Chemosphere 195 (2018) 29–39

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Waste-water treatment plants are implicated as an important source of flame retardants in insectivorous tree swallows (*Tachicyneta bicolor*)

Kimberly J. Fernie [a,*], Robert J. Letcher [b]

[a] *Ecotoxiciology and Wildlife Health Division, Environment and Climate Change Canada, Canada Center for Inland Waters, 867 Lakeshore Road, Burlington, Ontario L7R 1A1, Canada*

[b] *Ecotoxicology and Wildlife Health Division, Environment and Climate Change Canada, National Wildlife Research Centre, 1125 Colonel By Drive, Ottawa, Ontario K1A 0H3, Canada*

HIGHLIGHTS

- Flame retardants (FR) were assessed in bird eggs at wastewater treatment plants.
- Tree swallows had greater levels of legacy FR at these sites than reference site.
- *In ovo* legacy FR usually higher at secondary treatment vs tertiary treatment site.
- Novel FR only occurred in tree swallow eggs from the wastewater treatment sites.

ARTICLE INFO

Article history:
Available online 7 December 2017

Keywords:
Tree swallows
Halogenated flame retardants
Wastewater treatment plant
Sewage outflow
Tachycineta bicolor

ABSTRACT

Wastewater treatment plants (WWTPs) are an important source of anthropogenic chemicals, including organic flame retardants (FRs). Limited studies indicate birds can be exposed to FRs by feeding from waters receiving WWTP effluent or in fields receiving biosolids. Expanding on our earlier study, 47 legacy and 18 new FR contaminants were characterized in the eggs of insectivorous tree swallows (*Tachycineta bicolor*) feeding in water bodies receiving effluent from two WWTPs and compared to those from a reference site 19 km downstream of the nearest WWTP. Of the FRs measured, polybrominated diphenyl ethers (PBDEs) dominated the FR profile, specifically BDE-47, -99, -100, -153, -154, with considerably lower concentrations of hexabromocyclododecane (HBCDD), BDE-183 and BDE-209; each detected in 96–100% of the eggs overall except HBCDD (83%). FR concentrations were usually significantly greater in eggs from the secondary WWTP versus the tertiary WWTP and/or reference site. Despite low detection rates, concentrations of new FRs, specifically pentabromobenzyl acrylate (PBBA), 1,2,-bis-(2,4,6-tribromophenoxy)ethane (BTBPE), bis(2-ethylhexyl)-tetrabromophthalate (BEHTBP), tetrabromo-*o*-chlorotoluene (TBCT), hexabromobenzene (HBB), α- and β-1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane (DBE-DBCH), were greater than HBCDD or BDE-209. Additional evidence that WWTPs are an important source of exposure to new FR contaminants for birds utilizing associated water bodies is that only the WTTP eggs, not the reference eggs, had measureable concentrations of PBBA, TBCT, BEHTBP, HBB, α-DBE-DBCH, 2,2′,4,5,5′-pentabromobiphenyl (BB-101), pentabromoethyl benzene (PBEB), 2,4,6-tribromophenyl allyl ether (TBPAE), and tetrabromo-*p*-xylene (*p*TBX). Our study suggests that WWTPs are an important source of legacy and new FR contaminants for birds consuming prey that are associated with WWTP out-flows.

1. Introduction

Flame retardants (FRs) are ubiquitous chemicals that are used globally for industrial and household applications (e.g., de Wit, 2002). The halogenated organic FRs (HFRs) are primarily based on bromine and chlorine, and in the mid-to late-2000s, represented approximately 25% (by volume) of the total annual FR production (Segev et al., 2009). HFRs are divided into three classes: aromatic (e.g., tetrabromobisphenol A (TBBPA), polybrominated diphenyl ethers (PBDEs)), cycloaliphatic (e.g. hexabromocyclododecane

* Corresponding author.
E-mail address: kim.fernie@canada.ca (K.J. Fernie).

https://doi.org/10.1016/j.chemosphere.2017.12.037
0045-6535/

(HBCDD) isomers), and aliphatic (a minor group of substances). Brominated FRs are more numerous than chlorinated FRs and both are known to degrade in the environment (Segev et al., 2009). Additive HFRs (e.g., PBDEs, HBCDD) are most frequently used because they are less expensive to manufacture than reactive (e.g., TBBPA) HFRs, but greater use of the former FRs is of major concern because they leach from products and are released into the environment (de Wit et al., 2010).

HFRs and other chemicals in industrial and household wastewater can be released into the environment via the out-flow of wastewater treatment plants (WWTPs), particularly from those located in and servicing larger urban centers. WWTPs have been characterized as important point sources of metals, pharmaceuticals, personal care products, macronutrients (e.g., ammonia), and chemicals including FRs, to the aquatic environment (e.g., DesJardins-Anderson and MacRae, 2006; Song et al., 2006) and to terrestrial sites via the application of WWTP biosolids. Triclosan and tricarban were measured throughout a terrestrial food web, including the eggs of European starlings (*Sturnis vulgaris*), in agricultural lands repeatedly receiving WWTP sludge (Sherburne et al., 2016). Similarly, side-chain fluoropolymer surfactants were measured in soil samples collected in 2015 from farm field sites to which WWTP biosolids were applied in southern Ontario (Canada), and generally were found at much greater concentrations than at farm field sites not receiving biosolid applications (Chu and Letcher, 2017).

