Environmental Pollution 193 (2014) 254–261

Contents lists available at ScienceDirect

Environmental Pollution

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

Organophosphate flame retardants and organosiloxanes in predatory freshwater fish from locations across Canada

Daryl J. McGoldrick [a, *], Robert J. Letcher [b], Enzo Barresi [a], Michael J. Keir [a], Jeff Small [a], Mandi G. Clark [a], Ed Sverko [a], Sean M. Backus [a]

[a] *Water Science and Technology Directorate, Environment Canada, Burlington, ON, L7R 4A6, Canada*
[b] *Ecotoxicology and Wildlife Health Division, Science and Technology Branch, Environment Canada, National Wildlife Research Centre, Carleton University, Ottawa, ON, K1A 0H3, Canada*

ARTICLE INFO

Article history:
Received 5 May 2014
Received in revised form
20 June 2014
Accepted 23 June 2014
Available online 24 July 2014

Keywords:
Lake Trout
Walleye
Canadian locations
Organophosphate flame retardants
Organosiloxanes

ABSTRACT

Whole body homogenates of Lake Trout (*Salvelinus namaycush*) or Walleye (*Sander vitreus*) collected from Canadian lakes were screened for organophosphate flame retardant (OPFR) and organosiloxane compounds. Six OPFR and five siloxane compounds were detected above quantitation limits in at least one individual fish from sampled lakes. The OPFRs, tris(2-chloroethyl) phosphate (TCEP) and tris(2-butoxyethyl) phosphate (TBOEP), were most frequently quantified with concentrations ranging from <0.07 to 9.8 ng/g (ww). Levels of TBOEP were highest in fish from the Great Lakes region while TCEP was detected only in fish from the northernmost lakes in our network. Concentrations of the cyclic siloxanes, octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6), were above quantitation limits in all fish. D5 was the most abundant siloxane across all sampling locations with the highest concentrations (45–719 ng/g ww) observed in Lake Trout from the western end of Lake Ontario near the mouth of the Niagara River.

1. Introduction

Organophosphate flame retardants (OPFRs) are high production volume chemicals, in use since the 1970s, that are added to plastics, foams, textiles, floor polishes, waxes and furniture (Marklund et al., 2005; Reemtsma et al., 2008; Bergh et al., 2011). In recent years, it has been suggested that the production and use of certain OPFRs are increasing, and coincident with the regulation and phase-out of many brominated flame retardant substances (Reemtsma et al., 2008). Salamova et al. (Salamova et al., 2014) very recently reported the levels of 12 OPFRs in particle phase samples collected in the Great Lakes basin. Tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCIPP) and, tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) were the dominant components ΣOPFR which found at concentrations 2 to 3 orders of magnitude higher than other brominated flame retardants in similar samples. OPFRs enter waste water streams readily as they are not chemically bonded to the materials to which they are added to hinder the ignition of fire and are water soluble (Bester, 2007). Four OPFRs: TCEP, TCIPP, TDCIPP, and tris(2-butoxyethyl) phosphate (TBOEP) are routinely detected in rainfall and snow (Regnery and Puttmann, 2009) as well as waste water treatment plant influents and effluents (Meyer and Bester, 2004; Rodil et al., 2005).

Relatively few studies have investigated OPFRs in biota and particularly in fish and wildlife. Ma et al. (2013) very recently reported OPFR concentrations in muscle tissue of domestic chickens (*Gallus gallus domesticus*) and ducks (*Anas platyrhynchos domesticus*). Tri-n-butyl phosphate (TNBP), TCEP, TBOEP, and triphenyl phosphate (TPHP) were present at highest concentrations (up to 281 ng/g lipid weight; ~14 ng/g wet weight). Chen et al. (2012) also showed that of 12 OPFRs analyzed for, 5 were frequently quantifiable (including TPHP and TDCIPP) in individual herring gull eggs (*Larus argentatus*) collected from Lake Huron, and where TCIPP (0.21–4.1 ng/g ww), TCEP (0.02–0.55 ng/g ww), and TBOEP (0.16–2.2 ng/g ww) were most concentrated of all OPFRs detected. Among five colony sites in the Laurentian Great Lakes, of the same 12 OPFRs analyzed for, Letcher et al. (2011) reported the detection of TBOEP, TPHP, TCIPP and TCEP, with ΣOPFR concentrations ranging among the five sites from 2.02 ng/g ww (Chantry Island, Lake Huron) to 6.69 ng/g ww (Agawa Rock, Lake Superior) in 2010-collected egg pools. Greaves and Letcher (Greaves and Letcher, in press) very recently reported on the concentrations and

