Critical review of the analysis of brominated flame retardants and their environmental levels in Africa ‡

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‡ Electronic Supplementary Information (ESI) available: Table S1: Overview and summary of publications on BFRs in Africa.

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

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.

Keywords: Brominated flame retardants; Africa; Environmental levels, Sample preparation; Instrumental analysis

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 (Kemmlein *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 committedly developed, established and maintained.

Due to the differences in the physicochemical properties of BFRs and their prevalence in various matrices, a wide variety of analytical approaches for sample preparation have been developed. Recent reviews on analysis methods for BRFs applied worldwide are available in the literature (Covaci *et al*., 2003, 2007, 2011; Dirtu *et al*., 2013; Fulara and Czaplicka, 2012; Król *et al*., 2012; Papachlimitzou *et al*., 2012; Stapleton, 2006; Xu *et al*., 2013) and is not the scope of this paper.

The aim of this paper was to summarise published studies on BFR occurrence in environmental compartments from different African countries to present the current status on BFR levels; and to critically review the chemical analysis performance in Africa to analyse these compounds. In order to provide an overview of the current analytical status for the analysis of BFRs in Africa, twenty-four papers were selected where the procedure for BFR analysis was described and analysis performed in an African laboratory. The following sections summarise the analytical methods used for the determination of BFRs, including sample preparation, instrument detection techniques, general comments from an analytical quality assurance perspective and BFR levels in the African environment.

2. Analytical methods utilized in Africa

2.1. Sample preparation

Sample preparation is an important aspect of the analytical process. The analysis of target BFRs at low concentrations in complex environmental matrices often requires the inclusion of multi-step sample preparation. Depending on the nature of the matrix, sample preparation may vary, but the major steps would include one or a combination of the following requirements: to release and isolate the analytes of interest from the sample matrix through exhaustive extraction, removal of part of the sample matrix through selective clean-up (which may involve purification and fractionation) and pre-concentration of the analyte.

2.1.1. Extraction methods

In line with recommendations from previous international inter-laboratory comparisons (de Boer and Cofino, 2002; de Boer and Wells, 2006), most of the selected publications as summarized in Table 1 indicated that samples were collected in pre-cleaned amber or aluminium foil covered glass containers and stored at low temperatures (4 to -20 °C). Solid sample pre-treatment involved air drying (evaporation), sieving and grinding with a chemical drying agent, e.g. sodium sulphate (Na_2SO_4). Final extracts have also been treated with additional Na_2SO_4 to remove any residual moisture before analysis. Liquid sample pre-treatment involved filtration, to remove solid particles and acidification of the water samples (preservation). Extraction techniques employed included liquid-liquid extraction (LLE) and solid phase extraction (SPE) for liquid samples and Soxhlet extraction, ultrasound-assisted extraction (UAE) and liquid-solid extraction (LSE) for solid samples (Table 1). During extraction efficiency evaluation through recovery experiments, the terms recovery should be defined as recovery or apparent recovery to avoid confusion. Recovery refer to the yield from sample preparation steps of an analytical process compared to the amount of analyte in the original sample reported (Burns *et al*., 2002). Apparent recovery is reported, when the calculated value obtained using an analytical procedure that involves a calibration graph is compared to a reference value (Burns *et al*., 2002).

Liquid-liquid extraction is a simple and cost effective method for the extraction of BFRs from aqueous matrices. The choice of solvents to achieve exhaustive extraction of the analytes of interest is important. Other parameters include sample-solvent ratio, extraction time and the evaporation procedure (Moldoveanu and David, 2015). Because of the hydrophobicity of PBDEs and their relatively low concentrations in water, large sample volumes of up to 1 L are required for LLE (Fulara and Czaplicka, 2012). Odusanya *et al*. (2009) employed LLE and determined the extraction efficiencies of nine solvent systems using hexane, dichloromethane (DCM), petroleum ether, acetone and combinations of these solvents by spiking landfill leachates with BDEs. Liquid-liquid extraction of 100 mL sample using petroleum ether (60 – 80 °C), gave better apparent recoveries. Olukunle *et al*. (2014) similarly investigated the extraction efficiency of nine solvent systems using hexane, DCM, toluene and combinations of these solvents for the extraction of fourteen BDE congeners from ultrapure water. Even though this matrix is not representative of the matrix under investigation, they concluded that DCM provided adequate recoveries (75 to 101%). Dichloromethane was previously used for the extraction of selected PBDEs and PBB153 from river water (Daso *et al*., 2013a). In this study, spiked river water

Table 1
Summary of the sample preparation procedures used for the analysis for BFR analysis in Africa.