Another predominant means by which HFRs are released from WWTPs into the environment is the discharge of treated effluent (North, 2004), and concentrations of HFRs in WWTP effluent have been reported in a number of studies (e.g., DeBoer et al., 2000; DesJardins-Anderson and MacRae, 2006; Song et al., 2006). As a result of their relatively low water solubility and volatility, higher brominated FRs are associated with sediments or solid phases such as sewage sludge (Matscheko et al., 2002; Sellström et al., 2005; Banerji et al., 2009), while less brominated FRs, being more water soluble, are found in the effluent (North, 2004). As a result, aquatic invertebrates, fish and other wildlife inhabiting or feeding from waters receiving WWTP effluent may be exposed to and/or accumulate HFRs, particularly the lower brominated FRs as reported in fish (e.g., DesJardins-Anderson and MacRae, 2006; Gevao et al., 2011; Guerra et al., 2010). While the occurrence and accumulation of PBDEs and other HFRs are well-documented in birds from both aquatic and terrestrial ecosystems (e.g., Chen et al., 2013; Fernie et al., 2017; Su et al., 2017), the exposure of birds and their accumulation of FRs in relation to WWTPs as a potential source of exposure, is not well studied.

Tree swallows (*Tachycineta bicolor*) are mid-trophic passerine birds that feed within a 225 m radius around their nest box during egg laying (Stapleton and Robertson, 2006), primarily on aerial insects, many of which have aquatic larvae that develop in sediment (Dunn and Hannon, 1992). They have been widely used to characterize concentrations of PBDEs, polychlorinated biphenyls (PCBs), and polyaromatic hydrocarbons (PAHs), among other chemicals, in contaminated regions throughout North America, including Areas of Concern and Super Fund sites (e.g., Custer et al., 2017, 2016). Chemical burdens measured in passerine eggs reflect maternal exposure to chemicals (Dauwe et al., 2006) and with tree swallows, reflect sediment contamination within 1 km of their nest box (Custer et al., 2017, 2016), with significant associations for PCBs and PAHs evident among the nestlings' diet, carcasses and sediment as well (Custer et al., 2017). As a result, breeding tree swallows feeding from water bodies receiving WWTP effluent, provide a means to determine if FRs are transferred to avian biota from aquatic environments.

Previously we reported changes in the reproductive success of the same tree swallows used in this study, in relation to multiple stressors including their exposure to PBDEs, HBCDD, and other persistent organic pollutants, concluding that there was some influence of the PBDEs available in the WWTP outflows on early reproductive parameters but not reproductive output (Gilchrist et al., 2014). The aim of the current study was to enhance our understanding of the tree swallows' exposure to PBDEs by evaluating the congener patterns of the legacy PBDEs previously published (Gilchrist et al., 2014) and evaluating the composition of the new HFRs, thereby characterizing the exposure to legacy and new HFRs of insectivorous swallows as represented by their eggs, and source associations with WWTP effluent at nesting sites as compared to a reference site in a heavily populated region (southern Ontario, Canada).

2. Materials and methods

2.1. Study sites

This study was conducted and approved in accordance with the guidelines from the Canadian Council of Animal Care, and all necessary municipal, provincial and federal permits were obtained annually. Breeding populations of tree swallows were monitored at sites in southern Ontario, Canada, between March and July from 2007 to 2010. A total of 49 nest boxes were established adjacent to the reservoir at the reference site, Mountsberg Conservation Area, established in 1964 (Fig. 1). Another 27 nest boxes were also situated around the sewage lagoons of WWTP1, that at the time of this study was based on secondary treatment processes, and continues to serve Kitchener, Ontario, Canada (population: 250,000). An additional 71 nest boxes were located within 800 m immediately downstream of the effluent discharge pipe of the tertiary treatment plant, WWTP2, servicing Hamilton, Ontario, Canada (population: 500,000). All three sites were approximately 40 km equi-distant apart.

2.2. Egg collections

As well as the objectives of the current study, the objectives of the overall study included assessments of the growth and thyroid function of the nestling swallows (Fernie, unpublished data). Consequently, only one of the first three eggs laid within each clutch was collected for chemical analysis. The eggs were collected prior to clutch completion in order to minimize embryonic development and taken from first laid clutches only. By using one of the first 3 eggs laid in each first clutch, variations in lipid concentrations and hence contaminant concentrations were minimized since evidence suggests the occurrence of intra-clutch variation in lipids, PCBs, and elements, for tree swallows (Custer et al., 2010). We assumed inter-clutch variation in lipid and contaminant concentrations to be low. This is supported by studies in Great tits (*Parus major*), another passerine that lays large clutches of eggs like tree swallows; sum ($\sum$) PBDE concentrations varied only 3% within their first clutches regardless of laying order (Van den Steen et al., 2009a) compared to the 97% variation among-clutches (Van den Steen et al., 2006), and were significantly lower in their replacement clutches (Van den Steen et al., 2009a).

2.3. Chemical analysis

The preparation and chemical analysis of the tree swallow eggs has been fully described in Gilchrist et al. (2014). The analysis of BDE-183, total HBCDD, and BDE-209 and its metabolites, were restricted to the eggs collected in 2009 and 2010 only. Briefly, the contents of each egg was homogenized and stored in a chemically clean jar