Environmental Pollution 206 (2015) 306–314

Contents lists available at ScienceDirect

Environmental Pollution

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

Hexabromocyclododecane affects benthic-pelagic coupling in an experimental ecosystem

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ARTICLE INFO

Article history:
Received 3 May 2015
Received in revised form
9 July 2015
Accepted 12 July 2015
Available online 25 July 2015

Keywords:
HBCDD
Brominated flame retardants
Mesocosm study
Structural equation modelling
Baltic sea
Indirect ecosystem effects

ABSTRACT

Hexabromocyclododecane (HBCDD) is an additive brominated flame retardant and a recognized PBT chemical. However, little is known about its effects on coastal species, and even less on ecosystem effects. We investigated the dose–response effects of HBCDD over 8 months in 1000 L experimental mesocosms assembled from coastal Baltic Sea ecosystem components. HBCDD was added via spiked plankton material and a range of structural and functional endpoints were measured during the experiment. Increasing HBCDD concentration decreased the biomass of large *Macoma balthica*, resulting in a decreased recirculation of nutrients to the water. Changes in plankton communities were also observed, either due to direct toxic HBCDD effects or indirect via changes in benthic-pelagic coupling of nutrients. Such complex ecosystem responses can only be quantified and understood by using realistic experimental set-ups, and including knowledge of system-specific ecological interactions. This is the first study of HBCDD effects on ecosystem level.

1. Introduction

Hexabromocyclododecane is one of the most widely used brominated flame retardants. The estimated global production of HBCDD in 2011 was 31,000 tonnes (UNEP, 2012). It is used mainly as an additive in polystyrene foam produced for use as construction material but also in polymer dispersion for textiles and electronic appliances (mainly as an additive to high impact polystyrene) (ECHA, 2009). HBCDD is considered persistent, bioaccumulative and toxic, and was added to the Annex XIV list of the European Union Regulation REACH in 2011. In 2013 HBCDD was added to Annex A of the Stockholm Convention, with exemption for its main use (building insulation material) until 26 November 2019. HBCDD is thereby regulated by both EU and the contracting parties of the Stockholm Convention. In the United States, which has not yet ratified the Stockholm Convention, the Environmental Protection Agency has tried to steer industry towards the use of alternative compounds through stakeholder discussions (US EPA, 2014). It is difficult to estimate progress as US HBCDD production amounts are classified. However, future production is expected to decrease globally, even though US production decreases may take longer time.

As HBCDD is an additive flame retardant (i.e. not chemically bound in the matrix), with time it moves out of the matrix into the environment. According to a substance-flow analysis, diffuse release from construction materials account for the majority of HBCDD emissions (Morf et al., 2008). Approximately half of all emissions were estimated to consist of diffuse atmospheric emissions from installed insulation boards in buildings (Morf et al., 2008). As the global regulation of HBCDD use in building

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http://dx.doi.org/10.1016/j.envpol.2015.07.012
0269-7491/

insulation material will be under time-limited exemption until 2019, global emissions of newly produced HBCDD will continue. Although emissions will likely decrease over time as industry has started the transition to the use of alternative compounds, previously installed HBCDD containing insulation will continue emissions. Waste is also an important source of HBCDD (Eguchi et al., 2013; Zhang et al., 2009), and will continue to be important for years as HBCDD-containing products remain in product cycles. In addition, unregulated use has also been observed (Rani et al., 2014), with high concentrations of HBCDD found in food packages and aquaculture buoys.

HBCDD has a cyclic ring structure and the molecular formula is $C_{12}H_{18}Br_6$. The technical product comprises mainly three pairs of enantiomers, α- β- and γ-HBCDD (Heeb et al., 2005). The three isomers have different properties such as water solubility (48.8–2.1 $\mu g\ L^{-1}$), environmental persistence (half-lives varying from 44 days to infinite (no degradation detected during 112 days incubation), depending on isomer and test setting) and log Kow (5.07–5.47) (ECHA, 2008).

The physicochemical properties of HBCDD explain why it mainly partitions to sediment and particulate matter in the aquatic environment and that it accumulates in lipids and biomagnifies in aquatic food webs (Wu et al., 2010; Law et al., 2006; Sørmo et al., 2006; Tomy et al., 2004). These physiochemical properties indicate that lipid or particle-bound HBCDD is a major pathway for HBCDD to enter aquatic food-webs via e.g. accumulation in plankton (Poma et al., 2014). The highest concentrations of HBCDD in wildlife are generally found in species with a high trophic level position such as predatory birds, seals and cetaceans (Sellström et al., 2003; Hoguet et al., 2013; de Wit et al., 2006), implying that biomagnification occurs in natural food-webs. There is also evidence that long-range atmospheric transport occurs as HBCDD has been detected in remote areas such as the Tibetan Plateau (Zhu et al., 2013) and the Arctic (de Wit et al., 2006; Dietz et al., 2013).

