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Research article

Polychlorinated biphenyls (PCBs), hexabromocyclododecanes (HBCDDs) and degradation products in topsoil from Australia and the United Kingdom

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ABSTRACT

Hexabromocyclododecane (HBCDD) is listed under the Stockholm Convention on persistent organic pollutants, yet very few data are available on HBCDD concentrations in soil. Median concentrations of total hexabromocyclododecanes (ΣHBCDDs) from soils from the UK (n = 24) were 0.73 ng g^{-1} dry weight (range <0.01–430 ng g^{-1}) and exceed significantly (p = 0.002) those in Australian soils (n = 17, median = 0.10 ng g^{-1}, range <0.0002–5.6 ng g^{-1}). Concentrations of polychlorinated biphenyls (PCBs) (average = 4.7 ng ΣPCBs g^{-1}, range = 0.39–21 ng g^{-1}) were determined in 19 UK samples and found to be statistically indistinguishable (p > 0.05) from those of HBCDDs; thereby underlining the extent to which HBCDDs have migrated into the UK environment. Moreover, PCB concentrations in this study are not markedly lower than those recorded in UK soils sampled in the mid-1980s indicating that the initial rapid decline in UK contamination with PCBs following bans on their manufacture and use, has not been maintained. Degradation products of HBCDD: pentabromocyclododecenes (PBCDs) and tetrabromocyclododecadienes (TBCDs) were detected in some UK soil samples with semi-quantitative concentrations ranging between 0.01 and 7.3 ng g^{-1} for ΣPBCDs and 0.01–1.3 ng g^{-1} for ΣTBCDs. In Australian soils only ΣTBCDs were detected at concentrations ranging from 0.0023 to 0.45 ng g^{-1}. Chiral signatures of HBCDDs were racemic or non-racemic in all samples indicating minimal edaphic enantioselective degradation. A horizontal transect at the most contaminated UK location (a suburban garden) revealed a marked decrease in concentrations of HBCDDs with increasing distance from buildings.

1. Introduction

Hexabromocyclododecane (HBCDD) was a widely used brominated flame retardant (BFR) with a reported global market demand in 2001 of 16,700 metric tonnes, of which most (9500 t) was produced in Europe [1]. Major applications of HBCDD were as an additive to expanded and extruded polystyrene foams for thermal insulation of buildings and to a lesser degree to high impact polystyrene (HIPS) used in enclosures for electronic equipment such as TVs, along with back-coating of fabrics like sofa covers and curtains [2]. This has raised concerns because of the potential adverse health impacts of HBCDD in laboratory animals. These include: liver and thyroid hormone disruption [3,4] and reproductive disorders [5]. As a consequence of these health concerns, coupled with evidence of its persistence and capacity for bioaccumulation and long range environmental transport; in 2013, HBCDD was listed as a persistent organic pollutant (POP) by the United Nations Environment Programme (UNEP) under Annex A of the Stockholm Convention on POPs [6].

HBCDD was not bound to products chemically (i.e. it is an "additive" flame retardant) and is persistent; this coupled with its extensive use has led to demonstrable contamination of the environment and humans [7,8]. In the UK, HBCDDs have been

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quantified in a variety of matrices including air, lacustrine sediments and water [9,10], but hitherto have not been measured in soils. Although some data on HBCDD concentrations in background soil samples have emerged recently from China [11,12]; within Europe, knowledge of HBCDD contamination of soil is otherwise restricted to locations in the vicinity of industrial activities associated with HBCDD manufacture and use [13–16]. This is an important omission, given the known importance of soil as a sink for other persistent organohalogen compounds such as polychlorinated biphenyls (PCBs) [17].

We have reported previously on the presence of HBCDD degradation products, namely pentabromocyclododecenes (PBCDs) and tetrabromocyclododecadienes (TBCDs) in lacustrine sediments, indoor dust, and human milk [10,18,19]. However, there are no data on these compounds in soil that could help in further understanding the long-term environmental fate of HBCDD. In a similar vein, while enantioselective metabolism of chiral HBCDD diastereomers has been reported in humans, fish and other biota; a recent study reported no enantioselective degradation of HBCDDs in soils from China [13].

Given this background, this study reports concentrations of HBCDDs, PBCDs, and TBCDs, along with chiral signatures of HBCDDs in samples of topsoil from both the UK and Australia. To our knowledge, this study provides the first information on the presence of HBCDDs and its degradation products in Australia and the first data worldwide on HBCDD degradation products in soil. These two countries provide an opportunity to examine the extent of environmental contamination and environmental fate of HBCDD in two geographically and climatically distinct regions. Moreover, we hypothesised that the greater use of HBCDD in Europe than elsewhere, would be reflected in higher concentrations in UK than Australian soils. This study also compares HBCDD contamination of UK soils with concentrations of PCBs to provide a "benchmark" for the extent to which HBCDDs have migrated into the environment. Moreover, while PCBs are often viewed as a "legacy" contaminant following the cessation of their manufacture in the UK in the late 1970s, recent data suggests a slowing rate of decline in environmental contamination as a result of continuing emissions from buildings [20].

