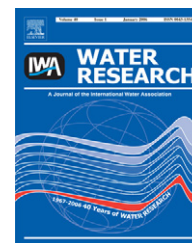


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Plasticizers and their degradation products in the process streams of a large urban physicochemical sewage treatment plant

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ABSTRACT

The plasticizers bis (2-ethylhexyl) phthalate (BEHP), bis (2-ethylhexyl) terephthalate (BEHTP) and bis (2-ethylhexyl) adipate (BEHA) were found in significant quantities in the influents, process streams, treated effluent and solid residues of a large physicochemical treatment plant in Montreal, Canada. Of these plasticizers, BEHA was the most abundant in the influent but most was removed during primary treatment. Evidence indicated that significant biodegradation occurred within the sewers and during treatment resulting in the formation of three biodegradation products that had been reported in earlier laboratory studies; namely, 2-ethylhexanol, 2-ethylhexanal and 2-ethylhexanoic acid. Significantly greater concentrations of 2-ethylhexanal were found in process streams than had been reported in earlier laboratory work. This was attributed to the fact that there were fewer opportunities for losses of this volatile compound over the course of wastewater treatment. The plasticizers were removed from the aqueous phase to varying degrees during treatment, with most ending up in the solid residues. All three metabolites and the parent plasticizers were observed in the effluent and most were found in the solids that were analyzed. Results suggest that the treatment plant does not effectively remove plasticizers from the influent and represents a significant source of these compounds and their degradation products in the environment.

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1. Introduction

Anthropogenic activities result in the release of organic compounds into wastewaters that can have toxic, carcinogenic, mutagenic or/and endocrine disrupting properties. These compounds eventually reach sewage treatment plants where they undergo physical, chemical or biological mechanisms of transformation or removal. In many cases, they may tend to concentrate in wastewater sludges, which would add constraints to the disposal or beneficial uses of these solids

(CEC, 2000; Birkett and Lester, 2003; Schowanek et al., 2004; Abad et al., 2005).

Plasticizers are a class of industrial chemicals that are a particular source of concern because of the extent of their use in commercial applications and the growing recognition of the potential threats that they pose to the health of humans and ecosystems (Gomez-Hens and Aguilar-Caballeros, 2003; Rahman and Brazel, 2004). Plasticizers are oily liquids that are used to impart properties such as flexibility and workability to plastics for effective processing and tailoring of plastic

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formulations (Sears and Darby, 1982). Their importance as industrial chemicals is demonstrated by their current rate of use, which has been estimated to be in the millions of tonnes annually (Bauer and Herrmann, 1997). Unfortunately, because they are not chemically bound to the polymers, plasticizers can migrate from plastic products during normal use and following their disposal (Fromme et al., 2002). Thus, as many studies have shown, they have become widely distributed in the environment and are frequently found in the influents, effluents and sludges of wastewater treatment plants, and in surface waters that receive treated effluents (Petrovic and Barcelo, 2001; Fromme et al., 2002; Fauser et al., 2003; Gavala et al., 2003; Marttinen et al., 2003a; Bago et al., 2005).

Bis (2-ethylhexyl) phthalate (BEHP), also known as di-octyl phthalate or di-(2-ethylhexyl) phthalate (DEHP), is the most commonly used plasticizer and is produced in millions of tonnes per year worldwide (Koch et al., 2003). It has been estimated that phthalate plasticizers comprise approximately 92% of plasticizer production in the world, with BEHP alone accounting for approximately 50% of this amount (Rahman and Brazel, 2004; Lunberg et al., 1992). This particular di-ester plasticizer is amongst the most abundant organic contaminants in urban wastewaters and sewage sludges and has been classified as a priority organic pollutant (CEC, 2000; Scrimshaw and Lester, 2003). Other plasticizers are also in common use, albeit in much lower quantities. An example of another common phthalate plasticizer is bis (2-ethylhexyl) terephthalate (BEHTP), which is an isomer of BEHP. This plasticizer is used as an alternative to BEHP since it is more resistant to migration (Rahman and Brazel, 2004). It also has a lower probability of forming a monoester (i.e., mono-ethylhexyl phthalate) that can result from the incomplete breakdown of BEHP (Barber et al., 1994). This monoester has been causally linked to cancer in higher organisms (Albro et al., 1989). Another plasticizer in widespread use is bis (2-ethylhexyl) adipate (BEHA). It accounts for approximately 5% of the plasticizer market (Edenbaum, 1992) and is used in a wide variety of plastic applications, particularly where flexibility is required at low temperatures (Rahman and Brazel, 2004). As such, it is frequently used in cling wraps, packaging and medical products (Keith et al., 1992).

