



## Review

# Critical review of the analysis of brominated flame retardants and their environmental levels in Africa<sup>☆</sup>



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## HIGHLIGHTS

- Current analytical techniques for BFR analysis in Africa were reviewed.
- BFR levels in the African environment were also reviewed.
- BFRs were ubiquitously present in the African environment.
- There was limited data on alt-BFRs as replacements for banned formulation in Africa.

## ARTICLE INFO

## Article history:

Received 23 May 2016

Received in revised form

15 August 2016

Accepted 21 August 2016

Handling Editor: Myrto Petreas

## Keywords:

Brominated flame retardants

Africa

Environmental levels

Sample preparation

Instrumental analysis

## ABSTRACT

World-wide, the prevalence of brominated flame retardants (BFRs) is well documented for routine analysis of environmental and biological matrices. There is, however, limited information on these compounds in the African environment and insufficient information on the analytical approaches used to obtain data. This paper presents a review on BFR levels in the African environment and the various analytical methodologies specifically applied in Africa for polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls and alternative-BFRs. The analyses include liquid sample preparation using liquid-liquid and solid phase extraction and solid sample preparation involving Soxhlet extraction, with ultrasound-assisted extraction increasingly being applied. Instrumental detection techniques were limited to gas chromatography coupled with electron capture detector and electron impact ionisation with single quadrupole mass spectrometers. Information on congener profile prevalence in indoor dust, soil, aquatic environment (water, sediment, and aquatic organisms), eggs, wastewater treatment plant compartments, landfills (leachate and sediment) and breast milk are presented. Although PBDEs were inconsistently detected, contamination was reported for all investigated matrices in the African environment. The manifestation in remote regions indicates the ubiquitous prevalence and long-range transport of these compounds. Levels in sediment, and breast milk from some African countries were higher than reported for Asia and Europe. Due to limited data or non-detection of alternative-BFRs, it is unclear whether banned formulations were replaced in Africa. Most of the data reported for BFR levels in Africa were obtained in non-African laboratories or in South Africa and formed the basis for our discussion of reported contamination levels and related methodologies.

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<sup>☆</sup> Electronic Supplementary Information (ESI) available: [Table S1](#): Overview and summary of publications on BFRs in Africa.

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## 1. Introduction

Flame retardants (FRs) are frequently applied to combustible materials to reduce their flammability, to delay ignition and to meet fire safety requirements. Brominated flame retardants (BFRs) exhibit a variety of beneficial physicochemical properties that can be favourably applied to combustible materials (e.g., polymers, plastics, wood, paper and textiles) and have been widely used in electronic and electric equipment, furniture, construction materials and other commercial products (Alaee et al., 2003). Depending on the FR characteristics, the physical and chemical combustion processes which involve preheating, volatilization/decomposition, combustion and propagation, can be either delayed or some steps can be prevented in the solid, liquid or gas phase (EHC 192, 1997). The physical actions involve fuel dilution (where large non-combustible gas volumes are released), cooling (where endothermic processes cool the process to below temperatures required to sustain propagation), and charring (where combustible layers are isolated from the fuel source and/or insulated to reduce heat transfer) (EHC 192, 1997). The chemical modes of action involve reactions in the solid phase, through the formation of low thermal conductive surface films (where heat transfer rates are reduced and the formation of char barriers are promoted), and in the gaseous phase through the free radical mechanism where the FR dissociates into radical species that interfere with the flame propagating step (EHC 192, 1997). Halogens have the ability to capture free radicals produced during the combustion process to remove the flames' capability to spread. The capturing efficiency increases with the size of the halogen atom ( $F < Cl < Br < I$ ) (Alaee et al., 2003). Organobromine, organochlorine and organofluorine compounds are commonly used as FRs since iodinated compounds are unstable and decompose to some extent at elevated temperatures (Alaee et al., 2003). Higher trapping efficiency and the ability to deliver halogen radicals at lower temperatures, make organobromines ideal FR candidates (Alaee et al., 2003). Because of their toxic effects and their persistence, the pervasive environmental distribution of BFRs have been a subject of concern over the past decades. The most commonly used BFRs are polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), tetrabromobisphenol-A (TBBPA) and polybrominated biphenyls (PBBs) (Alaee et al., 2003). However, PBB production stopped shortly after the 1973

disaster, where it was accidentally substituted for a non-toxic supplement in cattle feed and distributed to farms in the lower peninsula of Michigan (Carter, 1976).

Conventions and international governmental departments have introduced projects and guidelines to study the production, use and release of BFRs to provide information concerning environmental contamination, to evaluate the significance of the contamination and to assist with regulatory actions (Kemmlin et al., 2003, 2009). Despite these prohibitions, BFR levels continue to be reported in the environment. The stringent regulations on worldwide use of BFRs have resulted in the introduction of alternative-BFRs (alt-BFRs) as replacements for banned formulations. For example, decabromodiphenyl ethane (DBDPE) was introduced as a replacement for deca-BDE, 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) as a replacement for octa-BDE, bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEHTBP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB) as replacement for penta-BDE. Alternative FRs include tetrabromobisphenol A-bis(2,3-dibromopropylether) (TBBPA-DBPE) and hexachlorocyclopentadienyldibromocyclooctane (HCDBCO) (Alaee et al., 2003; Shaw et al., 2014). The HBCD and commercial penta- and octa-PBDE mixtures are restricted under the Stockholm Convention (SC), whereas deca-BDE is on the list of proposed chemicals to be added (<http://chm.pops.int/>).

Numerous overviews on the global levels and trends of BFRs in environmental samples have been published (Alaee et al., 2003; Covaci et al., 2003, 2011; Cruz et al., 2015; de Wit, 2002; de Wit et al., 2010; Law et al., 2014; Toms et al., 2012; Wu et al., 2012). Polder et al. (2008) presented one of the first reports on BFR levels in the African environment, in particular on PBDEs and HBCD in bird eggs from South Africa. Following this report, levels of BFRs were identified in abiotic and biotic environmental samples, collected from South Africa, Nigeria, Tanzania, Ghana, Congo, Egypt, Guinea-Bissau, Senegal, Tunisia, Uganda, Kenya and Ile Cocos, an island in the Indian Ocean (Table S1, Supporting information). Of the fifty papers reviewed here, twenty six of the papers describing BFR analysis were performed in non-African laboratories in Europe, North America and Asia. As stringent global regulations pose potential threats to international trade and industry in developing economies, African laboratories should ensure that the capability to accurately quantify persistent organic pollutants such as BFR's is

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