Analytes	Sample type and size	Sample pre-treatment	Extraction technique	Clean-up technique	Recovery (%)	Ref.
Tri- to hepta-BDE	Landfill leachate (100 mL)	Not provided	LLE: 3 × 15 mL petroleum ether	0.5 cm^3 Na_2SO_4 + 6 g Silica column Elute with petroleum ether	Spiked matrix 102.9 - 108.0%	(Odusanya *et al*., 2009)
Deca-BDE	Dust wipes (not provided)	Sieved (250 µm), homogenised	Soxhlet: hexane/acetone (2:1, v/v) for 8 h	Multi-layer silica column: 0.25 g Na_2SO_4, 0.25 g acid silica, 0.25 g basic silica, 0.25 g neutral silica, elute with hexane/acetone mixture	CRM: 84% Spiked matrix: 67 - 102%	(Kefeni *et al*., 2011)
Tri- to hepta-BDE BB153	Sediment (10 g)	Dried and sieved (1 mm)	2 g Cu powder added to sample LSE: 120 mL hexane/acetone (2:1, v/v) for 12 h	Multi-layer silica column: 0.1 g Na_2SO_4, 0.1 g activated silica, 0.4 g acid silica, (44% w/w, conc. H_2SO_4) 0.1 g activated silica, 0.2 g (30% w/w, 1 N NaOH) basic silica, 0.1 g activated silica, elute with hexane	Spiked matrix: 84.4 - 110%	(Daso *et al*., 2011)
Tri- to Hepta-, Deca-BDE BB153	Effluent (800 mL), Sewage sludge (10 g)	Effluent – No pre-treatment Sewage sludge dried at 50 °C, ground and sieved (500 µm)	Effluent - LLE: 3 × 40 mL DCM Sewage sludge - Soxhlet: hexane/acetone (3:1, v/v) for 16 h, concentrated at 45 °C	Effluent - Multi-layer silica column: 0.1 g Na_2SO_4, 0.1 g activated silica, 0.4 g 44% acid silica, 0.1 g activated silica, 0.2 g basic silica, 0.1 g activated silica, elute with hexane Sludge - Multi-layer silica column: 4 g Na_2SO_4, 2 g activated silica, 8 g 44% acid silica (44% H_2SO_4, w/w), 1 g activated silica, 4 g basic silica (30% NaOH, w/w), 1 g activated silica, elute with hexane	Surrogates: 58 – 102% Spiked matrix: 65 – 112%	(Daso *et al*., 2012)
Tri- to hepta-, deca-BDE	Sediment (10 g)	Dried and sieved (150 µm)	Soxhlet: hexane/acetone (2:1, v/v) for 10 h	Extracts treated with 2 g Cu powder Multi-layer silica column: 0.2 g Na_2SO_4, 0.2 g neutral silica, 0.4 g acid silica, 0.2 g neutral silica, 0.2 g basic silica, 0.2 g neutral silica, elute with hexane/DCM (3:1, v/v)	Spiked matrix: 41.7% - 130%	(Olukunle *et al*., 2012)
Tetra- to hexa-, deca-BDE Mono- to Tri-, hexa-, deca-BB	Dust (0.89 - 2.4 g)	Sieved (250 µm), homogenised with Cu powder	Soxhlet: hexane/acetone (2:1, v/v) for 8 h	Multi-layer silica column: 0.2 g Na_2SO_4, 0.2 g acid silica, 0.2 g neutral silica, 0.2 g basic silica, 0.2 g neutral silica, elute with hexane/DCM (5:1, v/v)	CRM: 84 ± 5.7 – 137 ± 7.9%	(Kefeni and Okonkwo, 2012)
Penta-, octa-BDE Mono-BB	Landfill leachates (not provided)	Filtered	SPE: C18 Elute with 5 mL hexane	-	Not provided	(Nomngongo *et al*., 2012)
Mono- to tetra-BB HBCD TBBPA	Water (250 mL)	Acidified to pH 3, filtered using 0.47 µm pore size	SPE: Strata™-X Elute with 3 × 2 mL DCM/hexane (4:1, v/v) **Derivatization** HFBA heated to 55 °C for 2 h	-	Spiked matrix: 52.50 ± 6.23 – 117.50 ± 9.19%	(Chokwe *et al*., 2012)
Di- to hexa-, deca-BDE	Dust (1 g)	Sieved (250 µm), homogenised with Cu powder	Soxhlet: hexane/acetone (2:1, v/v) for 8 h	Multi-layer silica column: 0.2 g Na_2SO_4, 0.2 g acid silica, 0.2 g neutral silica, 0.2 g basic silica, 0.2 g neutral silica, elute with hexane/DCM (5:1, v/v)	CRM: 78 ± 5 – 112 ± 6% Surrogate: 72 – 112%	(Kefeni and Okonkwo, 2013)
Tri- to hepta-, deca-BDE Hexa-BB	Water (800 mL)	No pre-treatment	LLE: 3 × 40 mL DCM Concentrated at 45 °C	Multi-layer silica column: 1 g Na_2SO_4, 0.1 g activated silica, 0.4 g acid silica (44% conc. H_2SO_4, w/w), 0.1 g activated silica, 0.2 g basic silica (30% NaOH, w/w), 0.1 g activated silica, elute with hexane	Milli-Q water QC: 69 – 97% Spiked matrix: 106 – 131%	(Daso *et al*., 2013a)
Tri- to hepta-, deca-BDE BB153	Landfill leachate (800 mL)	No pre-treatment	LLE: 3 × 40 mL DCM Concentrated at 45 °C	Multi-layer silica column: 1 g Na_2SO_4, 0.1 g activated silica, 0.4 g 44% acid silica, 0.1 g activated silica, 0.2 g basic silica, 0.1 g activated silica, elute with hexane	Spiked matrix: 50.1 - 136% Surrogate: 54 - 92%	(Daso *et al*., 2013b)
Mono- to hexa-, deca-BDE Di-, deca-BB	Dust (2.3 - 3.5 g)	Sieved (250 µm) and homogenised	Add 0.3 g Cu powder Soxhlet: hexane/acetone (2:1, v/v) for 8 h	Multi-layer silica column: 0.2 g Na_2SO_4, 0.2 g acid silica, 0.2 g neutral silica, 0.2 g basic silica, 0.2 g neutral silica, elute with hexane/DCM (5:1, v/v)	CRM: 78 ± 5 – 112 ± 6% Surrogate: 72 - 112%	(Kefeni *et al*., 2014)
Mono- to hexa-, deca-BDE	Dust (2.3 - 3.5 g) Polymers (0.5 g)	Sieved (<45 µm to >150 µm)	Add 0.3 g Cu powder Soxhlet: hexane/acetone (2:1, v/v) for 8 h	Multi-layer silica column: 0.2 g Na_2SO_4, 0.2 g acid silica, 0.2 g neutral silica, 0.2 g basic silica, 0.2 g neutral silica, elute with hexane/DCM (5:1, v/v)	CRM: 78 ± 5 – 112 ± 6% Surrogate: 72 - 112%	(Kefeni and Okonkwo, 2014)
Tri- to hepta-, deca-BDE	leachates (500 mL) sediment (10 g)	Not provided	Leachates - LLE: 3 × 40 mL DCM, concentrated at 45 °C Sediment - Add 2 g Cu powder Soxhlet: hexane/acetone (2:1, v/v) for 16 h	Extracts treated with 2 g Cu powder. Multi-layer silica column: 0.2 g Na_2SO_4, 0.2 g neutral silica, 0.4 g acid silica, 0.2 g neutral silica, 0.2 g basic silica, 0.2 g neutral silica, elute with hexane/DCM (3:1, v/v)	Spiked matrix: 75 – 101% Surrogate: 81 – 90%	(Olukunle *et al*., 2014)

Tri- to hepta-, deca-BDE	Dust (0.8 g)	Sieved (212 µm) and homogenised	Sonication: 2 × 10 mL hexane/MeOH (1:3, v/v) for 30 min at a 40 °C	0.8 g Na_2SO_4, 3 g Silica, fraction 1 elute with 25 mL hexane, fraction 2 elute with diethyl ether/hexane (1:1 v/v)	CRM: 95.7 – 111.8%	(Abafe and Martincigh, 2014, 2015)
Tri- to hepta-, deca-BDE	Eggshells and egg membranes and albumen (1 - 2 g)	Dried, separated membranes and grounded	Sonication: 2 × 5 mL hexane/DCM (1:1, v/v) for 60 and 30 min at a 65 °C followed by 2 mL hexane/DCM (1:1, v/v) for 30 min at a 65 °C Concentrated at 45 °C	Florisil: 2 g, elute with hexane	Surrogate: 40.00 - 135.94%	(Daso *et al*., 2015)
Tri- to hepta-, deca-BDE	Dust (0.1 g)	Sieved	Add 2 g Cu powder Soxhlet: hexane/acetone (2:1, v/v) for 8 h	Multi-layer silica column: 0.5 g Na_2SO_4, 0.1 g silica, 0.16 g acid silica, 0.16 g silica, 0.16 g basic silica, 0.16 g silica, elute with hexane/DCM (5:1, v/v)	Surrogate: 65 - 90% CRM: 70 – 111%	(Olukunle *et al*., 2015a)
Tetra- to hepta-, deca-BDE	Dust (100 mg)	Dried and sieved (150 µm)	Sonication: 3 cycles toluene/DCM (1:1, v/v) at 55 °C for 15 min, centrifuged and reduced under a gentle flow of N2 to about 1 mL	Multi-layer silica column: 0.5 g Na_2SO_4, 0.16 g silica, 0.06 g Pesticarb, 0.16 g silica, elute with toluene/DCM (1:1, v/v)	Surrogate: 104 - 126% CRM: 70 – 111%	(Olukunle *et al*., 2015b)
Tri- to hepta-BDE PBB101 HBCD	Fish (5 g)	Grounded with 20 g Na_2SO_4	Sonication: 2 cycles, 20 mL hexane/acetone (4:1, v/v) at 55 °C for 45 min, treated with conc. H_2SO_4 and evaporated to dryness	Re-constituted in 2.5mL MeOH, diluted to 250 mL, and acidified with acetic acid SPE (Strata-X Polymeric Reverse Phase), elute with DCM/hexane (4:1, v/v) elutes were collected and reduced to dryness under gentle stream of nitrogen **Derivatization** TEA and HFBA heated to 50 °C for 30 min	Spiked matrix: 50.02 [a] - 90.88%	(Chokwe *et al*., 2015a)
Tetra- to hepta-BDE PBB101 HBCD	Water (250 mL) Sediment (5 g) Fish (5 g)	Water (acidified) Sediment (grinded with 20 g Na_2SO_4) Fish (Grinded with 20 g Na_2SO_4)	Water – SPE: Strata™-X Sediment –Sonication: 2 cycles, hexane/acetone (4:1, v/v) at 55 °C for 45 min, 2 g Cu added, evaporated to dryness Fish - Sonication: 2 cycles, 20 mL hexane/acetone (4:1, v/v) at 55 °C for 45 min, treated with conc. H_2SO_4 and evaporated to dryness	Re-constituted in 2.5mL MeOH, diluted to 250 mL, and acidified with acetic acid SPE (Strata-X Polymeric Reverse Phase), elute with DCM/hexane (4:1, v/v) elutes were collected and reduced to dryness under gentle stream of nitrogen **Derivatization** TEA and HFBA heated to 55 °C for 2 h	Spiked matrix: 63 – 99%	(Chokwe *et al*., 2015b)
Tri- to hepta-BDE Tri- to penta-BB TBBPA HBCD	Sewage sludge (5 g)	Centrifuged, precipitate mixed with 20 g Na_2SO_4	Sonication: 2 cycles, 30 mL hexane/acetone (4:1, v/v) at 55 °C for 45 min 3 g acid silica, elute with 40 mL DCM Add 2 g Cu concentrate	Re-constituted in 2.5mL MeOH, diluted to 250 mL, and acidified with acetic acid SPE (Strata-X Polymeric Reverse Phase), elute with DCM/hexane (4:1, v/v) elutes were collected and reduced to dryness under gentle stream of nitrogen **Derivatization** TEA and HFBA heated to 50 °C for 30 min	Spiked matrix: 38.65 - 78.63%	(Chokwe *et al*., 2015c)
EH-TBB, BTBPE, DBDPE, BEH-TEBP, HBCD	Sediment (10 g) Leachates (500 mL)	Sediment – Dried, ground sieved (150 µm) Leachates - filtered	Sediment – Soxhlet: 180 mL hexane/DCM (1:1, v/v) for 16 h Leachates - LLE: 3 × 40 mL DCM Concentrated at 45 °C	Multi-layer silica column: 0.5 g Na_2SO_4, 0.16 g silica, 0.06 g Pesticarb, 0.16 g silica, elute with hexane	Surrogate: 65% and 110%	(Olukunle and Okonkwo, 2015)
Tri- to hepta-, deca-BDE BB153	Sediment (10 g)	Dried and sieved (500 µm)	2 g Cu powder added to sample LSE: 120 mL hexane/acetone (2:1, v/v) for 12 h	Multi-layer silica column: 0.1 g Na_2SO_4, 0.1 g activated silica, 0.4 g acid silica, (44% w/w, conc. H_2SO_4) 0.1 g activated silica, 0.2 g (30% w/w, 1 N NaOH) basic silica, 0.1 g activated silica, elute with hexane	Spiked matrix: 90.3 - 130%	(Daso *et al*., 2016)