Important questions remain about the environmental implications of plasticizers in the environment (Rahman and Brazel, 2004). Also, at present, little is known about the degree of resistance of plasticizers to degradation in common wastewater treatment processes. Even less is known about the environmental impacts and fates of products arising from the breakdown of such pollutants in sewage and treated effluents. It has been recently demonstrated that several common soil micro-organisms can partially degrade bis (2-ethylhexyl) ester plasticizers such as BEHP, BEHA and BEHTP into metabolites including their related mono-ester, 2-ethylhexanol, 2-ethylhexanal and 2-ethylhexanoic acid (Nalli et al., 2002, 2006; Gartshore et al., 2003). The pathways for the degradation of bis (2-ethylhexyl) ester plasticizers that result in the formation of these metabolites are shown in Fig. 1. It has also been shown in controlled laboratory studies that these metabolites are more toxic than the original plasticizers and can resist further biodegradation (Horn et al., 2004; Nalli et al., 2006). Field studies also confirmed that BEHP and BEHA and two of the metabolites, 2-ethylhexanol and 2-ethylhexanoic acid, were

present in surface waters, river sediment, freshly fallen snow and even in tap water (Horn et al., 2004). The presence of the third metabolite, 2-ethylhexanal, was not reported in most early degradation studies, most likely due to the high volatility of this compound and its tendency to partition into the gas phase. However, the production of this compound and its role in the degradation pathway has recently been confirmed (Nalli et al., 2006). Despite the results of these laboratory and field studies, it is still not evident how readily the degradation products of plasticizers will form and/or persist in process streams as they pass through sewage treatment systems.

There are four potential modes of removal of organic compounds such as plasticizers during conventional wastewater treatment (Langford and Lester, 2003): (1) adsorption on suspended solids or into fats and oils; (2) aerobic and anaerobic biodegradation; (3) chemical degradation (e.g., surface-catalyzed hydrolysis, photo-oxidation); and (4) volatilization. It is expected that metabolites would be produced throughout the treatment process as the plasticizers are degraded by biological means. Given that plasticizers and their degradation products may pose a threat to ecosystems after they are released into receiving waters, a study of the fate of these compounds is warranted. In particular, it is essential to evaluate their prevalence in various treatment plant compartments and to identify processes that are most effective in reducing the environmental impacts associated with these compounds.

Therefore, the presence of bis (2-ethylhexyl) ester plasticizers (BEHP, BEHTP, BEHA) and their metabolic intermediates was investigated in the process streams and residues of a sewage treatment plant in Montreal, Canada. This treatment facility incorporates primary and physicochemical treatment steps and serves a large urban population. With a maximal capacity of about 7.6 million m³ per day and serving over 1 880 000 citizens, it is the largest primary-physicochemical sewage treatment plant in North America (City of Montréal, 2006). The study involved the quantification of plasticizers and their breakdown products entering the treatment plant in the influent sewage and estimation of the amounts ultimately released in treated effluents and process residues.