The Baltic Sea is one of the world's most polluted seas and HBCDD is commonly found its environmental compartments. A retrospectively analysed time series of HBCDD concentrations dating back to 1968 show a clear increase in guillemot (*Uria aalge*) eggs during the first decades, with a deceasing trend for the last ten years (Swedish Museum of Natural History (2014)). This is similar to the development in other environments after decreases in use (Johansson et al., 2011; Law et al., 2008). However, concentrations in Baltic Sea blue mussel (*Mytilus edulis* × *Mytilus trossulus*) and herring (*Clupea harengus*) muscle have been relatively stable since monitoring began in 2000 and concentrations in cod (*Gadus morhua*) liver are still increasing annually with about 6%. Global environmental time trends for HBCDD are mixed, with both evident increases and decreases in different matrices and regions (Law et al., 2014).

Reviews of the toxicity of HBCDD have been performed both during its EU Risk Assessment (ECHA, 2008) and by the POPs Review Committee of the Stockholm Convention (UNEP, 2010). HBCDD has been classified as very toxic to aquatic life with long-lasting effects (Aquatic Acute 1 and Aquatic Chronic 1) according to the EU Classification, labelling and packaging Regulation (ECHA, 2014). HBCDD has in vertebrates also been found to potentially affect liver function as well as thyroid gland and thyroid hormone homeostasis (ECHA, 2008). In the bivalve Baltic tellin (*Macoma balthica*) it has been shown to have a genotoxic potential and increases cell death (Smolarz and Berger, 2009). Little is known about HBCDD toxic effects on natural communities, and to the authors' best knowledge no published studies have previously examined direct or indirect effects on community or ecosystem level.

The use of mesocosms in ecotoxicology is well-established and mesocosms are often used in refined risk assessments, especially of pesticides, in order to increase the ecological relevance and reduce uncertainties in the necessary extrapolation from laboratory standard tests to field conditions (Clements and Newman, 2002). Mesocosms allow the simultaneous testing of toxicological effects on several species and communities, including indirect effects caused by e.g. modified predator-prey or competition relationships.

The aim of this study was to investigate potential direct and indirect effects of hexabromocyclododecane (HBCDD) on a coastal aquatic ecosystem at near natural conditions using an ecologically realistic exposure scenario. In the 8-month long (three seasons) study, mesocosms containing typical Baltic Sea organisms were exposed to a HBCDD gradient by applying a scenario of a contaminated plankton bloom.

2. Materials and methods

2.1. Experimental design

The experiment consisted of twelve mesocosms (1000 L each), which were exposed to a concentration gradient of HBCDD by addition of spiked plankton. Three control replicates only received unspiked plankton. The experiment was run for 8 months between October 2008 and May 2009.

2.2. Spiking of plankton material

A plankton sample was collected 13 weeks prior to the start of the experiment near the Stockholm University Askö Laboratory, (N 58.823°, E 17.637°), using a 90 μm mesh size plankton net. The sample mainly contained phytoplankton and was frozen until twelve days prior to the start of the experiment, when it was thawed out and thoroughly mixed. Four flasks of plankton material were prepared containing ‘high’, ‘medium’, ’low’ and no HBCDD. Technical HBCDD (99.5%, ICL-IP, Israel) was dissolved in a known volume of acetone and added to the first three plankton suspensions to obtain nominal concentrations of 68, 8.5 and 1.1 mg HBCDD gdw^{-1} (83.95, 10.76 and 1.31 mg g TOC^{-1}). The same volume of acetone was added to the fourth ([solvent] control) flask. To evaporate the acetone, suspensions were kept with continuous stirring in darkness at 4 °C for 12 days. Finally, to achieve nine plankton suspensions with a gradient of HBCDD concentrations, the control suspension was mixed in nine batches with the three suspensions containing HBCDD to achieve concentrations that, when added, would result in the following nominal amounts of HBCDD per mesocosm: 1.3, 2.7, 5.3, 10.6, 21.3, 42.5, 85, 170, 340 mg. Suspensions were prepared in such a way that each mesocosm (including the three controls) received the same volume of plankton suspension, (500 ml, 5 g dw, 4 g TOC).

2.3. Collection of sediment and organisms

Sediment and organisms were collected during the period 1 September to 2 October 2008. Surface sediment (mud according to Folk's ternary diagram) was collected at a water depth of 5 m (N 58.849°, E 17.537°) using a benthic sledge. Human population density in the area is very low and the sediment is fairly uncontaminated (Sundelin and Eriksson, 2001). The sediment was sieved to remove macrofauna >5 mm. No additional water was added during sieving in order to reduce changes in biogeochemical conditions.

Bivalves (*M. balthica* and *Cerastoderma glaucum*) were collected at 0.5 m water depth using a shovel and sieve. *Fucus vesiculosus*, and its associated fauna (*Idotea* spp.), was collected from shallow (0–0.5 m) hard bottoms using rakes. Soft bottom benthic angiosperms (*Stuckenia pectinata*, *Ruppia cf. cirrhosa*, and *Zannichellia*