[a] Recovery include nonylphenol penta ethoxylates isomer (NPPE2)

gave higher recoveries (106 to 131%) compared to ultrapure water (69 to 97%) (Daso *et al*., 2013a). Due to the low water solubility and high log octanol/water partition coefficient (Log K_{ow}) it is expected that PBDEs tend to bind to the organic fraction of particulate matter. This extraction technique also provided sufficient recoveries for the extraction of PBDEs and BB153 from matrix spiked sewage sludge (Daso *et al*., 2012) and alt-BFRs from landfill leachates (Olukunle and Okonkwo, 2015).

Solid phase extraction was also used for the extraction of PBDEs, PBBs, HBCD and TBBPA. Chokwe *et al*. (2012) evaluated the extraction efficiency of four different SPE cartridges using spiked wastewater samples. The recommended Strata™-X SPE product showed apparent recoveries from 53% (HBCD) to 110% (BB10). It was reported that recoveries improved when samples were spiked after filtration, this can be attributed to target analytes retained by particulate matter.

Soxhlet extraction is the well-established extraction technique for persistent organic pollutants (POPs). This continuous extraction process, often applied to solid or semi-solid samples, is used to extract organic analytes into a solvent. Samples are usually dried (e.g. with Na_2SO_4) and ground to increase the surface area of the particles prior to extraction. The number of extraction cycles used depends on the analyte solubility and the capacity of the solvent to penetrate the matrix (Moldoveanu and David, 2015). It is a cost-effective technique that allows for high process efficiency, but requires long extraction times and large volumes of solvent. As shown in Table 1, Soxhlet extraction was used for the extraction of BFRs from dust, sewage sludge and sediment. PBDEs and PBBs were extracted from dust using a mixture of hexane/acetone (2:1, v/v) for 8 h. This method was used to analyse a dust certified reference material (CRM) and apparent recoveries of between 78 ± 5 ng g^{-1} for BDE209 and 112 ± 6 ng g^{-1} for BDE17 were reported (Kefeni and Okonkwo, 2013, 2014; Kefeni *et al*., 2014). This solvent system was also used for the extraction of sediment, applying different extraction times (Olukunle *et al*., 2012, 2014). The 16 h extraction time gave sufficient recoveries (81 to 90%), while shorter extraction times had lower recoveries for BDE209. Alt-BFRs were extracted from sediment for 16 h using Soxhlet with hexane/DCM (1:1, v/v) and recoveries ranged from 65 to 110% (Olukunle and Okonkwo, 2015).

Ultrasound-assisted extraction (UAE), where high frequency electrical energy is converted into ultrasound waves, was used in a number of studies for the extraction of PBDEs, PBBs, HBCD and TBBPA. Four solvent system combinations comprising of hexane, DCM, acetone and toluene were evaluated by spiking Na_2SO_4 (Olukunle *et al*., 2015b). It was concluded that toluene/DCM (1:1, v/v)

using three 15 min cycles at 55 °C gave optimal recovery. Abafe and Martincigh (2015, 2014) used hexane/methanol (MeOH) (1:3, v/v) as solvent and extracted a dust CRM at 40 ^{0}C for 30 min and reported recoveries between 96 and 112%. Ultrasound-assisted extraction was also used for the extraction of PBDEs from eggshells, eggshell membranes and residual albumen using hexane/DCM (1:1, v/v) for 60 min and two further cycles of 30 min at 65 °C and a wider recovery range was reported (Daso *et al*., 2015). When comparing apparent recoveries obtained from the extraction of a dust CRM with Soxhlet extraction (hexane/acetone 2:1, v/v for 8 hours) and UAE (three 15 min cycles with toluene/ DCM 1:1, v/v at 55 °C), identical apparent recoveries were reported for the tri- to hepta- and deca-BDEs ranging from 70% for BDE153 to 111% for BDE183 (Olukunle *et al*., 2015a, 2015b).

Liquid-solid extraction was employed in a single study for the extraction of tri- to hepta-BDEs and BB153 from sediment by mechanical shaking with a mixture of hexane/acetone (2:1, v/v) for 12 h (Daso *et al*., 2011, 2016).

2.1.2. Clean-up methods

Sulphur removal from abiotic and lipid removal from biotic matrices should be included in the clean-up step to improve chromatographic separation of BFRs. For the removal of sulphur from dust and sediment, metallic copper powder was either added to the sample during the homogenisation step before extraction (Daso *et al*., 2016; Kefeni and Okonkwo, 2012, 2013), mixed during extraction (Kefeni and Okonkwo, 2014; Kefeni *et al*., 2014; Olukunle *et al*., 2014, 2015a) or added after extraction (Chokwe *et al*., 2015b). Non-destructive lipid removal was applied to eggshells, eggshell membranes and remaining albumin using Florisil® as fat retainer (Daso *et al*., 2015). Destructive methods using concentrated sulphuric acid were used for the remove of fat from fish (Chokwe *et al*., 2015a, 2015b; Daso *et al*., 2015).