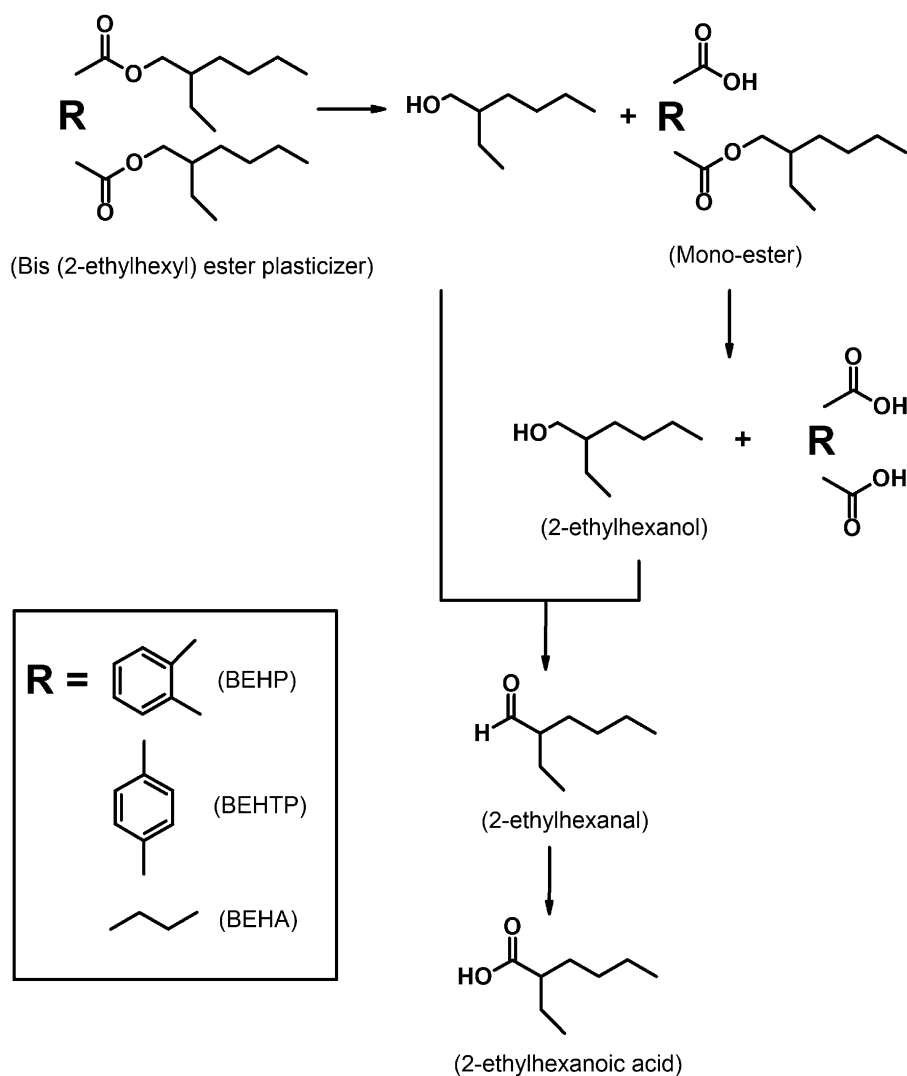
2. Materials and methods

2.1. Reagents

BEHP (98%) was obtained from Fluka/Sigma-Aldrich Co. (Oakville, Ontario). BEHA (99%), BEHTP (98%), 2-ethylhexanol (99.6%), 2-ethylhexanal (96%) and 2-ethylhexanoic acid (99%) were obtained from Sigma-Aldrich Co. (Oakville, Ontario). HPLC-grade water, acetone and chloroform were purchased from Fisher Scientific (Montreal, Quebec) and were used for cleaning and extraction purposes. All solvents were tested for potential contamination with plasticizers and related breakdown products using gas chromatograph (GC) analysis, as will be described below.

2.2. Sample collection and preparation

Samples were collected from the Montreal sewage treatment plant (Quebec, Canada), which accepts wastewaters from



across the Island of Montreal. Wastewaters originated from domestic areas, industrial operations, institutions and commercial enterprises as well as urban runoff and waters from rainfall and snow melt and were delivered through two interceptors systems (City of Montréal, 2006). The “North influent” consists of sewage collected via the Northern and South-Western interceptors, which predominantly serve residential regions. The Northern interceptor is a combined sewer system collecting storm waters and sanitary wastewaters from a region of approximately 740 000 inhabitants (1998 estimate). The South-Western interceptor is a separate sewer system that delivers only sanitary sewage to the sewage treatment facility from a region of approximately 64 000 inhabitants (1998 estimate). The “South influent” consists of sewage collected via the South-Eastern interceptor on the Island of Montreal. It is a combined sewer network that serves approximately 1 million inhabitants (1998 estimate).

The Montreal treatment plant accomplishes primary and physicochemical treatment of sewage before discharging

the treated water into the Saint-Lawrence River. A schematic of the treatment processes and the sampling locations is shown in Fig. 2. Sampling was performed on March 11, 2005 between 9:00 and 10:00 a.m. There was no rain or snow precipitation on the day of sampling or on the preceding day. The North and South influents were sampled separately just before the point in the sewage treatment facility where the streams were combined and pumped through screening and grit removal systems. A mixture of coagulants (i.e., ferric chloride and alum) was injected upstream of the screens to destabilize the colloids and an anionic acrylamide polymer was subsequently injected at the exit of the grit chambers to agglomerate the destabilized particles for flocculation, which rapidly sediment in the clarifiers. The coagulant and the coagulant aid were injected in amounts proportional to the total phosphorus load and the flow of raw water. In March 2005, the alum, ferric chloride and the anionic acrylamide polymer doses were about 3.2, 7.8 and 0.37 mgL⁻¹, respectively. Sludges originating from the sedimentation

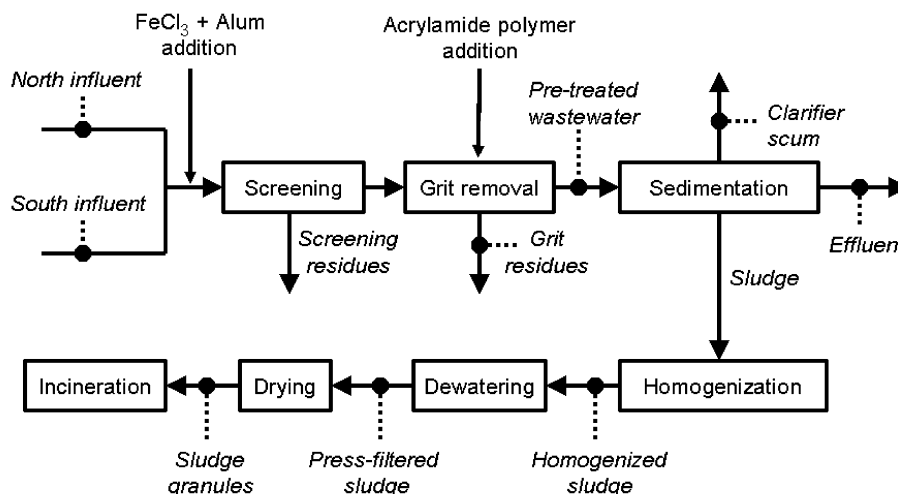


Fig. 2 – Schematic of the physicochemical treatment plant located in Montreal, Québec, Canada. Sampling locations are labeled (●).

