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# Detection of novel brominated flame retardants (NBFRs) in the urban soils of Melbourne, Australia

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ABSTRACT

A range of brominated flame retardants (BFRs) have been incorporated into polymeric materials like plastics, electronic equipment, foams and textiles to prevent fires. The most common of these, polybrominated diphenyl ethers (PBDEs), have been subject to legislated bans and voluntary withdrawal by manufacturers in North America, Europe and Australia over the past decade due to long-range atmospheric transport, persistence in the environment, and toxicity. Evidence has shown that replacement novel brominated flame retardants (NBFRs) are released to the environment by the same mechanisms as PBDEs and share similar hazardous properties. The objective of the current research was to characterize soil contamination by NBFRs in the urban soils of Melbourne, Australia. A variety of industrial and non-industrial land-uses were investigated with the secondary objective of determining likely point sources of pollution. Six NBFRs; pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and decabromodiphenyl ethane (DBDPE) were measured in 30 soil samples using selective pressurized liquid extraction (S-PLE) and gas chromatography coupled to triple quadrupole mass spectrometry (GC-MS/MS). NBFRs were detected in 24/30 soil samples with $\Sigma_5$NBFR concentrations ranging from nd-385 ng/g dw. HBB was the most frequently detected compound (14/30), while the highest concentrations were observed for DBDPE, followed by BTBPE. Electronic waste recycling and polymer manufacturing appear to be key contributors to NBFR soil contamination in the city of Melbourne. A significant positive correlation between $\Sigma_8$PBDEs and $\Sigma_5$NBFR soil concentrations was observed at waste disposal sites to suggest that both BFR classes are present in Melbourne's waste streams, while no association was determined among manufacturing sites. This research provides the first account of NBFRs in Australian soils and indicates that these emerging contaminants possess a similar potential to contaminate Melbourne soils as PBDEs.



## 1. Introduction

A range of brominated flame retardants (BFRs) have been incorporated into plastics, electronic equipment, foams and textiles to prevent fires [1,2]. The most common of these, polybrominated diphenyl ethers (PBDEs), have come under a great deal of scientific and regulatory scrutiny due to long-range atmospheric transport, persistence in the environment and evidence of bioaccumulation in humans and wildlife [3,4]. Toxicological reports have described a range of adverse effects in humans and animals exposed to PBDEs, including endocrine disruption and neurodevelopmental toxicity [5,6]. In light of environmental and health hazards, PBDEs have been subject to legislated bans and voluntary withdrawal by manufacturers in North America [7,8], Europe [9,10] and Australia [11] over the past decade. Commercial PBDE formulations Penta-BDE and Octa-BDE were listed as United Nations Persistent Organic Pollutants (POPs) under the Stockholm Convention of 2009 [12], while registration of the remaining product, Deca-BDE, has been officially proposed [13]. Restriction and regulation of PBDEs, however, has driven a rise in manufacture and use of replacement products, known as “novel” brominated flame retardants (NBFRs). Many of the compounds described as “novel” have been in

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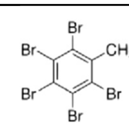
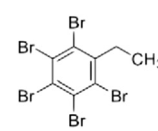
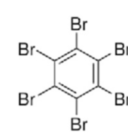
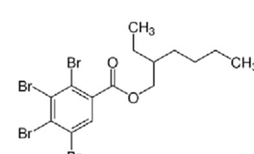
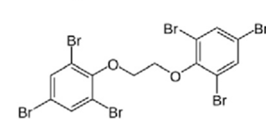
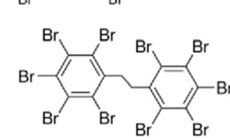
production for decades, but have only been recognized as significant environmental contaminants recently, since replacing PBDEs in a range of products. Most NBFRs have comparable vapour pressures and log $K_{OW}$ values to PBDEs and are, likewise, not chemically bound within polymers [2]. Consequently, research has shown that NBFRs are likely to be released to the environment by the same mechanisms as PBDEs and share a similar fate as persistent pollutants in air, soil and sediments [14–17]. Industries involved in the manufacture or disposal of flame retarded goods are expected to be key emission sources [18–21]. Many NBFRs also exhibit analogous bioaccumulation potential and toxicity to PBDEs [22]. Experimental evidence has identified hazards of NBFRs to include endocrine disruption of the thyroid and reproductive systems [22], neurotoxicity and genotoxicity [2,23,24].