Clean-up and fractionation of BFRs are summarised in Table 1. The process mainly involved the use of multi-layer silica columns containing Na_2SO_4 (0.1 to 1 g), neutral activated silica (0.25 to 4 g), sulphuric acid impregnated silica (0.16 to 8 g), potassium hydroxide impregnated silica (0.16 to 4 g) or combinations thereof. The multi-layer silica columns were modified by replacing the acid- and basic silica combinations with Pesticarb (0.06 g) for the clean-up of PBDEs from dust extracts (Olukunle *et al*., 2015b) and alt-BFRs from landfill sediment and leachates (Olukunle and Okonkwo, 2015). A column system consisting of Na_2SO_4 and activated silica was used for PBDEs cleaned-up from landfill leachate

extracts (Odusanya *et al*., 2009). Abafe and Martincigh (2014, 2015) used Na_2SO_4, activated silica and Florisil® for clean-up and fractionation of dust extracts. The first fraction was eluted with hexane, containing BDE 209 and the second fraction eluted using diethyl ether/hexane (1:1, v/v) to collect the remaining PBDEs.

2.2. Instrumental analysis

Injection and detection techniques and column characteristics are imperative for the analysis of BFRs. Where gas chromatography (GC) analysis is used as a separation technique, identification and quantitation of BFRs is often performed using electron capture detector (ECD), a sensitive detection technique for organohalogenated compounds. Although, compound co-elution is an important consideration for complex samples (Stapleton, 2006). The disadvantage of GC-ECD is poor selectivity; all halogen containing compounds produce a signal and the presence of PCBs at high concentrations may influence the accurate quantitation of PBDEs (Alaee *et al*., 2001). The ECD is not isotope selective. Therefore, the use of $^{13}C_{12}$-labelled internal standards is impractical due to co-elution with the native compounds. Alaee *et al*. (2001) used GC-ECD configured with a 30 m 5-MS (diphenyl dimethylpolysiloxane) type column to investigate the co-elution of thirty-four di- to hepta-BDE congeners with commonly occurring PCBs and other organochlorine (OC) compounds. Potential co-elutions for ten PBDE congeners with PCBs and OCs were reported, and of particular concern is the interference of CB180 with BDE47. While these considerations have to be taken into account when using GC-ECD, co-elutions may be resolved by using mass spectrometry (MS). The determination of PBDEs using low resolution mass spectrometry (LR-MS) is typically performed with either electron capture negative ionisation (ECNI) or electron impact ionisation (EI), either in full scan, selective ion monitoring (SIM) or selective reaction monitoring modes in MS/MS instruments. As shown in Table 2, a number of studies have reported BFR analysis using GC-ECD and electron impact ionisation with single quadrupole mass spectrometers (GC-EI-MS) in full scan and SIM modes. In some studies GC-ECD was solely used for the analysis of BDE209 (Kefeni and Okonkwo, 2012; Olukunle *et al*., 2012). GC-time-of-flight mass spectrometry (GC-TOFMS) was also used but limited to structural confirmation of target compounds (Daso *et al*., 2013a, 2016). For the analysis of BFRs using GC-EI-MS in full-scan and SIM mode, the molecular ions $[M]^{+\bullet}$ were used for quantitation and identification was confirmed by retention time comparison and the presence of two qualifier ions (Kefeni and Okonkwo, 2012, 2013, 2014; Kefeni *et al*., 2014; Olukunle *et al*., 2012, 2014, 2015a). Ions formed during EI ionisation depend on the degree

Table 2
Summary of the analytical procedures used for the analysis for BFR analysis in Africa.

Analyte groups	Injection volume (µL), mode, temp (°C)	Carrier gas, flow rate (mL/min)	Column (m × mm × µm)	GC oven conditions	Separation and detection	LOD	Ref.
Tri- to hepta-BDE	1, Splitless, 250	He, 3	ZB-5 (30 × 0.25 × 0.25)	90 °C (1 min), 210 °C at 30 °C/min, 290 °C at 10 °C/min	GC-ECD	10 - 500 pg L^{-1a}	(Odusanya *et al*., 2009)
Deca-BDE	1, Splitless, 290	N_2/ He, 1.5 (for 30 m column), 2.5 (for 15 m column)	ZB-5 (15 × 0.25 × 0.25) ZB-5 (30 × 0.25 × 0.25)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (4.5 min for 15 m) (32 min for 30 m)	GC-ECD	0.5 ng g^{-1b}	(Kefeni *et al*., 2011)
Tri- to hepta-BDE BB153	1, Splitless, 280	He, 1.5	DB-5 MS (60 × 0.25 × 0.1)	100 °C (2 min), 220 °C at 20 °C/min, 300 °C at 4 °C/min (7 min)	GC-ECD	0.03 - 0.13 ng g^{-1b}	(Daso *et al*., 2011)
Tri- to Hepta-, Deca-BDE BB153	1, Splitless, 280 (BDE209 – 250)	He, 1.5 (BDE209: He, 3.0)	DB-5 MS (60 × 0.25 × 0.1) BDE209 - DB-5 MS (15 × 0.25 × 0.1)	100 °C (2 min), 220 °C at 20 °C/min, 300 °C at 4 °C/min (7 min) BDE209: 100 °C (1 min), 150 °C at 50 °C/min, 310 °C at 12.5 °C/min	GC-ECD	Not provided	(Daso *et al*., 2012)
Tri- to hepta-, deca-BDE	1, Splitless, 290	He, 1.5 (BDE209: N_2, 2.5)	DB-5 (30 × 0.25 × 0.10). BDE209 - ZB-5 (15 × 0.25 × 0.25)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (1 min), for BDE209 (3 min) Transfer line: 300 °C	GC-EI-MS (full scan) and ECD	0.03 - 0.32 ng g^{-1} BDE209: 4.66 ng g^{-1}	(Olukunle *et al*., 2012)
Tetra- to hexa-, deca-BDE Mono- to Tri-, hexa-, deca-BB	1, Splitless, 290	He, 1.5 (BDE209: N_2, 2.5)	DB-5 (30 × 0.25 × 0.10). BDE209 - ZB-5 (15 × 0.25 × 0.25)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (1 min), for BDE209 (3 min) Transfer line: 300 °C	GC-EI-MS (full scan) and ECD	0.3 - 0.5 ng g^{-1b} BB209: 0.8 ng g^{-1b} BDE209: 1.2 ng g^{-1b}	(Kefeni and Okonkwo, 2012)
Penta-, octa-BDE Mono-BB	Not provided	He, 1	BPX5 (30 × 0.25 × 0.25)	80 °C (2 min), 140 °C at 50 °C/ (1.5 min), 220 °C at 20 °C/min (1 min), 280 °C at 2 °C/min, 300 °C at 30 ° °C/min (10 min) Transfer line: 280 °C	GC-EI-MS (full scan)	Not provided	(Nomngongo *et al*., 2012)
Mono- to tetra-BB HBCD TBBPA	1, Splitless, 275	He, 40 cm/ s	DB-5 (15 and 30 × 0.25 × 0.25) Rtx-1614 (15 × 0.25 × 0.10)	50 °C to 120 °C at 7.5 °C/min , 275 °C at 15 °C/min , 300 °C at 25 C/min (2 min) Transfer line: 300 °C	GC-EI-MS[c]	0.01 - 0.1 µg L^{-1b}	(Chokwe *et al*., 2012)
Di- to hexa-, deca-BDE	1, Splitless, 290	He, 1.5	HP-5MS (30 × 0.25 × 0.25) BDE209 - ZB-5 (15 × 0.25 × 0.1)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (1 min) Transfer line: 300 °C	GC-EI-MS (SIM)	0.04 - 0.7 ng g^{-1} BDE209: 1.3 ng g^{-1}	(Kefeni and Okonkwo, 2013)
Tri- to hepta-, deca-BDE Hexa-BB	1, Splitless, 280 (BDE209 – 250)	He, 1.5 (BDE209: He, 3.0)	DB-5 MS (60 × 0.25 × 0.1) BDE209 - DB-5 MS (15 × 0.25 × 0.1)	100 °C (2 min), 220 °C at 20 °C/min, 300 °C at 4 °C/min (7 min) BDE209: 100 °C (1 min), 150 °C at 50 °C/min, 310 °C at 12.5 °C/min	GC-EI-TOFMS (Identification) GC-ECD (Quantification)	0.16 - 1.54 ng L^{-1b}	(Daso *et al*., 2013a)
Tri- to hepta-, deca-BDE BB153	1, Splitless, 280 (BDE209 – 250)	He, 1.5 (BDE209: He, 3.0)	DB-5 MS (60 × 0.25 × 0.1) BDE209 - DB-5 MS: (15 × 0.25 × 0.1)	100 °C (2 min), 220 °C at 20 °C/min, 300 °C at 4 °C/min (7 min) BDE209: 100 °C (1 min), 150 °C at 50 °C/min, 310 °C at 12.5 °C/min	GC-ECD	0.1 - 1 ng mL^{-1a} BDE209: 5 ng mL^{-1a}	(Daso *et al*., 2013b)
Mono- to hexa-, deca-BDE Di-, deca-BB	1, Splitless, 290	He, 1.5	HP-5MS (30 × 0.25 × 0.25) BDE209 - ZB-5 (15 × 0.25 × 0.1)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (1 min) Transfer line: 300 °C	GC-EI-MS (SIM)	0.13 – 1.8 ng g^{-1}	(Kefeni *et al*., 2014)
Mono- to hexa-, deca-BDE	1, splitless, 290	He, 1.5	HP-5MS (30 × 0.25 × 0.25). BDE209 - ZB-5 (15 × 0.25 × 0.1)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (1 min) Transfer line: 300 °C	GC-EI-MS (SIM)	0.04 to 0.7 ng g^{-1} BDE209: 1.8 ng g^{-1}	(Kefeni and Okonkwo, 2014)
Tri- to hepta-, deca-BDE	1, Splitless, 290	He, 1.5	ZB-5 (15 × 0.25 × 0.25)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (10 min) Transfer line: 300 °C	GC-EI-MS (SIM)	0.02 - 0.3 ng $µL^{-1}$ BDE209: 0.9 ng $µL^{-1}$	(Olukunle *et al*., 2014)