Table 1 – General water quality data of the influents and effluent of the Montreal physicochemical treatment plant in March 2005 and on the day of sampling of March 11 2005

Parameters	North influent		South influent		Effluent	
	Mean	March 11	Mean	March 11	Mean	March 11
Suspended solids (mgL^{-1})	110 ± 30	150	120 ± 30	123	20 ± 4	20
Total phosphorus (mgL^{-1})	1.8 ± 0.4	2.7	1.7 ± 0.2	2.0	0.5 ± 0.1	0.5
Ammoniacal nitrogen (mgL^{-1})	n.a.	n.a.	n.a.	n.a.	5.1 ± 1.4	n.a.
PH	7.5 ± 0.2	n.a.	7.4 ± 0.1	n.a.	7.4 ± 0.1	n.a.
Alcalinity (mgL^{-1})	160 ± 10	n.a.	160 ± 10	n.a.	140 ± 10	n.a.
Chemical oxygen demand (mgL^{-1})	200 ± 40	240	250 ± 40	270	140 ± 50	150
Biochemical oxygen demand (mgL^{-1})	70 ± 20	90	110 ± 20	110	60 ± 10	60
Turbidity (NTU)	n.a.	n.a.	n.a.	n.a.	14 ± 2	15

*n.a. = not available.

processes were homogenized and, during the day of sampling, were dewatered by filter presses and then incinerated. Residual waters from dewatering and other processes were returned to the influent at a location downstream of the sampling point. Surface scum in the clarifiers was recovered and mixed with the sludge before dewatering. The treatment plant was also equipped to make granules by drying the dewatered sludge. Even though no granules were produced in March 2005, samples of granules produced during earlier performance tests of the drying systems were collected for analysis. General water quality data describing the influent and effluent in March 2005 and on the day of sampling are presented in Table 1.

Samples were manually collected in stainless-steel containers and poured into glass vials that were covered with aluminum foil to prevent exposure to light. All glassware was pre-rinsed with HPLC-grade water, acetone and chloroform to avoid potential contamination of samples with plasticizers. No contact with plastics was allowed during sampling and aluminum foil was used as a barrier between

screw tops and the samples. Liquid samples were maintained at 4°C after collection and during transport and storage until extraction. Liquid samples were prepared for analysis approximately 3–20 h after sampling. Semi-solid and solid samples were stored at -20°C until they were freeze dried before undergoing subsequent extraction and analysis.

Three and a half liters of each liquid sample (i.e., influent sewage, wastewater after grit removal and effluent) were passed through a G4 Fisherbrand acetone-washed glass-fiber filter from Fisher Scientific (Montreal, Quebec). The filtrate was then acidified to pH 2 with H_2SO_4 and extracted twice with HPLC-grade chloroform (1:10 v/v). The organic phases were mixed and concentrated in a rotary evaporator and then concentrated further under a gentle stream of nitrogen to a volume of about 2 mL. The remaining residue was dissolved in HPLC-grade chloroform to a final volume of either 2 or 4 mL and kept in glass vials at -20°C until analysis.

For freeze-dried samples, a Soxhlet extraction was performed on 5-g samples using chloroform. The extract was concentrated using the method outlined above for liquid samples.

2.3. GC analysis

A model CP-3800 GC from Varian Canada Inc. (Mississauga, Ontario) equipped with a flame ionization detector was used to detect and measure the concentration of the plasticizers and their degradation products. A SPB-5 fused silica column (30 m × 0.32 mm, with a 0.25 µm film thickness) from Supelco/Sigma-Aldrich (Oakville, Ontario) was used. GC settings were similar to those used by Horn et al. (2004) with slight adjustments: i.e., an injector temperature of 300 °C, an initial column temperature of 40 °C, a hold time of 2 min, a temperature ramp rate of 10 °C per minute with a final temperature of 300 °C and a detector temperature of 300 °C.

Method validation was performed according to Government of Québec (1995) recommendations. In order to evaluate compound recovery following extraction, 0.01% v/v of *n*-pentadecane was introduced into every sample as an internal standard. In the case of sludge analyses, a spiked sludge sample was treated (i.e., freeze drying, extraction and analysis) to compare results with the unspiked sample. To ensure analytical reliability, the detection and measurement of the compounds were achieved with and without spiking the samples with a mixture of the target compounds. Also, all samples were analyzed at least three times and multiple standard curves were drawn and standard solutions were used. Method repeatability and intermediate precision were evaluated based on six replicates. Repeatability was determined for BEHP, BEHTP and BEHA as 6%, 4% and 14%, respectively. For 2-ethylhexanol, 2-ethylhexanal and 2-ethylhexanoic acid, it was determined to be 8%, 4% and 2%, respectively. Intermediate precision was determined for DEHP, DEHTP and DEHA as 12%, 6% and 10%, respectively. For 2-ethylhexanol, 2-ethylhexanal and 2-ethylhexanoic acid, it was determined to be 5%, 5% and 6%, respectively. The percentage recovery for all samples was approximately 80%, according to internal standards and spiked samples.

3. Results

As shown in Table 2, BEHP, BEHTP and BEHA were consistently detected in all aqueous process streams of the treatment plant. BEHA was detected at the highest concentration, especially in the sewage of the North influent where a concentration of 10 300 µg L⁻¹ was observed. However, most of this was removed with the solids. All of the plasticizers are hydrophobic and this is the most dramatic example of the removal of these compounds during primary treatment after addition of coagulants and a coagulant aid.