To date, as many as 75 NBFRs have been manufactured. A subset of these are considered to be priority contaminants due to high production volume, prevalence in the environment and bioaccumulation potential (Table 1) [4,22,25]. Among the most widely utilized of the NBFRs is decabromodiphenylethane (DBDPE), which is marketed as a direct replacement for Deca-BDE commercial mixtures in a range of plastics, resins, rubbers, adhesives and textiles [1,2]. 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) constitutes the main replacement for Octa-BDE mixtures, used mostly in hard plastics while 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) is used in conjunction with other flame retardants in soft polymer materials like polyurethane foams as replacements for Penta-BDE [2,26]. Pentabromotoluene (PBT), pentabromoethylbenzene (PBEB) and hexabromobenzene (HBB) are each used in a wide range of materials such as hard plastics, flexible foams and textiles to meet flammability standards [25].

Although primary production of NBFRs has not taken place in Australia to date, these compounds may be imported in their raw form for incorporation into secondary materials by local manufacturers. Australia's peak chemical regulation body, the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) maintains the Australian Inventory of Chemical Substances (AICS), in which chemicals approved for manufacture or import are listed. BTBPE, PBEB and PBT are currently included in the inventory while BTBPE is the only NBFR to have been reviewed as part of a Priority Existing Chemical (PEC) assessment [27]. The 2001 assessment estimated the import of BTBPE during the years 1998–1999 to be 17 metric t/y, though this number has not been updated in recent years. No domestic import estimates are currently available for any of the other NBFRs analysed in this study. Flame-retarded precursor materials imported to Australia may also contain NBFRs not documented by the AICS [27].

The NBFRs described above have been detected in atmospheric samples from Europe [16], USA [28], Asia [29] and Africa [30] at concentrations similar to and exceeding those of PBDEs. As with PBDEs, evidence suggests that most NBFRs undergo net atmospheric deposition to land [31–33]. NBFR soil levels have rarely been studied, although contamination has been reported in the

**Table 1**
Novel brominated flame retardants (NBFRs) of emerging environmental concern.

| Compound | Abbreviation[a] | Vapour pressure (Pa) (25 °C) | Octanol-water coefficient (log $K_{OW}$) | Chemical structure |
|---|---|---|---|---|
| Pentabromotoluene | PBT | 1.22E-03[c] | 5.87 ± 0.62[c] |  |
| Pentabromoethylbenzene | PBEB | 3.2E-04[c] | 6.40 ± 0.62[c] |  |
| Hexabromobenzene | HBB | 7.5E-04[b]<br>1.14E-04[c] | 5.85 ± 0.67[c] |  |
| 2-Ethylhexyl-2,3,4,5-tetrabromobenzoate | EH-TBB | 6.33E-08 -<br>4.58E-06[d] | 8.72–8.75[d] |  |
| 1,2-Bis(2,4,6-tribromophenoxy)ethane | BTBPE | 3.88E-10[c] | 7.88 ± 0.86[c] |  |
| Decabromodiphenylethane | DBDPE | 6.0E-15[c] | 11.1[c] |  |

[a] Organobromine flame retardant abbreviation standard proposed by Bergman et al. [68].
[b] Tittlemier et al. [69], experimental results.
[c] Covaci et al. [25], from SciFinder Database calculation.
[d] Kuramochi et al. [65], calculation.