Tri- to hepta-, deca-BDE	1, Pulsed Splitless, 285	He – 1.2	Rtx-1614 (15 × 0.25 × 0.10)	90 °C (2 min), 270 °C at 20 °C/min, 325 °C at 10 °C/min (5 min) Transfer line: 350 °C	GC-EI-MS (SIM)	0.03 – 0.16 ng g^{-1}	(Abafe and Martincigh, 2014, 2015)
Tri- to hepta-, deca-BDE	1, Splitless, 270	He, 2.33	ZB-5 (15 × 0.25 × 0.25)	90 °C (1 min), 200 °C at 40 °C/min, 250 °C at 25 °C/min, 310 °C at 7.5 °C/min (5 min) Transfer line: 280 °C	GC-EI-MS (SIM)	0.03 – 8.88 ng g^{-1b}	(Daso *et al*., 2015)
Tri- to hepta-, deca-BDE	1, Splitless, 290	He, 1.5	ZB-5 (15 × 0.25 × 0.25)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (10 min) Transfer line: 300 °C	GC-EI-MS (SIM)	0.01 - 0.024 ng μL^{-1a}	(Olukunle *et al*., 2015a)
Tetra- to hepta-, deca-BDE	1, Splitless, 290	He, 1.5	DB 5 (15 × 0.25 × 0.1)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (10 min) Transfer line: 300 °C	GC-EI-MS (SIM)	0.009 - 0.025 ng μL^{-1a}	(Olukunle *et al*., 2015b)
Tri- to hepta-BDE PBB101 HBCD	1, Splitless, 275	He - linear velocity 40 cm/ s	Rtx-1614 (15 × 0.25 × 0.10)	50 °C to 120 °C at 7.5 °C/min, 275 °C at 15 °C/min, 280 °C at 25 °C/min (1 min) Transfer line: 280 °C	GC-EI-MS[c]	Not provided	(Chokwe *et al*., 2015a)
Tetra- to hepta-BDE PBB101 HBCD	Not provided, 280	He - linear velocity 40 cm/ s	Rtx-1614 (15 × 0.25 × 0.10)	50 °C to 120 °C at 7.5 °C/min, 275 °C at 15 °C/min, 300 °C at 25 °C/min (2 min) Transfer line: 300 °C	GC-EI-MS[c]	0.01 – 0.2 µg L^{-1} 0.12 – 0.48 ng g^{-1}	(Chokwe *et al*., 2015b)
Tri- to hepta-BDE Tri- to penta-BB TBBPA HBCD	1, Splitless, 300	He - linear velocity 40 cm/ s	Rtx-1614 (15 × 0.25 × 0.10)	50 °C to120 °C at 7.5 °C/min, 275 °C at 15 °C/min, 300 °C at 25 °C/min (2min) Transfer line: 275 C	GC-EI-MS[c]	0.30 - 4.50 ng g^{-1b}	(Chokwe *et al*., 2015c)
EH-TBB, BTBPE, DBDPE, BEH-TEBP, HBCD	1, Splitless, 225	He, 2	DB 5 (15 × 0.25 × 0.1)	100 °C (2 min), 160 °C at 10 °C/min (2 min), 300 °C at 40 °C/min (10 min) Transfer line: 280 °C	GC-EI-MS (SIM)	0.005 - 0.025 ng μL^{-1a}	(Olukunle and Okonkwo, 2015)
Tri- to hepta-, deca-BDE BB153	1, Splitless, 280 (BDE209 – 250)	He, 1.5 (BDE209: He, 3.0)	DB-5 MS (60 × 0.25 × 0.1) BDE209 - DB-5 MS (15 × 0.25 × 0.1)	100 °C (2 min), 220 °C at 20 °C/min, 300 °C at 4 °C/min (7 min) BDE209: 100 °C (1 min), 150 °C at 50 °C/min, 310 °C at 12.5 °C/min	GC-EI-TOFMS (Identification) GC-ECD (Quantification)	0.03 - 0.13 ng g^{-1b}	(Daso *et al*., 2016)

[a] Instrument detection limit
[b] Method detection limit
[c] Instrument scan mode not provided

of bromination and the intensity of the molecular ion $[M]^{+\bullet}$ decrease with an increase in the number of bromine atoms. The mass spectra of higher brominated BDEs are mostly dominated by fragment ions e.g. $[M\text{-}Br_2]^{+\bullet}$. Only three studies specified the use of fragment ions $[M\text{-}Br_2]^{+\bullet}$ and/ or molecular ions $[M]^{+\bullet}$ as quantitation ions for SIM analysis of PBDEs (Abafe and Martincigh, 2014, 2015; Daso *et al*., 2015)

2.2.1. Injection technique

The injection technique applied to introduce analytes into a GC column needs to be carefully selected and optimised to ensure sample integrity. The most frequently used injection techniques for the analysis of PBDEs include splitless or pulsed splitless injection, on-column injection and programmed temperature vaporizing (PTV) injection (Król *et al*., 2012; Stapleton, 2006). Splitless injection mode allows for the introduction of low analyte concentrations, but this method may be limited by smaller injection volumes and high inlet temperatures (Björklund *et al*., 2004; Król *et al*., 2012; Stapleton, 2006). The temperature and the injection time prior to column transfer are important factors contributing to the response (Björklund *et al*., 2004). Pressure-pulsed splitless injection is recommended to reduce injector residence times at high temperatures for BDE209 and other higher brominated BDEs (de Boer and Wells, 2006; Stapleton, 2006). As shown in Table 2, splitless injection with volumes of 1 µl is the most frequently used injection technique. For the analysis of PBDEs, PBBs and HBCD the injector temperatures ranged from 250 to 300 °C, whereas 225 °C was used for the analysis of alt-BFRs (Olukunle and Okonkwo, 2015). Abafe and Martincigh (2014, 2015) used pulsed splitless injection with the injector temperature at 285 °C. Kefeni *et al*. (2011) optimised various chromatographic parameters for the analysis of BDE209, and demonstrated an increase in response with increased inlet temperatures from 250 to 300 °C.