The very high concentrations of BEHA and the fact that most of these are removed after the coagulation procedures imply that this particular plasticizer is strongly associated with oily solids and droplets suspended in the influent wastewaters. This makes it likely that the samples collected were inhomogeneous given that oily materials would tend to be present at higher concentrations near the surface of the aqueous streams when mixing is not sufficient to keep them evenly dispersed. Because of the necessities of sampling, this would lead to an over-estimation of the amounts of BEHA present in the entire streams. Thus, the very high values for some influent BEHA concentration and mass flow rates are probably inflated. In general, these data can still be used to conclude that BEHA is present in much higher concentrations than the two phthalate plasticizers. All three of the plasticizers being studied are hydrophobic so the percentage errors are expected to be similar. It should also be noted that the influents of six other wastewater treatment plants in Quebec had an average BEHA concentration of 3460 µg L⁻¹ with a standard deviation of 2160 µg L⁻¹ (data not shown). These results confirm that BEHA concentrations in wastewaters from urban regions were consistently high.

In addition to the plasticizers, the metabolites that have been shown to arise from the biodegradation of bis (2-ethylhexyl) ester plasticizers were consistently observed in all aqueous process streams (see Table 2). Of these,

Table 2 – Concentrations of plasticizers and related biological degradation products in the aqueous process streams of the Montreal sewage treatment plant

Compounds	Concentration in the water phase (µg L ⁻¹)				
	Wastewater influents			Pre-treated wastewater (after grit removal)	Wastewater effluent (after physico-chemical treatment)
	North	South	Total		
BEHA	10 300 ± 400	3000 ± 120	6170 ± 250	1640 ± 70	147 ± 6
BEHP	57.0 ± 7.4	80.0 ± 10.4	70.0 ± 9.1	41.0 ± 5.3	54.0 ± 7.0
BEHTP	41.0 ± 2.1	58.0 ± 2.9	51.0 ± 2.6	32.0 ± 1.6	14.2 ± 0.7
2-ethylhexanol	10.3 ± 0.7	3.40 ± 0.24	6.0 ± 0.4	2.70 ± 0.19	2.30 ± 0.16
2-ethylhexanal	16.0 ± 0.6	4.10 ± 0.16	9.0 ± 0.4	2.20 ± 0.09	24.0 ± 1.0
2-ethylhexanoic acid	48.0 ± 1	25.9 ± 0.52	36.0 ± 0.7	23.0 ± 0.5	14.8 ± 0.3

2-ethylhexanol, which is released by the hydrolysis of the ester bonds in the plasticizers (see Fig. 1), was found at a concentration of $6.0\mu\text{g L}^{-1}$ in the total influent of the treatment plant. The concentration of this alcohol decreased by approximately 55% as the wastewater underwent grit removal and then declined by a further 7% before leaving in the effluent at a concentration of $2.3\mu\text{g L}^{-1}$. The concentration of 2-ethylhexanal, which is a volatile intermediate produced from 2-ethylhexanol (Nalli et al., 2006), was present in the influent at a concentration of $9.0\mu\text{g L}^{-1}$. This concentration decreased by 75% during grit removal but then underwent a subsequent 10-fold increase to $24\mu\text{g L}^{-1}$ before being released in the effluent. Of all the metabolites investigated, 2-ethylhexanoic acid, which is a recalcitrant product of plasticizer degradation (Nalli et al., 2006), was found in the highest concentration in the influent at a concentration of $36\mu\text{g L}^{-1}$. Its concentration gradually declined by 59% over the course of treatment resulting in an effluent concentration of $14.8\mu\text{g L}^{-1}$.

Table 3 presents a summary of the concentrations of plasticizers and related breakdown products that were measured in residues produced during treatment. Grit residues arising from the pre-treatment process contained all three plasticizers plus 2-ethylhexanol and 2-ethylhexanoic acid, but 2-ethylhexanal was not detected. Of the three plasticizers, the highest concentration observed was for BEHA at 79mg kg^{-1} , followed by BEHP and BEHTP at 11.8 and 10mg kg^{-1} , respectively. All target compounds were detected in homogenized sludge and dewatered sludge. The plasticizers were measured in the homogenized sludge in concentrations ranging from 34 to 80mg kg^{-1} while the degradation products were present at $12.5\text{--}34\text{mg kg}^{-1}$. In the dewatered sludge, the target plasticizers were found at higher concentrations of 340, 104 and 90mg kg^{-1} of BEHA, BEHTP and BEHP, respectively. 2-ethylhexanol was also found at a surprisingly high concentration of 85mg kg^{-1} . Except for 2-ethylhexanoic acid, all other target compounds were detected in the scum sampled from the surface of clarifiers, with an especially high concentration of 2-ethylhexanal at 98mg kg^{-1} . Plasticizers were detected in dried sludge (granules) at relatively low concentrations ranging from 12.2 to 19.3mg kg^{-1} , but no metabolites were detected.

In this work, the use of single samples of process streams adds error to the estimation of mass flows. However, the results presented in Table 4 can be considered as preliminary estimates of a mass balance that is a reasonable estimation of how plasticizers and their toxic intermediates are distributed in various streams in the STP. This preliminary estimate shows the magnitude of the problem regarding the discharge of plasticizer parent compounds.

