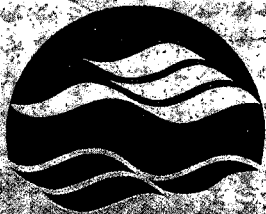06-228

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Polycyclic and Nitro Musks in
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Occurance and Removal in Wastewater
Treatment
BY:

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Polycyclic and Nitro Musks in Canadian Municipal Wastewater: Occurrence and Removal in Wastewater Treatment

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The removal and/or partitioning (to sludge) of six polycyclic and five nitro musks through the liquid treatment train of a conventional Canadian secondary activated sludge wastewater treatment plant is characterized. Raw influent, primary effluent, secondary effluent, primary sludge, and waste activated sludge concentrations were correlated to seasonal process temperatures (warm, 22°C; cold, 15°C). Maximum influent concentrations of polycyclic and nitro musks were 7,030 ± 2,120 ng/L for Galaxolide (HHCB) and 158 ± 89 ng/L for musk ketone respectively. Maximum secondary effluent concentrations were 2,000 ± 686 ng/L for HHCB and 51 ± 14 ng/L for musk ketone. Temperature appeared to influence the degree of removal of musks from wastewater during primary clarification (40% median removal at warm temperatures and 9% at cold temperatures) and overall treatment (82% median removal at warm temperatures and 74% at cold temperatures) but not secondary activated sludge treatment (71% median removal at warm temperatures and 70% at cold temperatures). In primary sludge, polycyclic musks were found at concentrations up to 35,000 ng/g for HHCB, and nitro musks were found at concentrations up to 490 ng/g for musk ketone. In waste activated sludge, polycyclic musks were found at concentrations up to 52,000 ng/g (HHCB), and nitro musks were found at concentrations up to 1,100 ng/g (musk ketone). The hydraulic retention time and the suspended solids of the treatment process appeared to influence the degree of partitioning of musks to sludge.

Key words: polycyclic musks, nitro musks, wastewater, sludge, removal, temperature, hydraulic retention time

Introduction

Polycyclic and nitro musks (PNMs) are widely used synthetic fragrances in Europe and North America (OSPAR Commission, 2004). They can be found in almost all consumer products such as perfumes, deodorants, cosmetics, soaps, shampoos, laundry detergents, fabric softeners, household cleaners, and air fresheners (Reiner and Kannan 2006). They are relatively lipophilic in a similar manner to polycyclic aromatic hydrocarbons (Rimkus 2004). Since the early 1980s, they have been measured in marine and freshwater biota, sediments, and water (Eschke 2004; Kolpin et al. 2004; OSPAR Commission 2004; Peck and Hornbuckle 2004), and have also been detected in human adipose tissue and human milk (Kannan et al. 2005). It is evident from the literature that PNMs are persistent, bioaccumulative, and ubiquitous in the environment (Daughton and Ternes 1999).

The toxicity of selected PNMs has been investigated on several aquatic species. One review concluded that there was no immediate threat to aquatic ecosystems based on the concentrations of PNMs reported in surface waters (Heberer 2002). The predicted no-effect concentrations of HHCB and AHTN (see Table 1 for a list of PNM abbreviations used in this paper) have been reported as 6,800 ng/L and 3,500 ng/L respectively (HERA 2004). Luckenbach and Epel (2005) reported that exposure of marine mussels to PNM concentrations above 22,000 ng/L inhibited excretion of other xenobiotics. The European community has limited the use of nitro musks in consumer products as a result of toxicological concerns for humans and the environment (Rimkus 2004). The *Canadian Environmental Protection Act* requires reduction of the releases of persistent, bioaccumulative, toxic substances that are primarily the result of human activities (Environment Canada 2004). Since there is evidence of persistence and bioaccumulation of PNMs in the environment, as well as indications of toxicity, discharges of PNMs may need to be reduced.

PNMs are produced by human activities and are released into wastewater after the use of consumer products (Salvito et al. 2004). Consequently, their presence in the environment is due to wastewater effluent discharges and land application of biosolids (Eschke 2004; Yang and Metcalfe 2006). Reduction of PNM discharges to the environment requires an understanding of their occurrence and fate during wastewater treatment.

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Previous investigators in Europe and North America have examined musk removal from wastewater and the presence of musks in sludge (Simonich et al. 2002; Artola-Garicano et al. 2003; Bester 2004; Kupper et al. 2004; Lishman et al. 2006; Yang and Metcalfe 2006). HHCB and AHTN are the most prevalent PNMs reported, with effluent concentrations in the microgram per litre range and sludge concentrations in the microgram per gram range. Most previous reports have been based on one-time sampling sequences of influent and effluent, and/or have been conducted in geographic regions with moderate climates. There is a need to examine the fate of PNMs during wastewater treatment in temperate climates such as Canada, and to amass larger data sets to assess the variability of PNM measurements in wastewater and sludge. The purpose of this research was to create a large data set for determination of the removal and/or partitioning to sludge of PNMs through the primary and secondary wastewater treatment processes of a conventional activated sludge plant, and to correlate removal and partitioning with seasonal process temperatures.

Materials and Methods

Treatment Plant Characteristics

Approximately 74% of Canadians are serviced by municipal sewers, and approximately 78% of the sewered population's waste receives secondary or tertiary treatment (Environment Canada, 2001). Secondary (activated sludge) treatment is generally defined as

biological treatment of wastewater using a controlled population of microorganisms under aerobic conditions; tertiary treatment is generally defined as additional treatment to remove suspended and dissolved substances remaining after secondary treatment (Environment Canada, 2001). The municipal wastewater treatment plant (WWTP) employed in this study was a large conventional secondary treatment plant in Ontario, Canada, representing the type of treatment applied to about 58% of Canadian municipal wastewater.

The treatment plant selected for this research serves a population of 310,000 and has a treatment capacity of 219,000 m^3/day. At present, typical average flows are 160,000 to 165,000 m^3/day. The inputs to the plant are approximately 60% from residential sources and 40% from industrial, commercial, and institutional sources. Unit operations include aerated grit removal, screening, primary settling, activated sludge treatment with secondary clarification, and disinfection with chlorine. The aeration tanks for activated sludge treatment are covered for odour control. Phosphorus is removed by adding ferrous chloride to the raw influent. Although the plant is not operated to nitrify, partial to full nitrification was observed during most sampling events. Sludge is digested anaerobically, then dewatered by centrifugation and incinerated. The centrate, representing about 1% of the plant flow, is fed back to the plant influent channel.

This study examined a single train of the treatment plant, representing approximately 5% of the overall plant flow. Mean flow through the study train was 7,900 m^3/day (range 3,800 to 12,000 m^3/day). Waste activated sludge (WAS) was removed directly from this train rather than being pumped back to the primary clarifier for co-thickening.