2.2.2. GC column system

The GC capillary column stationary phase, length, film thickness, inner diameter and carrier gas flow rate are considerations influencing the separation characteristics and response of PBDEs. Although a range of different columns have been used for the determination of PBDEs in environmental samples, the most widely used GC columns for the analysis of BFRs are non-polar to mid-polarity stationary phases (Björklund *et al*., 2004; Korytár *et al*., 2005). Thicker stationary phase columns (> 0.25 µm) require increased elution temperatures and long GC columns (> 30 m) results in extended exposure time at elevated temperatures and may contribute to thermal degradation of the higher brominated

congeners (Björklund *et al*., 2004). De Boer *et al*. (2001) reported that good separation for the majority of PBDEs can be obtained by using a 50 m column, and a shorter (15 m) column for deca-BDE. Shorter GC columns produce narrower chromatographic peaks and more compressed chromatograms and depending on the detector used, sufficient data points should be recorded over the peak detected (Van Leeuwen and de Boer, 2008). The GC analysis times can be reduced by using higher carrier gas flow rate, increased temperature program heating rates and by using shorter column lengths, thinner column diameters and thinner stationary phases (Klee and Blumberg, 2002). Narrow bore columns (< 0.15 mm) provide more theoretical plates per length of column resulting in improved chromatographic resolution, but restrict the amount of sample to be loaded on the column.

Björklund *et al*. (2004) proposed that due to the high boiling point of BDE209, a final oven temperature of 300 °C should be used to compromise between PBDE degradation and peak broadening since the GC oven temperature program affects the chromatographic resolving power, peak shape and response. Kefeni *et al*. (2011) investigated different final GC oven temperatures and concluded that temperatures between 300 and 310 °C, using a 5% phenyl-methylpolysiloxane stationary phase column (15 m × 0.25 mm × 0.25 µm), provide good chromatographic resolution and improved response for BDE209. As shown in Table 2, final GC oven temperatures employed for the analysis of PBDEs range from 290 to 310 °C. Typical column diameters employed included 0.25 mm diameter with film thickness ranging from 0.1 to 0.25 µm with non-polar stationary phases. Limited information on the behaviour and degradation of congeners with higher degree of bromination and BDE209 was provided; some studies discussed the problems associated with BDE209 analysis and the reasons for not analysing the congener (Chokwe *et al*., 2015a, 2015b; Daso *et al*., 2011; Odusanya *et al*., 2009). BDE209 response was evaluated using two columns with different lengths (15 and 30 m) with identical stationary phase and dimensions and a threefold increase in response was reported when using the shorter column (Kefeni *et al*., 2011). Improved chromatographic resolution was achieved for columns with thin film thickness (0.1 µm) compared to identical columns with film thickness of 0.25 µm (Kefeni and Okonkwo, 2012). BDE209 breakdown during analysis was also observed when using a 60 meter thin film (0.1 µm) column (Daso *et al*., 2012).

Korytár *et al*. (2005) compiled an extensive retention-time database for PBDE congeners using different capillary GC columns and reported on elution patterns for the hundred twenty-six PBDE congeners analysed. Sixty-three co-elutions were reported for the DB-5 (30 m × 0.25 mm × 0.25 µm) column

including the co-elution of BDE154 with BB153 and dimethylated tetrabromobisphenol-A (Me-TBBP-A). Covaci *et al*. (2003) provided a detailed summary of several potential chromatographic interferences and showed that BDE153 co-elutes with TBBP-A on a DB-5-type column and also suggested that BDE47 and BDE99 may have interferences with breakdown products of HBCD. Daso *et al*. (2011) reported on the co-elution of BDE154 and BB153 using a 30 m (0.25 mm × 0.25 µm) column, this co-elution was resolved by using a longer thin film column (60 m × 0.25 mm × 0.1 µm). Olukunle *et al*. (2012) analysed 16 PBDE congeners using a 30 m DB-5 column and found that BDE85 co-elutes with BDE126.

2.3. Quality assurance/ quality control

Accurate analysis of BFRs is important to facilitate scientists in providing reliable data for environmental policy makers. In order to minimize errors and ensure sufficient quality of data obtained, a number of quality assurance (QA) procedures, that include quality control (QC) measures, should be applied prior and during analysis. This includes the use of high quality calibrants such as certified reference materials (CRM), blank analysis (procedural and method blanks), recovery experiments, analysis of matrix matched CRMs and the participation in inter-laboratory studies (Covaci *et al*., 2003).

In the reviewed papers, where analysis was performed in Africa, special reference was made to ensure that glassware used during the analysis was sufficiently cleaned to eliminate any contamination (de Boer and Cofino, 2002; de Boer and Wells, 2006). Solvent and method blanks were regularly analysed and authors typically reported on the absence of any BFRs, with one exception where detectable levels were found in the method blanks and blank correction was applied (Daso *et al*., 2015). Blank correction procedure is not recommended as the background should preferably be clean enough to provide minimal blank values. Depending on the sample clean-up procedure and the detection method employed, column selection should also include the evaluation of possible co-elution of target analytes and structurally related analytes present in the sample. Limited information on chromatographic interferences with BFR target analytes were reported in the reviewed papers.

The reliability of the obtained result significantly increases with the use of $^{13}C_{12}$-labelled standards as internal standards (IS) and/ or syringe standards (SS) (de Boer and Cofino, 2002), but these standards do have additional financial implications on the analysis. Only one study described the use of $^{13}C_{12}$-labelled BDE analogues added prior to extraction where recoveries were used to assess method

accuracy (Daso *et al*., 2015). Matrix matched CRMs are commercially available from different suppliers and used to assess precision and trueness of measurement methods, calibration, establishing traceability, and generally to assist in method validation (ISO GUIDE 33, 2015). Due to limited availability of CRMs for some of the investigated matrices, matrix matched QC samples were used (Chokwe *et al*., 2012, 2015a, 2015b; Daso *et al*., 2013a, 2016; Odusanya *et al*., 2009; Olukunle and Okonkwo, 2015; Olukunle *et al*., 2012, 2014). For the analysis of dust, a dust CRM was regularly used to assess apparent recoveries (Kefeni and Okonkwo, 2013, 2014; Kefeni *et al*., 2014; Olukunle *et al*., 2015a, 2015b). Abafe and Martincigh (2014, 2015) used this CRM to assess the method accuracy and it is not clear if this was included in the result uncertainties. Although matrix matched CRMs were included for PBDE analysis, the results were mainly used for recovery studies. The obtained values often did not overlap within the uncertainty of the reference value, indicating that the methods might not be fully mastered and more routine analyses are needed. Data reliability has to be seriously addressed. In one case it was found that identical CRM recovery data were presented for two different extraction techniques giving a false indication of the method performance (Olukunle *et al*., 2015a, 2015b). Results from the second round (2012/ 2013) of the biennial global inter-laboratory assessment on persistent organic pollutants showed very low participation from Africa and only one laboratory submitted results for PBDEs (http://www.unep.org/chemicalsandwaste/Science/tabid/268/Default.aspx). This study concluded that training and capacity building for POP analysis are still needed in developing regions, including Africa.

As shown in Table 2, various detection limits were reported and included instrumental detection limit (IDL), method detection limit (MDL) and limit of detection (LOD). These detection limits are dependent on the instrument detection technique, sample amount used and blank interferences. Limit of quantification (LOQ) was only reported in four studies (Abafe and Martincigh, 2014; Chokwe *et al*., 2012, 2015c; Kefeni *et al*., 2011).

