×10^5 pg/m^3, which were lower but close to that of measured concentrations with the values ranged from 86 to 7.1×10^5 pg/m^3. The predicted air concentrations of target compounds and the measurements were significantly correlated with each other (r = 0.93, p < 0.05), implying the good fit between measured and estimated concentrations of target compounds in air. Further optimization of parameters for some target compounds (e.g. their physical-chemical properties and their biotransformation rates) would further improve model performance.

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