Approximately 150, 110 and $13\,000\text{kg d}^{-1}$ of BEHP, BEHTP and BEHA, respectively, were received by the sewage treatment plant on the day of sampling. Following treatment, approximately 2%, 80% and 28% of the BEHA, BEHP and BEHTP received in the influent, respectively, were discharged in the effluent into receiving surface waters (i.e., the Saint-Lawrence River). Of the degradation products, about 36% and 43% of 2-ethylhexanol and 2-ethylhexanoic acid inputs, respectively, were discharged. In contrast, approximately 2.65 times more 2-ethylhexanal was released from the treatment plant than was present in the influent, thereby indicating that 2-ethylhexanal was generated during sewage treatment.

Grit residues did not represent an important output for plasticizers and their breakdown products. In contrast, about 1%, 5%, 8%, 15% and 25% of the inputs of BEHA, 2-ethylhexanol, 2-ethylhexanoic acid, BEHP and BEHTP, respectively, were found in the dewatered sludge, which was subsequently incinerated. Similar to the observations noted above, more 2-ethylhexanal was found in these residues than in the influent. In the case of sludge granules, no data on their production rate were available from which the daily emission rates of plasticizers into the environment could be estimated. While the land application of these sludge granules could represent a source of plasticizers in the environment, the Montreal treatment plant did not produce a significant amount in the year 2005 for land application and, instead, opted for incineration.

The effluent from the Montreal wastewater treatment plant is discharged into the St. Lawrence River. In an earlier study (Horn et al., 2004), the quantities of BEHA and BEHP and the degradation products were measured in this same river, at a point several kilometers upstream of the sewer outfall. A summary of the quantities of these compounds observed

Table 3 – Concentrations of plasticizers and related biological degradation products in the residues of the Montreal sewage treatment plant

Compounds	Concentration (mg kg^{-1}) ^a				
	Grit residues	Scum at surface of clarifiers	Homogenized sludge	Press-filtered sludge	Granules
BEHA	79 ± 3	84 ± 3	34 ± 1.0	340 ± 10	19.3 ± 1.0
BEHP	10 ± 1.3	22 ± 2.9	80 ± 10	90 ± 12	15 ± 2.0
BEHTP	11.8 ± 0.6	20 ± 1.0	45 ± 2.3	104 ± 5	12.2 ± 0.6
2-ethylhexanol	n.d.	16 ± 1.1	12.5 ± 0.9	4.5 ± 0.3	n.d.
2-ethylhexanal	4.9 ± 0.2	98 ± 3.9	34 ± 1.4	85 ± 3.4	n.d.
2-ethylhexanoic acid	2.25 ± 0.05	n.d.	20.7 ± 0.4	14.6 ± 0.3	n.d.

^a n.d. = not detected.

Table 4 – Estimates of daily mass flows on the day of sampling of plasticizers and related biological degradation products in the influent, effluent and solid residues of the Montreal treatment plant and quantities in these streams expressed relative to those observed in the influent (in %)

Compartments	Stream flow	Mass flows (in kg d ⁻¹) (and residual quantities relative to influent, in %)					
		BEHP	BEHTP	BEHA	2-ethylhexanol	2-ethylhexanal	2-ethylhexanoic acid
Influent ^a	2.2 × 10 ⁶ m ³ d ⁻¹	150	110	13 000	14	20	76
Effluent ^b	2.2 × 10 ⁶ m ³ d ⁻¹	120 (80%)	31 (28%)	320 (2%)	5.1 (36%)	53 (265%)	33 (43%)
Grit residues ^c	8.1 tons d ⁻¹	8.1 × 10 ⁻⁵ (~0%)	9.6 × 10 ⁻⁵ (~0%)	6.4 × 10 ⁻⁴ (~0%)	0 (~0%)	4.0 × 10 ⁻⁵ (~0%)	1.8 × 10 ⁻⁵ (~0%)
Dewatered sludge ^d	798 tons d ⁻¹	23 (15%)	27 (25%)	87 (1%)	1.1 (8%)	22 (110%)	3.7 (5%)

^a Sum of North and South influents mass flows were estimated using the daily flow rates on the day of sampling (March 11, 2005); i.e., 10.4 and 14.9 m³ s⁻¹ for the North and South influents, respectively, totalizing 25.3 m³ s⁻¹. The specific flow rates of North and South influents at the moment of sampling were 9.0 and 13.7 m³ s⁻¹, respectively. According to the data obtained from Montreal sewage treatment plant, the average flow rates of the North and South influents in March 2005 were 12.6 and 16.9 m³ s⁻¹.

^b Values were estimated using the daily flow rate on March 11, 2005.

^c Values were estimated based on the amount disposed in March 2005 (i.e., 250.3 tons).

^d Values were measured with the daily amount generated on March 11, 2005 with about 32% of total solids. The average amount of dewatered sludge generated in March 2005 was 827 tons d⁻¹.

