Distribution of thirty-nine non-BDE flame retardants and plasticizers in a secondary wastewater treatment system

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1.0 BACKGROUND AND OBJECTIVES

- Restrictions in the use of brominated diphenyl ether (BDE) flame retardants has increased demand for a number of currently used flame retardants. Some of these flame retardants have been in use since the 1970s and are suitable replacements for BDEs and some are high production volume chemicals.
- Municipal wastewater treatment plants (WWTPs) have been identified as point sources of a broad range of environmental contaminants.
- In the present work, using LC-MS/MS and GC-ECNI-MS approaches, we have measured the concentration and distribution of thirty-nine currently used flame retardants in a secondary wastewater treatment plant.

2.0 ANALYTICAL METHODS

2.1 Target analytes

A total of 39 target analytes including: 13 organophosphorus (OPs), 7 chlorinated, 12 monoaromatic and 7 miscellaneous brominated flame retardants were investigated. The list of analytes were derived from targets of interest to national agencies such as Canada's CMP, and USEPA's TSCA and literature review of leading researchers in the field.

Table 1. Target analytes – OP flame retardants.

Compound	Shorthand	CAS #
Triethyl phosphate	TEP	78-40-0
Tris(2-chloroethyl) phosphate	TCEP	115-96-8
Tripropyl phosphate	TPrP	513-08-6
Tris(2-chloroisopropyl) phosphate	TCPP	13674-84-5
Tris(1,3-dichloro-2-propyl) phosphate	TDCPP	13674-87-8
Triphenyl phosphate	TPP	115-86-6
Tris(2,3-dibromopropyl) phosphate	TDBPP	126-72-7
Tributyl phosphate	TBP	126-73-8
Tricresyl phosphate	TCrP	1330-78-5
2-Ethylhexyl diphenyl phosphate	EHDPP	1241-94-7
Tris(2-butoxyethyl) phosphate	TBEP	78-51-3
Tris(2-ethylhexyl) phosphate	TEHP	78-42-2
Tetrakis(2-chloroethyl)dichloroisopentyldiphosphate	V6	38051-10-4

Table 2a. Target analytes – Chlorinated flame retardants.

Compound	Shorthand	CAS #
Dechlorane	Dec	2385-85-5
Dechlorane plus® (DP) Anti	DP Anti	135821-74-8
Dechlorane plus® (DP) Syn	DP Syn	135821-03-3
Dechlorane 602	Dec 602	31107-44-5
Dechlorane 603	Dec 603	13560-92-4
Dechlorane 604	Dec 604	34571-16-9
Hexachlorocyclopentadienyl-dibromocyclooctane	HCDBCO	51936-55-1

Table 2b. Target analytes – Monoaromatic flame retardants.

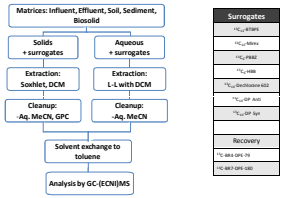
Compound	Shorthand	CAS #
Hexabromobenzene	HBB	87-82-1
Pentabromobenzene	PBBZ	608-90-2
1,2,4,5-tetrabromobenzene	1,2,4,5-TBB	636-28-2
1,2,3,5-tetrabromobenzene	1,2,3,5-TBB	634-89-9
1,2,4-tribromobenzene	1,2,4-TriBB	615-54-3
1,2-dibromobenzene	1,2-DiBB	583-53-9
1,4-dibromobenzene	1,4-DiBB	106-37-6
Pentabromotoluene	PBT	87-83-2
Pentabromoethylbenzene	PBEB	85-22-3
Pentabromobenzyl bromide	PBBB	38521-51-6
Tetrabromo-p-Xylene	pTBX	23488-38-2
Tetrabromo-o-chlorotoluene	TBCT	39569-21-6

Table 2c. Target analytes –Miscellaneous flame retardants

Compound	Shorthand	CAS #
2,4,6-Tribromophenylallyl ether	ATE	3278-89-5
2-Bromoallyl 2,4,6-tribromophenyl ether	BATE	99717-56-3
2,3-Dibromopropyl 2,4,6-tribromophenyl ether	DPTE	35109-60-5
1,2-Bis(2,4,6-tribromophenoxy)ethane	BTBPE	37853-59-1
Di(2-ethylhexyl) tetrabromophthalate	BEHTBP	26040-51-7
2-Ethylhexyl 2,3,4,5-tetrabromobenzoate	EHTBB	183658-27-7
1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane	Total TBECH	3322-93-8

2.2 Extraction and analysis

- A single LC-MS/MS method was used for the OP flame retardants (Table 1). All aspects of extraction and analysis for the OP flame retardants have been published [1].
- A single GC-(ECNI)MS method was used for analysis of targets in Table 2a, 2b and 2c. Details of extraction and cleanup are provided in the flow chart below.



2.3 Instrumental analysis

GC-Column : DB-5 capillary column (60 m, 0.25 mm i.d., 0.10 µm film thickness)

GC Temperature Program		General GC Conditions:	
Temp (°C)	60	Injector Temp (°C)	240
Hold time (min)	1.0	Carrier Gas	Helium
Rate (°C/min)	12.0	Ionization gas	Methane
Temp (°C)	320.0	Source Temp (°C)	142
Hold time (min)	13.33	Quadrupole Temp (°C)	106

3.0 SAMPLE COLLECTION

SAMPLING

- WWTP samples were collected from a secondary wastewater treatment plant with UV disinfection. An example schematic is shown in Figure 1.
- Composite samples (24 hrs composites) were collected for the raw influent and final effluent samples on two consecutive days.
- Grab samples were collected for the primary effluent, raw sludge and biosolid samples. Raw sludge and biosolid samples were collected on two consecutive days.
- All samples were stored at 4°C prior to extraction and analysis.