* Corresponding author.
E-mail address: daryl.mcgoldrick@ec.gc.ca (D.J. McGoldrick).

http://dx.doi.org/10.1016/j.envpol.2014.06.024
0269-7491/

distribution of 16 OPFR triesters in eight tissues from female herring gulls (*Larus argentatus*) and their entire clutches of eggs.

Organosiloxanes are also high production volume chemicals and are common components of many personal care products, cosmetics, as well as many other materials such as dry cleaning solvents, industrial cleaning fluids (Environment Canada and Health Canada, 2008a,b,c; Horii and Kannan, 2008; Wang et al., 2009). Due to the usage patterns and physiochemical properties of organosiloxane materials, the majority of releases to the environment are through solid and water waste streams where they are volatilized to the atmosphere or adsorbed to aquatic sediments (Wang et al., 2013a,b). Cyclic [hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6)] and/or linear [hexamethyldisiloxane (MM), octamethyltrisiloxane (MDM), decamethyltetrasiloxane (MD2M), and dodecamethylpentasiloxane (MD3M)] siloxanes have been detected in many different media such as, sewage and landfill biogas (Oshita et al., 2010; Rasi et al., 2010), waste water influents and effluents (Wang et al., 2013a,b; Bletsou et al., 2013), air (McLachlan et al., 2010; Genualdi et al., 2011), and biota (Kaj et al., 2005; Schlabach et al., 2007; Borgå et al., 2012; Kierkegaard et al., 2013). Where detected, linear siloxanes are found at lower concentrations than cyclic siloxanes and in aquatic biota linear siloxanes have only been detected in cod livers (Kaj et al., 2005; Schlabach et al., 2007; Zhang et al., 2011).

OPFRs and siloxanes are both produced in large volumes, share release pathways to the environment and, due to their physiochemical properties, some compounds within these chemical classes have been the subject of screening assessments by government regulatory agencies in several countries. Among the siloxanes D4, D5, D6, MD3M, and M4Q are identified are listed as “Top 10 priority siloxanes” by Howard and Muir (Howard and Muir, 2010) due to their potential for environmental persistence and bioaccumulation. The OPFRs, TCEP and TCIPP, are persistent environmental contaminants, suspected carcinogens and ubiquitous aquatic contaminants (Bester, 2007; Regnery and Puttmann, 2010; Bergh et al., 2011).

Environment Canada conducts routine monitoring and surveillance for priority contaminants in tissues of freshwater fish in water bodies across Canada in part to provide data to assess environmental risk and/or the effectiveness of risk management actions (Environment Canada, 2011). Whole body homogenates of predatory fish collected from select water bodies across Canada were selected for screening of OPFRs and organosiloxanes to determine the current status of environmental contamination and target future monitoring and surveillance activities.

2. Methods

2.1. Fish collection

Fish were collected from 16 water bodies across Canada (Fig. 1; Table S1). The water bodies consist of lakes, rivers, and reservoirs that are part of a network of stations routinely monitored by Environment Canada's National Fish Contaminants Monitoring and Surveillance Program (FCMSP) (Environment Canada, 2011). The water bodies range from remote northern lakes with minimal human influence (ex. Kusawa Lake) to lakes in heavily populated areas with intense agricultural and industrial activities (ex. Lake Ontario). Fish were captured using bottom set gill nets in 2009 or 2010 between June and October with the exception of fish from Lake Athabasca and Cold Lake which were collected through the ice in December. Lake trout (*Salvelinus namaycush*) are the preferred biomonitor in the FCMSP and were the most common species collected across the monitoring network; however, at locations where Lake Trout are not present, Walleye (*Sander vitreus*) were collected instead (Table S1). Lake Trout and Walleye are piscivorous species that generally occupy the uppermost trophic levels of the water bodies where they are found.

Fig. 1. Map of Canada showing the water bodies where fish were collected for this study.