TABLE 1. Characteristics and method detection limits of polycyclic and nitro musks

Musk type	Abbr.	Trade Names	CAS #	Log K_{ow}	Method detection limit	
					Wastewater (ng/L)	Sludge (ng/g)
Polycyclic	DPMI	Cashmeran	33704-61-9	5.9[a]	21	27
	ADBI	Celestolide Crysolide	13171-00-1	5.4[a]	16	36
	AHDI	Phantolide	15323-35-0	5.9[a]	17	27
	ATII	Traseolide	68140-48-7	6.3[a]	13	39
	HHCB	Galaxolide Abbalide Pearlide	1222-05-5	5.9[a]	11	41
	AHTN	Tonalide Fixolide Astralide	21145-77-7 or 1506-02-1	5.7[a]	8.4	32
Nitro	MA	Musk Ambrette	83-66-9	—	1.7	4
	MX	Musk Xylene	81-15-2	4.9[b]	1.8	4
	MM	Musk Moskene	116-66-5	—	1.6	4
	MT	Musk Tibetene	145-39-1	—	1.6	3
	MK	Musk Ketone	81-14-1	4.3[b]	1.6	4

[a] Osemwengie and Steinberg (2001).
[b] Simonich et al. (2000).

TABLE 2. Conventional wastewater parameters and treatment efficiency, warm and cold sampling periods[a]

Sample	pH (range)	Total COD (mg/L)	Filtered COD (mg/L)	TSS (mg/L)	Total cBOD5 (mg/L)	Filtered cBOD5 (mg/L)	Alkalinity (mg/L CaCO3)	Total Kjeldahl nitrogen (mg/L N)	Ammonia (mg/L N)	Nitrate (mg/L N)
WARM[b]										
Raw Influent	6.70 – 8.53	455	190	200	165	128	221	36.5	21.3	—
Primary Effluent	6.93 – 7.77	267	169	119	116	74	—	29.2	21.0	—
Secondary Effluent	6.61 – 7.92	41	27	16	7	6	91	3.3	0.5	14
COLD[c]										
Raw Influent	7.42 – 8.14	416	182	178	140	71	246	37.1	20.9	—
Primary Effluent	6.69 – 7.81	279	160	123	110	57	—	36.4	24.4	—
Secondary Effluent	6.60 – 7.86	44	34	16	6	5	83	2.6	0.2	20.4

[a] Values represent median values.
[b] Temperature mean, 22°C; n = 13.
[c] Temperature mean, 15°C; n = 12.

Sample Collection

Twenty-five sampling events were completed over a 20 month period (August 2003 to April 2005). Samples were collected at the following points of the WWTP (Fig. 1):

- L1: Raw influent, downstream of centrate addition but upstream of ferrous chloride addition;
- L2: Primary effluent from the outlet of the primary clarifier;
- L3: Secondary effluent from the secondary clarifiers;
- S1: Primary sludge from the primary clarifier underflow;
- S2: WAS from the secondary clarifier underflow.

L1, L2, and L3 were 24-hour equal volume composite samples. S1 and S2 were grab samples. Replicate sampling events were employed to quantify temperature variations through the seasons and to investigate temperature-related trends and removal efficiencies in musk concentrations.

Bulk composite wastewater samples were collected on-site directly into stainless steel 20-L canisters which had been cleaned with Contrad 70 detergent (Decon Laboratories Inc., Bryn Mawr, U.S.A.), deionised water, and methanol (Caledon Laboratories, Georgetown, Canada). Sample collection tubing was lined with Teflon, with the exception of about 1 m of silicone pump tubing. The intake strainers were stainless steel. The Sigma 900 refrigerated autosamplers (Hach Company, Loveland, U.S.A.) maintained the sample temperature at approximately 4°C over the 24-hour sampling period. The autosamplers were programmed to collect 350 mL of sample every 30 minutes over the 24-hour period, with one rinse of the intake tubing before sample collection. The process temperatures of the wastewater at each sampling point were recorded during each sampling day.

Grab sludge samples were collected into stainless steel 20-L canisters which had been cleaned as described above. The sludge pumping lines were flushed prior to sample collection.

Sample Preparation and Chemical Analysis

For conventional wastewater parameters, all subsamples were preserved, stored, and analyzed in accordance with *Standard Methods for the Examination of Water and Wastewater* (APHA et al., 1999). Wastewater samples were analyzed for chemical oxygen demand (COD), five-
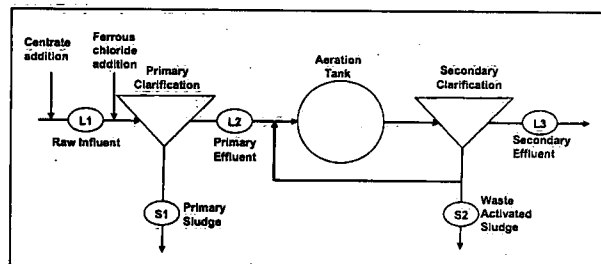

Fig. 1. Process diagram and sampling points.

day carbonaceous biochemical oxygen demand (cBOD$_5$), total Kjeldahl nitrogen, nitrate, ammonia, pH, alkalinity, total suspended solids (TSS), and volatile suspended solids. Sludge samples were analyzed for total solids and volatile solids.

Six polycyclic and five nitro musks, as listed in Table 1, were analyzed for this study. Stock solutions of polycyclic musks (at 100 μg/mL) and nitro musks (at 10 μg/mL), prepared in cyclohexane, were purchased from Promochem GmbH (Wesel, Germany). Anthracene-d10 and phenanthrene-d10 for surrogates were acquired from Sigma-Aldrich Corp. (St. Louis, USA). Analyses of musks in wastewater were completed as reported by Lee et al. (2003) with some modifications: either phenanthrene-d10 or anthracene-d10 was used as the surrogate for extraction. Briefly, samples were subjected to liquid-liquid extraction with petroleum ether, extracts were cleaned up on a 5% deactivated silica gel column, and elution was done with 10 mL of 5% acetone in hexane. The concentrated extracts were analyzed by gas chromatography-mass spectrometry (GC/MS).

The first 3 sets of sludge samples (2 warm, 22°C; 1 cold, 15°C) were analyzed by supercritical fluid extraction (SFE) and GC/MS analysis as reported by Lee et al. (2003). This method required that the sludge samples be air-dried, ground, and sieved before extraction; however, the air-drying possibly allowed for degradation or evaporation of the compounds of interest. A second analytical method was developed using microwave-assisted extraction (MAE) (Svoboda et al. 2007) and used to analyze the 5 remaining sample sets. Comparison of these two methods demonstrated that while the SFE and MAE extraction methods were equivalent, the sample drying step required for SFE caused losses of about 50% of the musk concentrations (Smyth et al. 2007). SFE results from the first 3 sample sets were therefore corrected (doubled) in order to compare with MAE results.

Sludge samples were stored in precleaned amber glass jars with Teflon-lined lids at -18°C before preparation and analysis. A stability study confirmed that the musk concentrations in sludge samples did not change significantly during frozen storage. Further, preparation of frozen sludge samples for MAE extraction showed that filtration provided a more satisfactory phase separation than centrifugation (Smyth et al. 2007). The liquid phase of sludge samples was analyzed by liquid-liquid extraction as described by Lee et al. (2003), without filtration.

The presence of musks in personal care products used by field and laboratory personnel creates the potential for contamination of field samples (Simonich et al. 2000; Kupper et al. 2004). Field blanks, in which deionised distilled water was run through the sampler tubing from one 20-L stainless steel canister into another, showed low concentrations of HHCB, AHTN, and MX. These concentrations were 2 to 3 orders of magnitude below concentrations measured in raw influent and primary effluent, and 1 to 2 orders of magnitude below concentrations measured in secondary effluent; hence, background contamination was considered negligible.