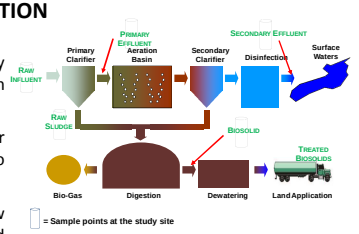


Figure 1. Wastewater treatment plant schematics and sampling locations.

4.0 RESULTS: METHOD PERFORMANCE DATA

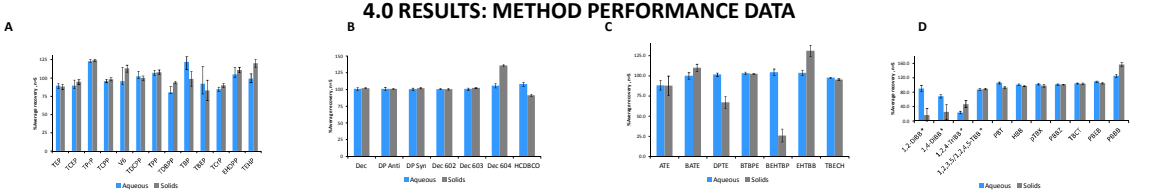


Figure 2. Replicate spike recovery for spiked aqueous and sediment samples: A = OP flame retardants, B= Chlorinated flame retardants, C = Miscellaneous flame retardants and D = Monoaromatic flame retardants. Notably low recoveries were observed for BEHTBP, and the volatile analytes 1,2-DiBB, 1,4-DiBB, and 1,2,4-TriBB in the solid matrices.

5.0 RESULTS: CONCENTRATION AND DISTRIBUTION OF FLAME RETARDANTS IN WWTP SAMPLES

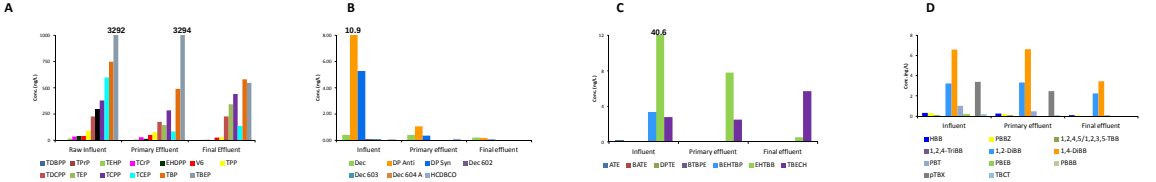


Figure 3. Concentrations and distributions of flame retardants in aqueous waste stream in a secondary wastewater treatment system. A = OP flame retardants, B = Chlorinated flame retardants, C = Miscellaneous flame retardants and D = Monoaromatic flame retardants.

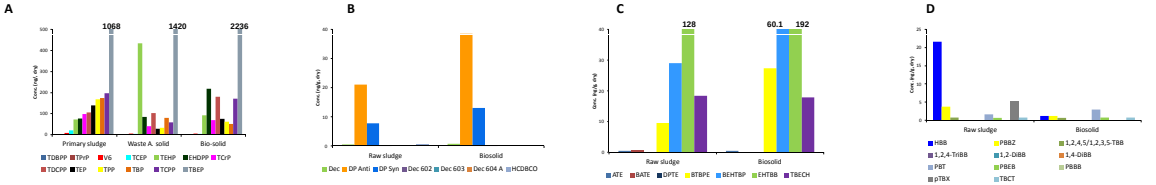


Figure 4. Concentrations and distributions of flame retardants in solid waste stream in a secondary wastewater treatment system. A = OP flame retardants, B = Chlorinated flame retardants, C = Miscellaneous flame retardants and D = Monoaromatic flame retardants.

6.0 SUMMARY

- Using LC-MS/MS and GC-(ECNI)-MS platforms reliable isotope dilution / internal standard methods were developed for quantitative measurement of thirty-nine non-BDE flame retardants.
- Target analytes include: 13 OPs, 7 chlorinated, 12 monoaromatic and 7 miscellaneous flame retardants.
- The methods were validated for measuring these contaminants in aqueous, solids and biosolid matrices.
- The developed methods were applied for measuring the concentration and distribution of these flame retardants in secondary wastewater treamtment system.
- OP flame retardants were shown to have the highest total concentration of any flame retardant in influent, effluent and biosolid samples.
- A number of flame retardants were detected in the final effluent and biosolid samples. Some flame retardants e.g. TBEP, Dec Anti, BTBPE and EHTBB concentrated into the solid phase whereas TBECH was observed to concetrate into the aqueous phase.
- Both liquid and solid waste from WWTP are sources of flame retardants in the environment.

FUTURE WORK

- Recently commercialized isope labeled standard for d17, $^{13}C_6$ -BEHTBP will be tested to improve recovery for BEHTBP.
- Measuremeing these contaminants in tissue is a focus for future study.

REFERENCES

1. Woudneh, M.B. et al. J. Chrom A. 2015, 1400: 149-155.
2. Chen, Da, et al. J. Chrom A. 2012, 1220: 167-174.
3. Sverko, Ed et al. ES&T. 2011, 45: 5088-5098.

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