

Sources and Significance of Human Dietary Exposure to “Novel” Brominated Flame Retardants

Supervisor: Prof. Stuart Harrad, School of Geography, Earth & Environmental Sciences, University of Birmingham (for more information and/or to apply contact S.J.Harrad@bham.ac.uk)

Abstract

Recent years have seen mounting concerns about the presence of brominated flame retardant (BFR) chemicals in the environment, their impacts on human and wildlife exposure and the consequent risks for health. These concerns have led to restrictions within the EU (and elsewhere) on the manufacture and new use of some of these chemicals (the polybrominated diphenyl ethers - PBDEs). As a result of these restrictions, it is hypothesised that there has been an increased demand for alternative (or novel) BFRs (NBFRs) to meet flammability standards. The project will test the hypothesis that recent and potential future regulatory controls placed on the manufacture and use of BFRs like PBDEs have – in the absence of accompanying relaxations of UK flame retardancy regulations - led to increased use of NBFRs, and that these chemicals have migrated into the environment and the UK diet. *Objective 1* is to assess UK dietary exposure to NBFRs and place it in context against: (a) existing assessments of exposure via other pathways, and (b) provide a benchmark against which the health impacts of and future trends in such exposure may be gauged. *Objective 2* is to identify which foodstuffs contribute most to dietary exposure. *Objective 3* is to elucidate the contribution of dietary exposure to UK human body burdens of NBFRs. This information will inform action to minimise exposure. To test our hypothesis, we propose an experimental programme to measure NBFRs in a variety of foodstuffs consumed in the UK. Combined with knowledge of consumption rates of such foodstuffs this will provide an assessment of dietary exposure and the relative contribution of different components. Our estimate of dietary exposure will be interpreted alongside measurements of body burden via analysis of human milk using pharmacokinetic modelling to indicate the influence of dietary exposure on body burden.

Introduction. Recent years have seen mounting concerns about the presence of brominated flame retardant (BFR) chemicals in the environment, their impacts on human and wildlife exposure and the consequent risks for health. These concerns have led to restrictions within the EU (and elsewhere) on the manufacture and new use of some of these chemicals (e.g. the polybrominated diphenyl ethers - PBDEs). As a result of these restrictions, it is hypothesised that there has been an increased demand for alternative (or novel) FRs to meet flammability standards. Precise estimates of production of these “novel” BFRs (NBFRs) are not yet available, but one study cited in (1) has put annual global production of NBFRs in the mid-2000s to amount to ~100,000 t. Despite their widespread usage to flame-retard consumer goods and materials like electronics and fabrics, as well as building materials like wall insulation; there is to date comparatively little known about whether and to what extent these chemicals have migrated into the environment. Of particular concern is that such chemicals are – due to their hydrophobicity and environmental persistence – capable of accumulation in the food chain, leading to contamination of the human diet.

Aims. The project tests the hypothesis that recent and potential regulatory controls placed on PBDEs and HBCD have increased use of NBFRs, leading to their migration into the environment, where they bioaccumulate and enter the diet to the extent that it constitutes the major pathway of exposure to NBFRs. *Objective 1* is to assess UK dietary exposure to NBFRs and place it in context against: (a) existing assessments of exposure via other pathways (2), and (b) provide a benchmark against which the health impacts of and future trends in such exposure may be gauged. *Objective 2* is to identify which foodstuffs contribute most to dietary exposure. *Objective 3* is to elucidate the contribution of dietary exposure to UK human body burdens of NBFRs. This information will inform action to minimise exposure. To test our hypothesis, we propose an experimental programme to measure NBFRs in a variety of foodstuffs consumed in the UK. Combined with knowledge of consumption rates of such foodstuffs this will provide an assessment of dietary exposure and the relative contribution of different components. Our estimate of dietary exposure will be interpreted alongside measurements of body burden via analysis of human milk using pharmacokinetic modelling to indicate the

influence of dietary exposure on body burden, as conducted successfully for HBCDs and TBBP-A (3).

Methods. The student will learn, optimise, and apply analytical methods to determine concentrations of emerging BFRs in UK diet samples provided by our collaborators at the UK's Food Standards Agency (FSA). These samples will reflect current exposure, but if possible, we will also measure NBFrs in food samples archived by the FSA, thereby elucidating recent temporal trends in dietary exposure in response to the changing regulatory landscape. The student will also measure NBFrs in human milk samples (n=30) archived at Birmingham. This component of the project will allow our estimate of dietary exposure to be interpreted alongside measurements of body burden indicated by human milk using pharmacokinetic modelling to indicate the influence of dietary exposure on body burden, as conducted successfully for HBCDs and TBBP-A (2). At the outset, we will target a number of NBFrs selected on the basis of their production volume and known presence in UK indoor dust samples (3); but this list will be amended during the course of the project as and when relevant new information emerges. Our initial list comprises: decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), tetrabromobisphenol A-bis(2,3 dibromopropylether) (TBBPA-DBPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), and bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH). The analytical methods are likely to be based on GC-MS as these have been applied successfully to dust samples (2), but LC/MS-MS will be evaluated where it is suspected to offer advantages.

Training. While previous experience of trace analytical chemistry (e.g. GC/MS) would be an advantage, training will be provided in the laboratory techniques required, and potential applicants without such experience should not be deterred from applying. The student will join the internationally-respected Persistent Organic Pollutants (POPs) Research Group. Currently, the group co-ordinates the major EU-funded Marie Curie Initial Training Network INFLAME on issues related to the sources, exposure and effects of flame retardant chemicals in the environment (www.birmingham.ac.uk/inflame). The POPs group encourages international collaboration strongly (several group members have spent time working in overseas labs in recent years), and it is envisaged that such research visits will be possible within this project. In particular, we have a long-standing and fruitful collaboration with the University of Antwerp with whom we are working actively in this area. Moreover, we also co-ordinate the EU-funded International Research Staff Exchange project INTERFLAME, within which doctoral researchers from the POPs group have the opportunity to undergo secondments to partners in Australia, Canada, China, Egypt, and Japan.

Selected References.

1. Covaci, A., Harrad, S. et al *Environment International* 37, 532–556 (2011).
2. Ali, N., Harrad, S. et al *Chemosphere*, 83, 1360–1365 (2011).
3. Abdallah, M., Harrad, S. *Environment International*, 37, 443–448 (2011).