Table 5 – Concentrations of plasticizers and their related biological degradation products measured in the effluent from the Montreal sewage treatment plant and in the water and sediment of the Saint-Lawrence River

Compounds	Concentration		
	Effluent (µg L ⁻¹)	River water (µg L ⁻¹) ^a	River sediment (µg kg ⁻¹) ^a
BEHP	54	180	110 000
BEHTP	14.2	n.a.	n.a.
BEHA	147	14	4400
2-ethylhexanol	2.3	0.85	100
2-ethylhexanal	24	n.d.	n.d.
2-ethylhexanoic acid	14.8	3.2	110

^a Horn et al. (2004); n.a. = not available; n.d. = not detected.

in the effluent and in the water and sediment of the St. Lawrence River is shown in Table 5.

4. Discussion

Plasticizers were consistently found in appreciable concentrations in the influents, process streams and effluents of the wastewater treatment plant (see Table 2). Thus, as indicated by the mass flows of plasticizers (see Table 4), sewage from urban sources can represent a significant source of plasticizers in the environment. Given the earlier reports of plasticizers in effluents (Fromme et al., 2002; Fauser et al., 2003; Martinen et al., 2003a), this finding was not unexpected; however, the relative quantities of the three plasticizers in the wastewaters were surprising.

The very high concentrations of BEHA observed in the treatment plant influents (see Table 2) were a particularly unexpected result of these investigations. That is, given that

92% of plasticizers in use worldwide are phthalates (Rahman and Brazel, 2004), it was surprising that the concentrations of BEHA were several orders of magnitude higher than those observed for BEHP and BEHTP. Furthermore, earlier work had demonstrated that BEHA was much more susceptible to biodegradation by common soil organisms than BEHP (Nalli et al., 2002). Since BEHA is used in much smaller quantities and is more readily biodegraded than other plasticizers, the findings presented in Table 2 suggest that (1) the sources of BEHA in urban wastewaters (particularly in food wraps, packaging and foods that had been exposed to such plastics) are very significant and/or (2) that BEHA must be significantly more mobile than BEHP and tends to leach out of plastic products and into the environment more quickly.

Under the sampling conditions of this study, since no precipitation was recorded in the region served by the municipal sewer system in the days preceding the sampling, the flows mainly consisted of domestic, commercial and industrial discharges. Given that one of the most common

uses for BEHA is in plastic films, such as those used for food wrapping (Keith et al., 1992), higher concentrations of BEHA were expected in regions that primarily serve residential populations. This is consistent with the observations here in which higher concentrations of BEHA were observed in the North influent that is expected to include wastewaters that originate from more residential regions compared to those of the South influent.

It was also unexpected to find BEHTP in concentrations similar in magnitude to BEHP, given that this phthalate plasticizer is not in a widespread use and it has been reported to be less susceptible to migration from plastic products than BEHP (Rahman and Brazel, 2004). Moreover, in earlier studies (Nalli et al., 2002), BEHTP was found to be more readily biodegraded than BEHP. The significant amounts of 2-ethylhexanol, 2-ethylhexanal and 2-ethylhexanoic acid show that there had been significant biodegradation in the interceptors from source to influent. Collectively, these results indicate that there are significant sources of BEHTP in the urban wastewaters that we have not been able to identify.

It can be seen that appreciable amounts of all three plasticizers were removed by primary treatment. Some of this appears in the dewatered sludge and the grit but much of the solid materials removed could not be analyzed and, therefore, it was not possible to complete a mass balance. BEHA, BEHP and BEHTP were removed from the aqueous phase with efficiencies of 98%, 20% and 72%, respectively. Given the physicochemical nature of the treatment process and the relatively short time scale of treatment, it is unlikely that the decreases in plasticizer concentrations were primarily due to biodegradation.

The biodegradation of adipate and phthalate plasticizers has been shown to result in the production of the metabolites 2-ethylhexanol, 2-ethylhexanal and 2-ethylhexanoic acid in laboratory studies with common soil organisms, as shown in Fig. 1 (Horn et al., 2004; Nalli et al., 2002, 2006). Field work (see Table 5) has confirmed that 2-ethylhexanol and 2-ethylhexanoic acid are also found in the environment. The present study has demonstrated that these same products are contained in the influents, process streams, treated effluent and solid residues of the Montreal wastewater treatment plant. As stated above, since there were relatively high concentrations of the degradation products in the influent, it is very likely that a significant portion of the plasticizers originally introduced into the sewer system were biodegraded before they reach the sewage treatment facility.

There is one unexpected result in the measurements of the biodegradation products. This is the presence of significant amounts of 2-ethylhexanal. In some situations, this was present in even higher quantities than the concentration of 2-ethylhexanol. The aldehyde is relatively volatile and easily oxidized to 2-ethylhexanoic acid (Nalli et al., 2006). As such, it was not observed in significant quantities in laboratory degradation studies which were done with a large flow of air through the reactor (e.g., Nalli et al., 2002). The aldehyde was also not observed in field samples (Horn et al., 2004). The situation presented by the current data is much different. The biodegradation occurring in the interceptors is in a closed pipe and it can be seen that appreciable amounts of the aldehyde are not lost.

Another surprising result is that the ratio of aldehyde to alcohol actually increases during the treatment steps. It appears that alcohol is being oxidized to the aldehyde faster than the aldehyde is being oxidized to 2-ethylhexanoic acid. This could indicate that once the alcohol has been released from the diester plasticizers by enzymatic hydrolysis, it is susceptible to non-biological oxidation to the aldehyde during primary treatment.