In order to assess the effectiveness of the extraction and analytical procedures, anthracene-d10 or phenanthrene-d10 was spiked into each liquid and sludge sample immediately before extraction. A total of 102 liquid samples were analyzed by liquid-liquid extraction (wastewater and sludge liquid phase); the mean recovery of the surrogate was 93.0% with a standard deviation (SD) of 20.5%. All liquid method blanks and all spiked blanks were also spiked with the surrogate; these 58 "clean" samples showed a mean recovery of 84.2% with a SD of 16.7%. A total of 60 sludge samples were analyzed by SFE and MAE for this study; the average recovery of the surrogate was 88.3% with a SD of 13.2%. All MAE sludge method blanks and spiked blanks (microwave cells loaded with sodium sulfate) were also spiked with the surrogate; these 13 "clean" samples showed a mean recovery of 80.2 % with a SD of 18.5%. These surrogate recoveries were very consistent between method blanks and field samples, and typical for trace analysis. Results reported in this study were not corrected for recovery of the deuterated surrogate.

Method detection limits (MDLs) for all musks in liquid and sludge samples are listed in Table 1. All MDLs were determined according to the United States Environmental Protection Agency (U.S. EPA) definition and method for MDL (U.S. EPA 2000), using 8 replicates prepared in laboratory-grade water for the wastewater MDL, and 8 replicates of clean sediment for the sludge MDL.

Results

Conventional Parameters and Temperature

A description of the wastewater treatment system performance provides the context for observations of removal of trace contaminants. Table 2 lists the median concentrations of aggregate organic and nitrogen species in each stage of the treatment process at this conventional secondary treatment plant. This plant was receiving medium to high strength wastewater (Metcalf and Eddy Inc. 2003), achieving typical removals of COD (90%), cBOD$_5$ (95%), and TSS (91%), and achieving partial to full nitrification as evidenced by the low effluent ammonia values. Fig. 2 summarizes the temperatures at each liquid sampling-point for each sampling period. Process temperatures were divided into two ranges for data analysis: Warm (mean 22°C) and cold (mean 15°). As Table 2 indicates, concentrations of conventional parameters and removals of COD, cBOD$_5$, and TSS were essentially the same during the warm and cold sampling periods.

Median values for mixed liquor suspended solids (MLSS) were 1,900 mg/L in the warm sampling periods and 2,020 mg/L in the cold sampling periods. Median hydraulic retention time (HRT) in the aeration tank was 9 hours at both temperature ranges. Solids retention time (SRT) for each sampling event was estimated using measured values for COD removal, mixed liquor volatile

suspended solids, and aeration tank HRT, and tabulated values of 0.45 g of volatile suspended solids per g of COD and 0.05 d⁻¹ for the yield and decay coefficients respectively (Metcalf and Eddy Inc. 2003). This estimation exercise showed that the median SRT in the aeration tank was 7.5 days at both temperature ranges.

Musk Concentrations in Wastewater and Sludge

Table 3 summarizes mean musk concentrations in the wastewater. The coefficient of variation (CoV) ranged from 2 to 92% for the 6 data sets (3 wastewater locations, 2 temperatures) and 10 musks detected in wastewater, with most CoV values between 20 and 50%. This level of variability in results is typical to somewhat high for trace analysis; however, the wastewater matrix is much more variable than other types of environmental samples such as surface water. Among the polycyclic musks, HHCB was detected at the highest concentrations in both warm (7,030 ng/L) and cold (6,660 ng/L) sampling periods, while DPMI was consistently the lowest detected musk. The nitro musks MX and MK were detected in the wastewater with the greatest frequency, while MA and MM were occasionally detected in raw influent and primary effluent and MT was never detected. MX was found in the highest concentration in both the warm (126 ng/L) and cold (158 ng/L) sampling periods.

Table 4 summarizes mean musk concentrations in sludge samples. Of the polycyclic musks, HHCB was detected at the highest concentrations in both the primary sludge (26,600 ng/g warm, 24,800 ng/g cold) and WAS (25,200 ng/g warm, 38,800 ng/g cold). AHTN was the second highest detected musk in all sampling periods, AHDI was consistently detected in the lowest concentrations, and DPMI was never detected. Of the nitro musks, MK was detected at the highest concentrations in both the primary sludge (228 ng/g warm, 352 ng/g cold) and WAS (413 ng/g warm, 724 ng/g cold). MX was the second highest detected musk in all sampling periods, MA was detected in only 9 of 47 samples, and MM and MT were never detected. The CoV for sludge concentrations ranged from 22 to 104% for the 4 data sets (2 sludge locations, 2 temperatures) and 7 musks consistently detected in sludge, with most CoV
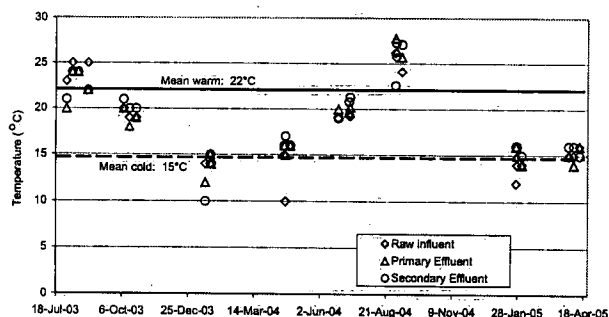

Fig. 2: Process temperatures during sample collection; Aug 2003 to Apr 2005.

values found between 22 and 45%. This level of variability in results is typical to somewhat high for trace analysis since the sludge matrix can be more variable than other environmental samples such as sediment.

Correlations between Conventional Wastewater Parameters and Musks

Musks tend to partition to wastewater solids (Bester 2004; Ternes et al. 2004); therefore musk concentrations in wastewater may be correlated with suspended solids concentrations. Previous investigators have reported correlations between musk concentrations and organic content in wastewater as measured by total five-day biochemical oxygen demand (BOD₅) and TOC (Yang and Metcalfe 2006); however, aggregate organic content in wastewater can be influenced by suspended solids concentrations. Pearson correlation coefficients were used to determine correlations between the conventional parameters COD and cBOD₅ to TSS, and between each of these conventional parameters and the 7 musks that were consistently detected (ADBI, AHDI, ATII, HHCB, AHTN, MX, and MK). Having only a maximum of 12 data pairs available for each correlation test required a relatively large absolute value of r to show a statistically significant (α = 0.05) correlation (McBean and Rovers 1998).

Correlations between aggregate organic content (as measured by COD and cBOD₅) and TSS were significant in raw influent, primary effluent, and secondary effluent at cold temperatures, while at warm temperatures only secondary effluent showed a significant correlation between COD and TSS. Significant correlations between conventional parameters and musks were likewise more frequent for the cold temperature data sets: in cold primary effluent, COD and TSS concentrations were correlated to ADBI, AHDI, ATII, and AHTN concentrations, and in cold secondary effluent, COD was correlated to HHCB. In warm primary effluent, COD concentrations were correlated to MX and MK concentrations, and in warm secondary effluent, TSS was correlated to HHCB and AHTN. Sample scatterplots of HHCB and AHTN concentrations versus TSS concentrations in warm secondary effluent are shown in Fig. 3.