Considerable efforts were undertaken to address general aspects of QA/QC which include precautionary measures with sample treatment, glassware cleaning and regular analysis of instrumental (solvent) and procedural blanks. More emphasis needs to be placed on information required to achieve acceptable accuracy and precision for the qualitative analysis and analysis performance relating to laboratory participation in international proficiency tests. Limited or incomplete information was often provided for QA/QC related to instrumentation. This needs to be critically

evaluated and reported to reach adequate chromatographic resolution of complex mixtures, reproducible mass spectra, reasonable detection limits and acceptable stability of target analyte response. Criteria should be set for analyte retention time deviation and identification based on definite abundance of analyte specific ion ratios.

3. BFR levels reported in environmental samples

Table 3 provides an overview of PBDE levels in various matrices sampled in Africa. The BFR levels reported in each matrix is discussed and include indoor dust, soil, aquatic environment (water, sediment, and aquatic organisms), eggs, wastewater treatment plant compartments, landfills (leachate and sediment), and human breast milk.

3.1. Indoor dust

Indoor dust is a complex heterogeneous mixture of organic compounds and particle-bound matter present in homes, schools, offices, hotels and cars. Indoor dust is always in close proximity to human activity. Dust in the indoor environment can therefore be a major source of human exposure to environmental contaminants and may even be the largest route of PBDE exposure to toddlers (Jones-Otazo *et al*., 2005).

BFR levels were reported for dust samples from South Africa, Nigeria and Egypt. Kefeni *et al*. (2011) reported on the presence of BDE209 in dust from a computer classroom, offices and hotel rooms in South Africa. Average concentrations obtained from office dust (103 ng g^{-1}) and hotel rooms (118 ng g^{-1}) were higher than reported for surface wipes from the computer classroom (26 ng g^{-1}). Subsequently, a comprehensive study was undertaken to determine the concentrations of sixteen PBDE and PBB congeners in pooled dust samples taken from offices at the same university (Kefeni and Okonkwo, 2012). Although BDE99 and 47 were the only congeners found with median concentrations above the LOD with detection frequencies of 81 and 63%, respectively. The mean concentration for the Σ_6PBDE was 169 ng g^{-1}, with BDE209 concentrations ranging from <LOD to 571 ng g^{-1}. BB209 was the dominant PBB congener and mean concentration for the Σ_5PBB was 38 ng g^{-1}. Abafe and Martincigh (2014) analysed PBDEs in dust from homes, computer laboratories and offices and reported mean Σ_8PBDE levels ranging from 818 to 1 710 ng g^{-1}. BDE209 was the dominant congener in the house and office samples, with BDE153 dominant in the samples collected from the computer rooms. Indoor dust was also collected from two e-waste dismantling and recycling facilities and an electronic repair workshop

Table 3
Summary of PBDE occurrence in Africa.

Matrix	Country	Samples	Congeners	Dominant congeners	ΣPBDE concentration range	ΣPBDE concentration	Ref.
Dust	South Africa	Offices	BDE209	-	-	103 ng g^{-1} (mean)	(Kefeni *et al*., 2011)
Dust	South Africa	Hotel rooms	BDE209	-	-	118 ng g^{-1} (mean)	(Kefeni *et al*., 2011)
Dust	South Africa	Computer room	BDE209	-	-	26 ng g^{-1} (mean)	(Kefeni *et al*., 2011)
Dust	South Africa	Offices	BDE47, 66, 85, 99, 153, 209	BDE99 > 47	21.4 - 578.6 ng g^{-1}	169.1 ng g^{-1} (mean)	(Kefeni and Okonkwo, 2012)
Dust	South Africa	Offices	BDE15, 47, 66, 85, 99, 100, 153, 154, 209	BDE99 > 47	5.8 – 86.3 ng g^{-1} (mean)	-	(Kefeni and Okonkwo, 2013)
Dust	South Africa	Homes	BDE15, 47, 66, 85, 99, 100, 153, 154, 209	BDE99 > 47	1.5 – 20.6 ng g^{-1} (mean)	-	(Kefeni and Okonkwo, 2013)
Dust	South Africa	Homes	BDE3, 15, 47, 66, 85, 99, 100, 153, 154, 209	BDE209 > 99	<0.3 – 234 ng g^{-1}	18.3 ng g^{-1} (median)	(Kefeni *et al*., 2014)
Dust	South Africa	Homes	BDE3, 15, 47, 66, 85, 99, 100, 153, 154, 209	BDE209 > 99	30.9 - 205 ng g^{-1}	-	(Kefeni and Okonkwo, 2014)
Dust	South Africa	Offices	BDE3, 15, 47, 66, 85, 99, 100, 153, 154, 209	BDE209 > 99	73.8–625 ng g^{-1}	-	(Kefeni and Okonkwo, 2014)
Dust	South Africa	Homes	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209	689 – 3 290 ng g^{-1} (mean)	1 710 ng g^{-1} (mean)	(Abafe and Martincigh, 2014)
Dust	South Africa	Computer rooms	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE153	319 – 2 720 ng g^{-1} (mean)	818 ng g^{-1} (mean)	(Abafe and Martincigh, 2014)
Dust	South Africa	Offices	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209	226 – 5 020 ng g^{-1} (mean)	1 520 ng g^{-1} (mean)	(Abafe and Martincigh, 2014)
Dust	South Africa	W/EEE facilities	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209 > 99	2 632 – 44 203 ng g^{-1}	20 094 ng/g (mean)	(Abafe and Martincigh, 2015)
Dust	Nigeria	Homes	BDE47, 99, 100, 153, 154, 183, 209	BDE209 > 47	-	57 ng g^{-1} (mean)	(Olukunle *et al*., 2015a)
Dust	Nigeria	Offices	BDE47, 99, 100, 153, 154, 183, 209	BDE209 > 153	-	79.8 ng g^{-1} (mean)	(Olukunle *et al*., 2015a)
Dust	Nigeria	Cars	BDE47, 99, 100, 153, 154, 183, 209	BDE209	159 – 736 ng g^{-1} (mean)	-	(Olukunle *et al*., 2015b)
Dust	Egypt	Homes	BDE17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 209	BDE209	5.04 – 1 918 ng g^{-1}	248 ng g^{-1} (mean)	(Hassan and Shoeib, 2015)
Dust	Egypt	Workplaces	BDE17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 209	BDE209	38.1 – 72 279 ng g^{-1}	14 993 ng g^{-1} (mean)	(Hassan and Shoeib, 2015)
Dust	Egypt	Cars	BDE17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 209	BDE209	171 – 37 440 ng g^{-1}	6 943 ng g^{-1} (mean)	(Hassan and Shoeib, 2015)
Soil	Tanzania	Mount Meru	BDE17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190	BDE47 > 99	136 – 952 pg g^{-1} dw	386 pg g^{-1} dw (mean)	(Parolini *et al*., 2013)
Soil	Kenya	Rural areas	BDE28, 47, 99, 100, 153, 154, 183	BDE99/47	2.54 – 13.65 ng g^{-1} dw (mean)	-	(Sun *et al*., 2016)
Soil	Kenya	Suburban area	BDE28, 47, 99, 100, 153, 154, 183	BDE47	1.12 – 4.20 ng g^{-1} dw	2.19 ng g^{-1} dw (mean)	(Sun *et al*., 2016)
Soil	Kenya	Conservancy	BDE28, 47, 99, 100, 153, 154, 183	BDE28	0.19 – 3.13 ng g^{-1} dw	1.03 ng g^{-1} dw (mean)	(Sun *et al*., 2016)
Water	South Africa	River	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE47	2.60 – 4.83 ng L^{-1} (mean)	-	(Daso *et al*., 2013a)
Water	South Africa	River	BDE99, 100, 153, 154, 183	-	0.09–0.26 µg L^{-1}	-	(Chokwe *et al*., 2015b)
Sediment	South Africa	River	BDE28, 47, 99, 100, 153, 154, 183	BDE99 > 153	-	4.63 ng g^{-1} dw (mean)	(Daso *et al*., 2011)
Sediment	South Africa	Rivers	BDE28, 47, 99, 100, 153, 154, 183	BDE183 > 99	0.00 - 4.43 ng g^{-1} dw (mean)		(Daso *et al*., 2011)
Sediment	South Africa	River	BDE17, 28, 47, 66, 77, 99, 85, 153, 138,183, 209	BDE209 > 99	0.92 - 6.76 ng g^{-1} dw	23.85 ng g^{-1} dw (sum)	(Olukunle *et al*., 2012)
Sediment	South Africa	Rivers	BDE28, 47, 66, 85, 99, 100, 153, 154, 183,206, 209	BDE209 > 99	ND – 46 300 ng g^{-1} TOC	3 750 ng g^{-1} TOC (mean)	(La Guardia *et al*., 2013)
Sediment	South Africa	Rivers	BDE17, 47, 99, 100, 153, 154, 183, 209	BDE100	0.8 - 44 ng g^{-1} (mean)	2.4 ng g^{-1} (mean)	(Olukunle *et al*., 2014)
Sediment	South Africa	River	BDE99, 100, 153, 154, 183	Not discussed	10.5 – 24.5 ng g^{-1} ww	-	(Chokwe *et al*., 2015b)
Sediment	South Africa	River	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209	0.06 – 2.47 ng g^{-1} (mean)	-	(Daso *et al*., 2016)
Sediment	South Africa	River	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE47	0.22 – 9.95 ng g^{-1} (mean)	-	(Daso *et al*., 2016)
Sediment	Senegal	Estuaries	BDE47, 99, 119, 153	BDE47/99	<LOQ – 1.2 ng g^{-1} dw (mean)	-	(Bodin *et al*., 2011)
Sediment	Tanzania	Rivers	BDE47, 99, 100, 153, 154, 183	BDE99> 47	38 – 2 175 pg g^{-1} dw	-	(Hellar-Kihampa *et al*., 2013)
Sediment	DRC	River Basin	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209 > 47	<LOQ – 0.49 ng g^{-1} dw (median)	-	(Verhaert *et al*., 2013)
Sediment	Uganda	Lake	BDE17, 28, 47, 66, 85, 99, 100, 138, 153, 154, 183	BDE47 > 99	60.8 – 179 pg g^{-1} dw (mean)	-	(Ssebugere *et al*., 2014)
Muscle	South Africa	Fish	BDE28, 47, 99, 100, 153, 154, 183	BDE99	11.58 - 18.68 ng g^{-1} (l.w)	-	(Chokwe *et al*., 2015a)
Muscle	South Africa	Fish	BDE47, 99, 100, 153, 154, 183	BDE99	4.63 –33 ng g^{-1} lw	-	(Chokwe *et al*., 2015b)
Muscle	Ghana	Fish	BDE15, 28, 47, 66, 99, 100, 154, 155, 197/204, 206, 207, 208, 209	BDE47 > 209	0.89 to 19 ng g^{-1} lw (mean)	7.3 ng g^{-1} lw (mean)	(Asante *et al*., 2013)
Muscle	DRC	Fish	BDE47, 99, 100, 153, 154	BDE99> 47	<LOQ - 188 ng g^{-1} lw	-	(Verhaert *et al*., 2013)
Muscle	Tanzania	Fish	BDE28, 47, 99, 100, 153, 154, 207, 208, 209	BDE209 > 47	1.5 – 34.3 ng g^{-1} lw (mean)	-	(Polder *et al*., 2014)
Muscle	Uganda	Fish	BDE17, 28, 47, 66, 85, 99, 100, 138, 153, 154, 183	BDE47 > 99	48.2 – 177 pg g^{-1} lw (mean)	-	(Ssebugere *et al*., 2014)
Eggs	South Africa	Birds	BDE28, 47, 99, 100, 153, 154, 183, 209	-	2.3 – 396 ng g^{-1} lw (mean)		(Polder *et al*., 2008)
Eggs	Rodrigues	Birds	BDE47, 99, 100, 153, 154, 183, 206, 207, 208	BDE47 > 100	0.7 – 0.8 ng g^{-1} lw (mean)		(Bouwman *et al*., 2012)
Eggs	South Africa	Birds	BDE28, 47, 99, 100, 153, 154, 183, 207, 208, 209	-	<LOQ – 61 ng g^{-1} lw (mean)	-	(Bouwman *et al*., 2013)
Eggs	South Africa	Birds	BDE47, 99, 100, 153, 154, 183, 206 207, 208, 209	-	0.33 – 2.3 ng g^{-1} ww (median)	-	(Bouwman *et al*., 2015)
Eggs	South Africa	Penguins	BDE47, 99, 100, 153, 154, 183, 206 207, 208, 209	-	0.14 – 2.3 ng g^{-1} ww (median)	-	(Bouwman *et al*., 2015)