Overall, even though the physicochemical treatment process did accomplish the removal of an appreciable fraction of the total influent load of plasticizers, the treated effluent still contained significant amounts of all three plasticizers and their degradation products. In addition, significant quantities of all three plasticizers were recovered in the dewatered sludge and other solid or semi-solid streams and more of these must be present in the unmeasured solids streams. All of these compounds and most of their degradation products are fairly hydrophobic and, as a result, physicochemical treatment resulted in their removal via adsorption onto solids. For example, it has been reported that adsorption of organic compounds onto solids is the most significant mechanism of removal during primary treatment for compounds with $\log K_{ow}$ values (i.e., K_{ow} = Octanol–water partition coefficients) greater than 4 (Langford and Lester, 2003). For example, BEHP and BEHA are expected to have high sorption potentials ($\log K_{ow} > 4.0$) (Staples et al., 1997; USEPA, 2006), followed by 2-ethylhexanal and 2-ethylhexanoic acid with intermediate sorption potentials ($\log K_{ow} \approx 2.5–4.0$) (BG Chemie, 2000, 2005) and 2-ethylhexanol with a low sorption potential ($\log K_{ow} < 2.5$) (BG Chemie, 1995). Earlier measurements of these compounds in river samples (Table 5), where it was shown that the relatively hydrophobic sediments tended to contain very high concentrations of these chemicals (Horn et al., 2004), are consistent with the sorption potentials of these compounds.

The last metabolite, 2-ethylhexanoic acid, is unlike the other species being considered because its hydrophobicity is pH dependent. At neutral pH, most of this compound will be charged and thus much more water soluble. In March 2005, the pH values of the Montreal sewage treatment plant influent and effluent were 7.4 while the pH of dewatered sludge was 6.3. This would explain why the amount of 2-ethylhexanoic acid found in some of the non-aqueous phases is relatively low. In addition, this is the most stable of the breakdown products (Nalli et al., 2002, 2006), so it is expected to be found anywhere in the environment where micro-organisms and appreciable quantities of plasticizers are present.

With respect to the analyzed solid residues (Table 3), grits and sludges were found to contain the toxic degradation products, but the granules did not. Grit residues contained plasticizers that were likely adsorbed onto fats, oils and greases but contained only relatively low concentrations of 2-ethylhexanal and 2-ethylhexanoic acid, and no 2-ethylhexanol (see Table 3). The residual plasticizers in the grit are expected to contribute to the plasticizer loads in landfill leachates and, ultimately, will contribute to the production of toxic degradation products. Indeed, landfill leachates are already known to contain large amounts of plasticizers (Marttinen et al., 2003b), which likely originate from wastewater treatment plant residues and plastic wastes.

The toxic metabolites were present in significant quantities in the homogenized and dewatered sludges (Table 3). At present, the dewatered sludges from the Montreal sewage treatment plant are incinerated at approximately 900 °C, which mineralizes organic components. Thus, it is presumed that plasticizers and their toxic degradation products would be absent from ash residues. However, if incineration were to be discontinued in favour of other disposal techniques or beneficial end use of residues (e.g., land application), the presence of significant quantities of plasticizers and their degradation products might pose a significant limitation. For example, even though large quantities of BEHA in sludges would be expected to degrade fairly rapidly in the environment, this degradation will ultimately result in the production of the toxic metabolites. In addition, given their greater resistance to degradation, the phthalate plasticizers (and especially BEHP) would be expected to gradually accumulate wherever this material is disposed. And, while it is fortunate that the dried sludge granules contained less plasticizers than the dewatered sludges and no toxic metabolites, they still contained appreciable quantities of plasticizers. Thus, if the granules are to be disposed by land application, the plasticizers within these granules will act as reservoirs for the production of toxic metabolites by soil micro-organisms.

5. Conclusion

This study demonstrated that there were significant quantities of BEHA, BEHP and BEHP in the influents, effluents and process streams of a large urban physicochemical sewage treatment plant. Furthermore, all of the expected biodegradation products, 2-ethylhexanol, 2-ethylhexanal and 2-ethylhexanoic acid, were found in all of the process streams. Unexpectedly, the amounts of BEHA observed were very large relative to those BEHP, which is by far the most commonly used plasticizer. Another surprise was the high concentrations of 2-ethylhexanal, which is a volatile metabolite that was expected to be easily converted to the acid. Fortunately, 2-ethylhexanal is not expected to persist in the environment, but will ultimately lead to the production of the acid either in water or air. The physicochemical treatment plant was able to accomplish the partial removal of these plasticizers from the aqueous phase, but significant quantities still remained in treated process streams and solid residues. Not only is the presence of these plasticizers in the effluent and residues a concern, but they are also acting as pollutant reservoirs, that slowly biodegrade to produce the more stable and toxic compounds, 2-ethylhexanol, 2-ethylhexanal and 2-ethylhexanoic acid. In general, it is recommended that the development of eco-friendly alternatives to common plasticizers should be pursued to minimize the introduction of these problematic plasticizers and their toxic degradation products in the environment.

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