The purpose of this correlation exercise was to determine if conventional wastewater parameters, particularly TSS, could serve as indicators of musk concentrations in wastewater since musk analysis is relatively resource-intensive. The frequency of correlations between conventional parameters and musks was lower than anticipated and there was a marked difference in frequency between the warm and cold sampling periods. However there is enough evidence of these correlations to warrant further investigation.

Removal of Musks from Wastewater

For the purposes of this study, "removal" was defined as the change in concentration of the parent musk compound

TABLE 3. Mean concentrations of polycyclic and nitro musks in wastewater, warm and cold sampling periods[a]

	Sample	DPMI (ng/L)	ADBI (ng/L)	AHDI (ng/L)	ATII (ng/L)	HHCB (ng/L)	AHTN (ng/L)	MA (ng/L)	MX (ng/L)	MM (ng/L)	MT (ng/L)	MK (ng/L)
WARM[b]	Raw Influent	31.4 ± 5.2 (4)	89.4 ± 29.7 (1)	44.0 ± 10.1 (4)	256 ± 96.1 (2)	7030 ± 2120 (0)	1760 ± 675 (0)	9.00 ± 7.6 (4)	126 ± 75.0 (0)	4.80 ± 2.6 (9)	ND[d] (13)	104 ± 43.9 (0)
	Primary Effluent	27.1 ± 5.2 (6)	58.5 ± 11.6 (4)	27.6 ± 6.1 (7)	161 ± 43.4 (1)	4640 ± 1260 (0)	1120 ± 284 (0)	4.4 ± 2.6 (6)	77.3 ± 70.9 (0)	2.2 ± 0.2 (10)	ND (13)	74.3 ± 36.4 (0)
	Secondary Effluent	38.0 (12)	19.7 ± 1.5 (9)	ND[d] (13)	37.6 ± 13.5 (1)	1300 ± 274 (0)	298 ± 68.8 (0)	4.5 (12)	8.1 ± 4.5 (1)	ND (13)	ND (13)	42.2 ± 12.5 (0)
COLD[c]	Raw Influent	30.2 ± 5.9 (6)	77.5 ± 15.4 (1)	39.5 ± 7.5 (3)	178 ± 65.7 (0)	6660 ± 1920 (0)	1560 ± 274 (0)	7.0 ± 2.7 (4)	158 ± 89.4 (0)	5.3 ± 2.6 (4)	ND (12)	152 ± 84.3 (0)
	Primary Effluent	24.1 ± 2.3 (4)	72.9 ± 28.3 (0)	37.7 ± 12.8 (2)	191 ± 101 (0)	6230 ± 1750 (0)	1350 ± 421 (0)	4.1 ± 2.1 (6)	110 ± 52.2 (0)	4.2 ± 2.3 (5)	4.1 (11)	151 ± 62.5 (0)
	Secondary Effluent	22.7 ± 0.4 (10)	27.6 ± 6.2 (1)	ND (12)	39.8 ± 9.2 (0)	2000 ± 686 (0)	393 ± 97.3 (0)	5.4 (11)	16.9 ± 8.9 (0)	ND (12)	ND (12)	50.8 ± 13.6 (0)

[a] Values represent mean ± SD, calculated from detectable values only; (n), values in parenthesis represent number of samples below the MDL.
[b] Temperature mean, 22°C; n = 13.
[c] Temperature mean, 15°C; n = 12.
[d] ND, nondetectable

TABLE 4. Mean concentrations of polycyclic and nitro musks in sludge; warm and cold sampling periods[a]

	Sample	ADBI (ng/L)	AHDI (ng/L)	ATII (ng/L)	HHCB (ng/L)	AHTN (ng/L)	MA (ng/L)	MX (ng/L)	MK (ng/L)
WARM[b]	Primary sludge	367 ± 158 (1)	170 ± 49 (0)	1,080 ± 332 (0)	26,600 ± 7,850 (0)	7,510 ± 2,120 (0)	33 ± 54 (8)	63 ± 51 (0)	228 ± 170 (0)
	Waste activated sludge	221 ± 71 (0)	153 ± 54 (0)	1,370 ± 342 (0)	25,200 ± 6,500 (0)	6,490 ± 1,530 (0)	40 ± 62 (8)	53 ± 45 (0)	413 ± 394 (0)
COLD[c]	Primary sludge	251 ± 95 (0)	173 ± 180 (3)	924 ± 392 (0)	24,800 ± 6,170 (0)	6,880 ± 1,520 (0)	— (11)	178 ± 160 (0)	352 ± 108 (0)
	Waste activated sludge	368 ± 158 (0)	160 ± 68 (3)	1,530 ± 504 (0)	38,800 ± 13,300 (0)	10,400 ± 3,180 (0)	— (11)	389 ± 378 (0)	724 ± 321 (0)

[a] Values represent mean ± SD; (n), values in parenthesis represent number of samples below the MDL.
[b] Temperature mean, 22°C; Primary sludge, n = 13; Waste activated sludge, n = 12.
[c] Temperature mean, 15°C; Primary sludge, n = 11; Waste activated sludge, n = 11.
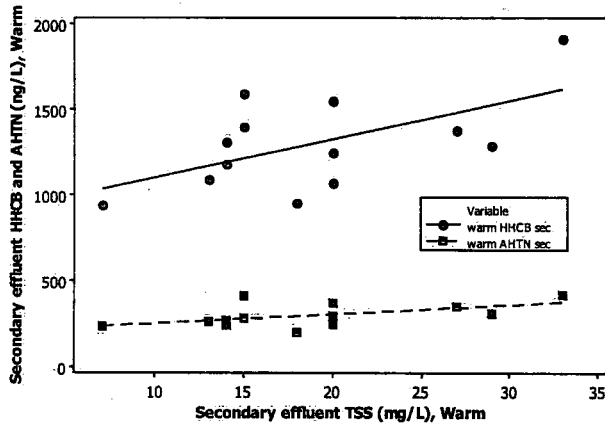
Fig. 3. Scatterplot of HHCB and AHTN concentrations (ng/L) versus TSS concentrations (mg/L) in secondary effluent at warm temperatures.

in the liquid phase of the wastewater. Removal was determined as a percentage of the raw influent or primary effluent concentration (influent to secondary treatment):

$$\% \text{ Removal} = \frac{(\text{Influent concentration} - \text{Effluent concentration})}{\text{Influent concentration}} \times 100 \quad (1)$$

As per Table 3, some musks were nondetectable at one or more sampling points. The location and frequency of nondetectable results provides important information on the ability of a treatment process to reduce parent musk concentrations to nondetectable levels, although calculation of a percent removal value becomes challenging. For this study, all nondetectable values were replaced by one-half of the MDL value for calculation of percent removals. For cases where a negative removal value was obtained, a value of zero was assigned as the percent removal. It may be possible to "create" musks due to desorption from solids or deconjugation of metabolites; it is also possible that negative values are the result of sampling and analytical variability.