2. Methods and materials

2.1. Sampling strategy

Soil samples from the UK were taken to 5 cm depth at 24 different locations from a range of rural, suburban, and urban locations. At each location, three sub-samples were taken within a 1 m^2 area. These were combined and homogenised for analysis. Most samples ($n = 20$) were taken in 2005, with the remainder taken in 2008 ($n = 2$), 2009, and 2010 ($n = 1$ in each year). In all cases samples were transferred immediately in the field to hexane-rinsed amber glass bottles, prior to transport to the University of Birmingham, where they were stored in the dark at 4 °C until analysis. PCBs were analysed in 19 samples in 2005, while HBCDDs were determined in all samples in 2008 and 2009.

Additional samples ($n = 4$) were taken from a suburban garden in West London where analysis of the initial sample revealed elevated levels of HBCDDs. Samples were taken in April 2010 at increasing distances from the house at approximately 3, 5, 7 and 12 m in a 14 m length garden. These samples were analysed for HBCDDs only.

The Australian soils were collected as part of the National Dioxin Program between 2002 and 2003 [21]. The samples were taken from industrial, urban, agricultural and remote locations across Australia. In this study, samples from 17 locations were selected for analysis. They were collected from the top 10 cm using aluminium tubes from 3 subsampling sites which were combined to form a composite sample. This was sealed in aluminium foil and freeze dried prior to storage. Australian samples were analysed for HBCDDs and degradation products only.

2.2. Analytical procedures for PCBs

Analysis of UK soil samples for PCBs was conducted in accordance with previously published methodology [20,22]. In summary, samples (50 g accurately weighed) were mixed with an equal mass of pre-extracted anhydrous Na_2SO_4 and 5 g Cu powder and treated with 10 ng of internal standards (PCBs 34, 62, 119, 131, and 173), prior to Soxhlet extraction for 16 h with dichloromethane. Concentrated crude extracts were eluted through a Florisil column (5 g) with dichloromethane (50 mL). Following concentration with solvent exchange to hexane, concentrates were washed with an equal volume of concentrated H_2SO_4, prior to further Florisil chromatography (1 g, eluted with 20 mL hexane), and lipid removal via solvent exchange between dimethyl sulfoxide and hexane. Final purification to remove residual sulfur was effected via elution through a Florisil column combined with 1 g of $AgNO_3$-impregnated aluminium oxide with hexane. After concentration and solvent exchange to nonane, GC/MS analysis was conducted on a Fisons MD-800 instrument fitted with a Varian Factor 4 VF-5ms column (60 m × 0.25 mm i.d., 0.25 μm film thickness). ΣPCB concentrations reported here are the sum of the 84 individual tri- through heptachlorinated PCBs monitored (the full list is available as Supplementary Data along with information on method accuracy, precision, and detection limits).

2.3. Analytical procedures for HBCDDs

For UK soils, all analysis was conducted at the University of Birmingham. For Australian soils, sample spiking and extraction was conducted at the University of Queensland using the same HBCDD internal standards as for UK soils. Following extraction, the crude extracts of the Australian soil samples were concentrated to 1 mL and shipped to the University of Birmingham where sample purification and analysis was conducted as for UK soils.

2.4. Sample extraction and extract purification

For UK soils approximately 50 g of soil was weighed accurately into a clean glass beaker and mixed with 50 g of pre-extracted anhydrous sodium sulfate and 5 g copper powder. More sodium sulfate was added if the sample was particularly wet. The soil was then transferred to a pre-cleaned soxhlet thimble (Whatman 41 mm id, 123 mm length), spiked with 10 ng of ^{13}C α-, β-, and γ-HBCDDs as internal (or surrogate) standards, and extracted with acetone:hexane (60:40, v/v) in soxhlet apparatus for 8 h. The acetone was removed by shaking with 2 × 50 mL of distilled water, the lower aqueous phase was discarded to waste and the hexane layer retained.

For the Australian soils approximately 100 g (accurately weighed) of each sample was treated with 10 ng of ^{13}C α-, β- and γ-HBCDDs and extracted using pressurized liquid extraction (ASE 300, Dionex). Extraction conditions were: temperature 50 °C, pressure 1500 psi, heat time 5 min, static time 5 min, flush volume 50%, purge time 60 s, static cycles 3, the solvent used was hexane:dichloromethane (40:60, v/v).

Crude sample extracts were reduced using a Turbovap sample concentrator to approximately 0.5 mL, prior to transfer to a pre-cleaned column containing 50 g of acid silica topped with 1 g sodium sulfate and 3 g of copper powder and eluted with 100 mL hexane:DCM (50:50, v/v). The eluate was concentrated in a Turbovap tube to 0.5 mL in hexane, and transferred to a finger vial with washes of 3 × 0.5 mL of hexane and 2 mL of sulfuric acid added. This