Fig. 4 and 5 illustrate all calculated and assigned percent removal values for ten musks during the warm and cold sampling periods respectively. As these figures illustrate, there was a high degree of variability in the removal values for each compound. Table 5 summarizes the median removal values. ADBI had the highest overall removal (87%) among the polycyclic musks while MX had the highest overall removal (92%) among the nitro musks at warm temperatures. ATII had the highest overall removal (80%) among the polycyclic musks and MX again had the highest overall removal (90%) among the nitro musks at cold temperatures.

The percent-removal data sets have nonnormal distributions; therefore a Mann-Whitney test was used to compare median removals. Median removal of all musks during primary clarification was 40% during warm periods and 9.4% during cold periods (different, p = 0.000). Median removal in secondary activated sludge treatment was not different (71% during warm periods and 70% during cold periods). Overall median removal of musks from liquid during conventional wastewater treatment was 82% during warm periods and 74% during cold periods (different, p = 0.001) due to the temperature effect in primary clarification. These results indicate that the considerable majority of musks are removed from wastewater, and that there is improved percentage removal during primary clarification at warmer temperatures compared to colder temperatures.

Musks in Primary and Waste Activated Sludge

Primary sludge consists largely of unstabilized organic material from human waste. WAS arises from the activated sludge process whereby soluble organics are metabolized by microorganisms and residual suspended matter become enmeshed in the microbial floc; hence WAS consists largely of microbial biomass which separates from the liquid stream during secondary clarification (Metcalf and Eddy Inc, 2003). The musk content of primary sludge is dependent on the PNM loading into the
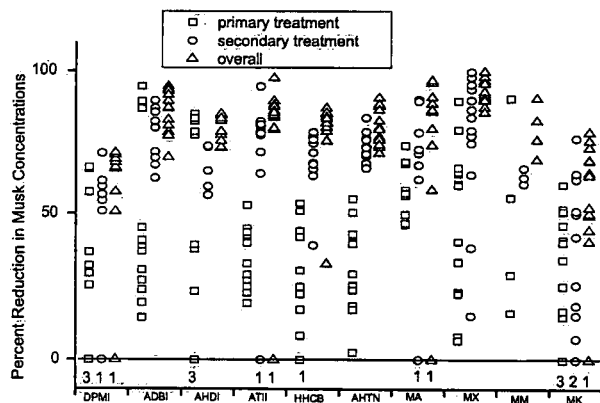

Fig. 4. Percent removal of musks from liquid phase, warm sampling periods. Numbers above each analyte indicate the number of "zero" removal values.
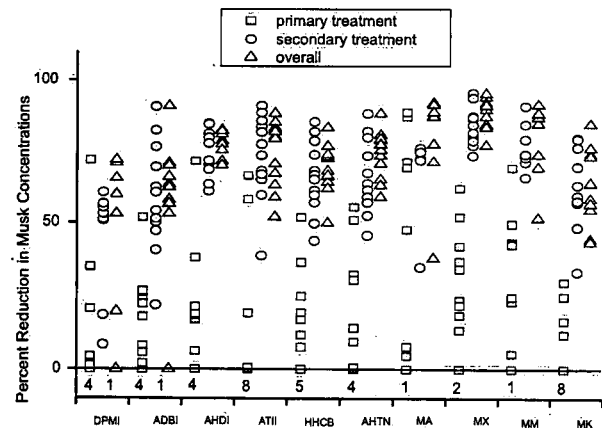

Fig. 5. Percent removal of musks from liquid phase, cold sampling periods. Numbers above each analyte indicate the number of "zero" removal values.

TABLE 5. Median removal values (%) for polycyclic and nitro musks in wastewater treatment[ab]

	Sample	DPMI %	(n)	ADBI %	(n)	AHDI %	(n)	ATII %	(n)	HHCB %	(n)	AHTN %	(n)	MA %	(n)	MX %	(n)	MM %	(n)	MK %	(n)	All data %	(n)
WARM[c]	Primary Treatment	31	(10)	38	(12)	58	(12)	33	(11)	31	(13)	29	(13)	57	(9)	60	(13)	42	(4)	34	(13)	40	(110)
	Secondary Treatment	57	(7)	80	(9)	69	(6)	78	(13)	75	(13)	71	(13)	72	(8)	84	(13)	63	(3)	42	(13)	71	(98)
	Overall	67	(10)	87	(12)	79	(9)	85	(12)	82	(13)	80	(13)	86	(10)	92	(13)	79	(4)	63	(13)	82	(109)
COLD[d]	Primary Treatment	1.4	(9)	7	(12)	17	(11)	0	(12)	9.7	(12)	9.4	(11)	59	(8)	24	(12)	34	(8)	0	(12)	9.4	(107)
	Secondary Treatment	52	(8)	57	(12)	75	(10)	76	(12)	66	(12)	66	(12)	74	(6)	83	(12)	74	(7)	63	(12)	70	(103)
	Overall	60	(7)	62	(12)	77	(9)	80	(12)	70	(12)	76	(12)	87	(8)	90	(12)	86	(8)	61	(12)	74	(104)

[a] ½ of MDL substituted for ND values to calculate removals. Zero substituted for negative removal values. MT never detected.
[b] %, percent median removal; (n), number of samples above the MDL.
[c] Temperature mean, 22°C; Primary sludge, n = 13; Waste activated sludge, n = 12.
[d] Temperature mean, 15°C; Primary sludge, n = 11; Waste activated sludge, n = 11.

plant and the degree of sorption to the primary sludge, while the musk content in WAS is determined by the musks remaining in the effluent from primary clarification and the degree of sorption to the WAS.

Using a mass balance approach, removal values based on Table 5, the assumption of no losses of musks through the treatment process, and the assumption that all musks partition to solids to the same extent, the fate of musks during wastewater treatment would be predicted as follows:

> WARM: 40% to primary sludge and 42% (70% of the remaining 60%) to WAS
> COLD: 10% to primary sludge and 63% (70% of the remaining 90%) to WAS

Therefore, one would expect to see approximately equal amounts (on a dry solids basis) of musks in primary sludge and WAS at warm temperatures, and significantly higher amounts in WAS compared to primary sludge at cold temperatures. Inspection of Table 4 shows that although there are no statistically significant differences between individual musk concentrations in the 4 sludge sample sets, the predicted trend is present for ATII, HHCB, MA and MX at warm temperatures and for ATII, HHCB, AHTN, MX, and MK at cold temperatures.

Hydraulic Retention Time and Sludge to Effluent Partitioning of Musks

Artola-Garicano and coworkers (2003) reported that neither biodegradation nor volatilization contributed significantly to the removal of HHCB and AHTN in wastewater treatment due to low microbial degradation rates combined with substantial binding to solids, and concluded that the HRT of the treatment process was more relevant to musk removal from wastewater than the SRT. Ternes et al. (2004) showed that equilibrium of HHCB and AHTN between the solid and liquid phases of wastewater strongly favoured the solid phase. Based on these reports, the extent of musk partitioning to solids during primary or secondary treatment would be determined by the HRT of the process, and by the surface area of solids available for sorption of the musk compounds. The process HRT and suspended solids conditions during this study were examined for two purposes: (1) a coincidental difference in primary or secondary HRT or suspended solids concentrations could account for the observed difference in removal of musks from the wastewater in warm and cold sampling periods, and (2) process HRT and suspended solids correlated with PNM partitioning to sludge would corroborate the previous reports.

The HRTs of the primary treatment and secondary treatment stages were calculated for each sampling day using the tank volume (primary clarifier for primary HRT, aeration tank and secondary clarifier for secondary HRT) and measured flow for that day. The mean HRT for primary treatment was 3.7 hours (range 2.2 to 7.0) during the warm sampling periods and 3.5 hours (range 2.5 to

5.2) during the cold sampling periods. Mean HRT for secondary treatment was 13.7 hours (range 8.0 to 25) during warm sampling periods and 12.8 hours (range 9.4 to 19) during cold sampling periods. Therefore, neither primary nor secondary treatment HRTs were different between the warm and cold periods. Pearson correlation tests between percent removals of individual musks and corresponding daily HRTs also showed no significant correlations ($\alpha = 0.05$); therefore, the observed differences in musk removal between warm and cold periods was not due to different HRTs.

Mean raw influent TSS concentrations were 204 mg/L (warm, range 116 to 304 mg/L) and 209 mg/L (cold, range 118 to 380 mg/L). Addition of ferrous chloride to the raw influent creates additional solids during primary clarification (Water Environment Federation, 1998). Mean ferrous chloride dosing was 11 mg/L (warm, range 7.4 to 20 mg/L) and 13 mg/L (cold, range 7.0 to 19 mg/L). Therefore suspended solids entering the primary clarifier were not different between warm and cold periods. Mean MLSS were 1,940 mg/L (warm, range 984 to 3,030 mg/L) and 2,060 mg/L (cold, range 1,180 to 2,950 mg/L) which indicates that suspended solids in the aeration tank were not different between warm and cold sampling periods. Primary clarification HRT and TSS were not different between warm and cold sampling periods, and secondary treatment HRT and MLSS were not different between warm and cold sampling periods. The HRT for secondary treatment was 3.5 times higher than that for primary clarification, while the MLSS for secondary treatment was 10 times higher than the TSS in primary clarification; based on the above-cited work, one would expect to see a higher proportion of musks in WAS than in primary sludge. Such a trend was observed for ADBI, ATII, HHCB, AHTN, MX, and MK during the cold sampling periods, but only for ATII, MA, and MK during warm periods (Table 4).

The extent of musk partitioning to sludge during primary and secondary treatment was estimated using a ratio of corresponding sludge and effluent concentrations (i.e., primary sludge to primary effluent; WAS to secondary effluent). The ratios for ADBI, ATII, HHCB, AHTN, MX, and MK are illustrated in Fig. 6. Each musk was considered individually, and comparisons were made between warm and cold periods and primary and secondary treatment using the mean values for each data set. Comparison of temperature ratios within the same treatment stage showed that ADBI and HHCB had different ($\alpha = 0.05$) sludge to effluent ratios during primary treatment while MX had a different ratio during secondary treatment. Comparison of treatment stage ratios within the same temperature showed that the partitioning ratios were different ($\alpha = 0.05$) between primary and secondary treatment for all musks at both temperatures. These results indicate that the characteristics of the treatment stage have more effect than process temperature on the partitioning of PNMs to sludge. The much higher degree of musk partitioning to sludge during secondary treatment could be attributed to the longer HRT and higher MLSS. Additionally, the
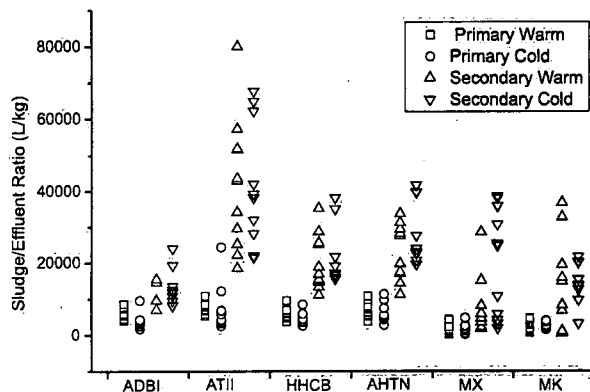
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Fig. 6. Concentration ratios of sludge to effluent (L/kg) for polycyclic and nitro musks in primary sludge to primary effluent and WAS to secondary effluent at warm and cold sampling periods.

recycling of activated sludge containing musks from the secondary clarifier back into the aeration tank will contribute to the higher sludge to effluent ratio observed in this treatment stage. At longer SRTs, a lower proportion of the activated sludge is wasted and a higher proportion is returned to the aeration tank to maintain a higher MLSS; therefore, the SRT of the process contributes to the accumulation of musks in WAS.

Discussion

Musks in Influent and Effluent

This study reports generally higher influent concentrations of musks than those reported in other Canadian work (Lee et al. 2003; Lishman et al. 2006; Yang and Metcalfe 2006). Maximum influent concentrations of polycyclic musks detected in this study were 9,150 ng/L (HHCB) and 2,440 ng/L (AHTN). The maximum concentrations of nitro musks in influent were 247 ng/L (MX) and 236 ng/L (MK). All previous Canadian reports have measured musk concentrations in filtered samples, whereas this study included the suspended solids. This study has demonstrated that since musks tend to partition to the solids stream, their inclusion in the analysis should be considered. Yang and Metcalfe (2006) conducted repeated sampling at one plant in Ontario, Canada; their reported influent musk concentrations (and the general water quality chemistry) were much lower than those measured in this study. Inspection of the water quality chemistry from their study indicates that the influent to that plant was of lower strength than that measured during this study. Yang and Metcalfe found that BOD$_5$ and TOC were significantly correlated with HHCB and AHTN concentrations in wastewater. The authors presented an equation which related musk concentrations to these two conventional wastewater parameters. COD, BOD$_5$, and TOC are all measures of the organic content of wastewater, and are all influenced by the presence of TSS. Results of their and the present work both indicate the presence of a correlation between conventional parameters (TSS, BOD) and musks;

however the amount and types of industrial inputs to the treatment plant can also affect influent concentrations of musks. Therefore, this type of correlation model would be plant-specific. Musk influent concentrations do not demonstrate any seasonal dependency (Table 3 and Yang and Metcalfe 2006). The influent concentrations of musks as reported by North American and European researchers vary widely and are generally much higher than those reported in this study (Table 6). This wide range of results supports previous observations that the concentration of PNMs in wastewater influent is a function of local usage patterns (Simonich et al. 2002).

This study reports generally similar effluent concentrations of musks to those reported for other Canadian treatment plants (Lee et al. 2003; Lishman et al. 2006). The maximum effluent concentrations of polycyclic musks detected in this study were 2,690 ng/L (HHCB) and 490 ng/L (AHTN). The maximum detected concentrations of nitro musks were 26 ng/L (MX) and 64 ng/L (MK). HHCB, AHTN, MX, and MK were consistently detected in all effluent samples. Since wastewater treatment plant effluents tend to contain very low levels of suspended solids (typically < 25 mg/L), the difference between soluble and total musk concentrations will be less pronounced in effluents than in influents. The first report of musks in Canadian effluent showed similar levels of polycyclic musks, but nondetectable levels (< 1 ng/L) of MX and MK (Ricking et al. 2003). Samples from that study were collected from conventional secondary treatment plants in the Maritime Provinces; there are frequently regional differences in the amounts and types of consumer products used, which could affect wastewater concentrations of PNMs. Effluent from the plant studied by Yang and Metcalfe (2006) showed musk concentrations about 10 times lower than those reported here, corresponding to lower influent concentrations. The effluent concentrations of musks as reported by both North American and European researchers are quite similar to those reported here (Table 6). This comparison is consistent with previous observations that effluent concentrations of musks are a function of the plant design and operation (Simonich et al. 2002).

Effluent samples for this study were collected from a stream representing only 5% of the total plant flow, and combined secondary effluent from this WWTP is chlorinated before discharge to the receiving water; therefore, comparison of effluent PNM concentrations from this study with reported toxicity values has limited relevance. However, the predicted no-effect concentrations for HHCB and AHTN in water of 6,800 ng/L and 3,500 ng/L, respectively (HERA 2004), are 2.5 times and 7 times higher than the maximum effluent concentrations detected in this study, indicating that PNM concentrations in this effluent would not cause toxicity in aquatic organisms.

Interstage Removal of Musks During Wastewater Treatment

Several previous investigators have studied the removal of

TABLE 6. Influent and effluent concentrations of HHCB, AHTN, MX, and MK as reported in North American and European Studies

Parameter	Influent concentration (ng/L)	Effluent concentration (ng/L)	Reference and comments
HHCB	16,600 ± 10,400[a]	980 – 3,750[b]	(Simonich et al. 2002)
AHTN	12,500 ± 7,350	620 – 2,670	• 15 plants in the U.S.A. and Europe;
MX	386 ± 299	6 – 284	lagoon results not included
MK	640 ± 395	ND[c] – 770	
HHCB	11,600	1,100 – 6,400	(Kanda et al. 2003)
AHTN	4,000	270 – 2,700	• United Kingdom
HHCB	1,780	915	(Lee et al. 2003)
AHTN	791	422	• 9 Canadian plants; filtered samples;
MX	7.5	6.2	median concentrations
MK	39	44	
HHCB	1,700	876	(Lishman et al. 2006)
AHTN	687	298	• 12 Canadian plants; filtered samples;
			median concentrations
HHCB	7,280	1,550	(This study)
AHTN	1,600	344	• 1 Canadian plant sampled 25 times;
MX	119	9.23	median concentrations
MK	113	45.6	

[a] Values represent the mean ± SD.

[b] Values represent a range of concentrations detectable from low to high.

[c] ND, nondetectable.

parent musk compounds through the stages of wastewater treatment. Reported removals of musks during primary treatment range from -50% (Artola-Garicano et al. 2003) to 51% (Simonich et al. 2000), with most values in the range of 15 to 40%. Median removal rates from this study are generally higher (Table 5). Median removals for polycyclic musks during primary treatment range up to 58% during warm periods and up to 17% during cold periods. The median removal of nitro musks was much higher, up to 60% during warm periods and up to 59% during cold periods. Reported removals of musks during secondary biological treatment range from 8% (Yang and Metcalfe 2006) to 98% (Simonich et al. 2000), with most values in the range of 25 to 80%. Removal rates for musks in secondary treatment from this study are consistent with previous studies. Median removal for polycyclic musks during secondary treatment ranges from 57 to 80% during warm periods and from 52 to 76% during cold periods. The removal rates for nitro musks ranged from 42 to 84% during warm periods and from 63 to 83% during cold periods. Therefore, one can conclude that the removal of musks following secondary biological treatment is much more consistent than that of primary treatment. Reasons for these observations may include less variability in secondary influent concentrations, more flow equalization, and more opportunity for partitioning to sludge due to longer HRTs and higher TSS/MLSS concentrations. Reported values for overall removal of

PNMs from these studies range from 12% (Artola-Garicano et al. 2003) to 99.7% (Simonich et al. 2002), with most values in the range of 40 to 90%. The findings reported herein compare well with these ranges.

With respect to comparing the removal rates of musks at warm and cold temperatures, the work by Yang and Metcalfe (2006) contains enough data to perform a similar comparison. February and April sampling periods were assumed to be cold, and July and October sampling periods assumed to be warm in like manner to the present study. Reported concentrations of DPMI, ADBI, AHDI, ATII, HHCB, MX, AHTN, and MK in raw influent, primary effluent, and secondary effluent prior to ultraviolet disinfection were used to calculate percent removals of all musks at each stage of treatment. Each resulting data set contained 16 values; median removals were 20% and 25% for primary treatment, 55% and 40% for secondary treatment, and 62% and 55% for overall treatment at warm and cold temperatures respectively. Mann-Whitney tests comparing each pair of medians for Yang and Metcalfe's work did not detect any temperature-related differences in removal of musks during primary treatment or overall treatment. However, removal during secondary treatment was not the same at warm and cold temperatures. Although their work indicates that there may be a temperature-related difference in removal, the treatment stage where this occurred contrasts with the present results which indicate temperature-related

differences during primary treatment. Another contrast between Yang and Metcalfe's work and that presented here is that the maximum overall removal they observed for any of the 8 detectable musks was 68% at cold temperatures and 88% at warm temperatures. Considering the same 8 musks, this study showed greater than 90% removal at both warm (21 out of 95 values) and cold (11 out of 88 values) temperatures (Fig. 4 and 5) in unfiltered samples. Plant influent and/or operating characteristics (e.g., HRT, SRT, dissolved oxygen levels) may be contributing to these differences.

As reported by Paasivirta et al. (2002) the temperature dependence of physical properties and degradation rates of musks are practically unknown thus far. Most reported values (vapour pressure, water solubility, Henry's law coefficient, octanol to water partition coefficient [K_{ow}]) are for one temperature only or without any given temperature. Modelling the fate of a compound at different climatic conditions or during different seasons will be more accurate if the temperature dependencies of the compound's physical properties are available.

The work by Paasivirta and coworkers demonstrated that the temperature dependence of solid vapour pressure, liquid vapour pressure, water solubility, and therefore the Henry's law constant were significant, while the temperature dependence of K_{ow} was small. The relationship between process temperature and removal of musks from the liquid phase during primary treatment has important implications for those Canadian wastewater treatment plants that only use primary treatment (about 14% of Canadian population [Environment Canada, 2001]).

Musks in Sludge

This study showed that the dominant PNMs found in primary sludge are HHCB (26,600 ng/g), AHTN (7,510 ng/g), MK (352 ng/g), and MX (178 ng/g) respectively. Blok and Rijs (cited in Fooken 2004) measured HHCB and AHTN in primary sludge from plants in the Netherlands and found concentrations similar to those reported here. Artola-Garicano and coworkers (2003) in the Netherlands measured HHCB and AHTN in primary sludge, however their results were reported in micrograms per litre. In order to compare those reported values to this study, a primary sludge solids content of 1 to 3% was assumed. The calculated concentration ranges from their work would be 1,300 to 26,000 ng/g for HHCB and 500 to 9,000 ng/g for AHTN, both being similar to those found in this study. In contrast, Ternes and coworkers (2005) in Germany measured HHCB and AHTN in dried primary sludge and found concentrations 10 times higher than those from this study. Llompart and coworkers (2003) measured 6 polycyclic and 2 nitro musks in primary sludge in Spain and reported concentrations about 10 times lower than those reported here. The wide range of results could be due to differences in usage patterns of products containing musks, differences

in retention times during primary treatment, and/or differences in the analytical methods used for measurement.

Similarly, there are some previous reports of musk concentrations in WAS. Reported concentrations vary more widely for this sludge type. This study showed maximum values of 52,100 ng/g (HHCB), 13,600 ng/g (AHTN), 1,050 ng/g (MK), and 767 ng/g (MX). Ternes and coworkers (2005), Blok and Rijs (cited in Fooken 2004), and Artola-Garicano and coworkers (2003) reported concentrations in the same order of magnitude as the present results. Once again, the work reported by Artola-Garicano and coworkers reported results in micrograms per litre; a WAS solids content of 0.5 to 1% was used to convert concentrations to ng/g. Yang and Metcalfe (2006) reported concentrations of 6 polycyclic and 2 nitro musks in WAS; their results were about 10 times lower than those reported here. In addition, Llompart and coworkers (2003) in Spain reported concentrations of 6 polycyclic and 2 nitro musks in WAS with results about 100 times lower than ours. This wide range of results is most likely due to differences in the secondary treatment process (e.g., extended aeration, nitrification/denitrification) and/or differences in the analytical methods used for measurement.

Sludge to Effluent Partitioning of Musks

In the present study, sludge to effluent ratios were used to determine correlations between musk content in sludge and the HRT of the process that generated the sludge. Ternes and coworkers (2004) reported a rapid method to measure the solid to water distribution coefficient (K_d) for HHCB and AHTN in sewage sludge. They used batch equilibrium tests and analyzed the water and solid phases of the sludge. Simonich and coworkers (2002) estimated K_d values using log K_{ow} values. These K_d values are listed in Table 7. For the current study, sludge to effluent ratios for polycyclic musks in primary treatment (6,450 L/kg for AHTN and 5,200 L/kg for HHCB) are similar to the K_d values reported by Ternes and coworkers (2004), while this study showed ratios for secondary treatment (25,300 L/kg for AHTN and 20,800 L/kg for HHCB) that are an order of magnitude higher. The CoV for both Ternes and coworkers' (2004) and the present values range from 29 to 42%; both data sets contained a similar amount of variability. The K_d values reported by Simonich and coworkers (2002) are not specific to a type of sludge, thus making comparisons less relevant; their values are lower than reported here, but greater than the values reported by Ternes et al. (2004) for HHCB and AHTN. Batch equilibrium K_d values have not been reported for MK and MX; ratios for primary treatment from this study (2,630 L/kg for MK and 1,300 L/kg for MX) compare reasonably well with those estimated by Simonich, while ratios for secondary treatment (12,900 L/kg for MK and 13,500 L/kg for MX) are much higher than the estimated values. The CoV for values from this study were very high, ranging from 44 to 100%. The primary and secondary

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treatment systems were not at equilibrium since they were continuously receiving fresh influent; however, the sludge to effluent ratio for primary treatment still agreed well with previous reports. The sludge to effluent ratio for the secondary treatment system was much higher than previous reports because the secondary treatment system was receiving musk-enriched return activated sludge from the clarifier.

Conclusions

The purposes of this investigation were to determine the removal of PNMs through the liquid treatment train of a conventional secondary activated sludge WWTP, to measure the PNM content in primary sludge and WAS, to correlate liquid removal and sludge content with seasonal process temperatures, and to amass large data sets of liquid and solids measurements to assess the variability of PNMs in wastewater and sludge.

Polycyclic musks were present in the raw influent at concentrations of up to 10,500 ng/L; nitro musks were present in the influent at concentrations of up to 391 ng/L. There were no seasonal trends in influent concentrations, suggesting no seasonal difference in the use of consumer products containing musk fragrances. The maximum effluent concentration of polycyclic musks was 3,230 ng/L and of nitro musks was 70.3 ng/L. Musk concentrations in wastewater were frequently correlated with total COD, total cBOD$_5$, and TSS concentrations.

Median removal of PNMs from wastewater during primary clarification was 40% at warm temperatures and 9% at cold temperatures. Median removal during secondary activated sludge treatment was 71% at warm temperatures and 70% at cold temperatures. Median overall removal of musks from wastewater during conventional activated sludge wastewater treatment was 82% at warm temperatures and 74% at cold temperatures.

This is the first study to report a correlation between process temperature and musk removal from wastewater during primary clarification. Controlled studies on the fate of PNMs during wastewater treatment at different process temperatures should be conducted to confirm these field observations. The relationship between process temperature and removal of PNMs from wastewater has important implications for WWTPs in more extreme climates such as Canada, especially for those jurisdictions that employ only primary clarification.

Polycyclic musks were present in primary sludge at concentrations of up to 35,000 ng/g, and nitro musks were present at up to 490 ng/g. Polycyclic musks were present in WAS at concentrations of up to 58,000 ng/g, and nitro musks were present at up to 1,100 ng/g. Within a treatment stage, the process parameters most likely to influence sorption of musks to sludge, namely TSS concentrations and HRTs, were not different between warm and cold sampling periods.

No significant temperature-related differences were observed between primary sludge concentrations or WAS concentrations of PNMs. The trend in sludge concentrations generally followed a simple mass balance prediction, with the assumptions of no losses of musks during treatment and equal solids partitioning for all musks. Longer HRT and higher suspended solids

TABLE 7. Measured and estimated solid-to-liquid distribution coefficients (K_d, L/kg) for AHTN, HHCB, MK, and MX in wastewater.

Musk	Sludge	K_d (L/kg)[a]	CoV (%)	Reference
AHTN	Primary	5,300 ± 1,900	36	Ternes et al. 2004
		6,450 ± 2,240	35	This study, all values
	Secondary	2,400 ± 960	40	Ternes et al. 2004
		25,300 ± 8,210	32	This study, all values
	Not applicable	12,020	—	Simonich et al. 2002
HHCB	Primary	4,920 ± 2,080	42	Ternes et al. 2004
		5,200 ± 1,680	32	This study, all values
	Secondary	1,810 ± 530	29	Ternes et al. 2004
		20,800 ± 7,690	37	This study, all values
	Not applicable	15,400	—	Simonich et al. 2002
MK	Primary	2,630 ± 1,170	44	This study, all values
	Secondary	12,900 ± 9,840	76	This study, all values
	Not applicable	2,081	—	Simonich et al. 2002
MX	Primary	1,300 ± 1,200	92	This study, all values
	Secondary	13,500 ± 13,500	100	This study, all values
	Not applicable	4,412	—	Simonich et al. 2002

[a] Values represent the mean ± SD.

concentrations in secondary treatment were associated with higher sludge to effluent ratios of PNM concentrations compared to primary treatment. More extensive, controlled studies are recommended to confirm that HRT and suspended solids are the key variables affecting musk partitioning to sludge in a wider range of treatment situations.

Acknowledgments

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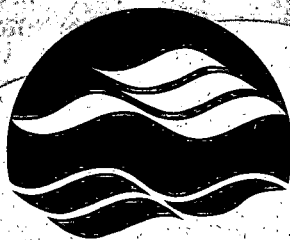
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