Eggs	South Africa	Crocodiles	BDE28, 47, 99, 100, 154, 183	-	1.6 – 3.3 ng g^{-1} lw (mean)	-	(Bouwman *et al*., 2014)
Eggshells	South Africa	Birds	BDE17, 47, 99, 100, 153, 154, 183, 209	BDE47/100	46.63 – 80.77 µg g^{-1} lw (mean)	-	(Daso *et al*., 2015)
Eggs	Tanzania	Chickens	BDE28, 47, 99, 100, 153, 154, 183, 206, 207, 208, 209	BDE209 > 183	19 – 81 ng g^{-1} lw (mean)	40 ng g^{-1} lw (median)	(Polder *et al*., 2016)
Leachate	South Africa	Landfills	BDE28, 47, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 183	BDE47 > 71	8392 – 54 761 pg L^{-1} (mean)	-	(Odusanya *et al*., 2009)
Leachate	South Africa	Landfills	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209	0.28 – 2 240 ng L^{-1} (mean)	-	(Daso *et al*., 2013b)
Leachate	South Africa	Landfills	BDE47, 99, 100, 153, 154, 183, 209	-	127 – 3 703 pg L^{-1}	-	(Olukunle *et al*., 2014)
Sediment	South Africa	Landfills	BDE47, 99, 100, 153, 154, 183, 209	BDE209 > 99	0.8 – 8.4 ng g^{-1} dw	-	(Olukunle *et al*., 2014)
Effluent	South Africa	WWTP	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209 > 99	2.48 – 1240 ng L^{-1} (mean)	-	(Daso *et al*., 2012)
Sludge	South Africa	WWTP	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209 > 47	2.09 – 48.4 ng g^{-1} (mean)	-	(Daso *et al*., 2012)
Breast milk	Ghana	Humans	BDE15 28, 47, 99, 100, 153, 154, 183, 196, 197, 206, 207, 209	BDE47	0.86 – 18 ng g^{-1} lw	4.5 ng g^{-1} lw (mean)	(Asante *et al*., 2011)
Breast milk	South Africa	Humans	BDE28, 47, 66, 99, 100, 153, 154, 183	BDE183	0.7 – 6.3 ng g^{-1} lw	1.7 ng g^{-1} lw (mean)	(Darnerud *et al*., 2011)
Breast milk	Tunisia	Humans	BDE28, 47, 66, 99, 100, 138, 153, 154, 183	BDE183 > 47	2.49 – 22.62 ng g^{-1} lw (mean)	10.74 ng g^{-1} lw (mean)	(Hassine *et al*., 2012)
Breast milk	Tanzania	Humans	BDE28, 47, 99, 100, 153, 154, 183	BDE99 > 47	<LOD – 785.8 ng g^{-1} lw (median)	19.8 ng g^{-1} lw (median)	(Müller *et al*., 2016)

(Abafe and Martincigh, 2015). Mean Σ_8PBDE levels were 20 094 ng g^{-1} and varied from 2 632 to 44 203 ng g^{-1}, with BDE209 and 99 as the dominant congeners with BDE209 levels ranging from 1 862 to 34 010 ng g^{-1}. The PBDE levels in dust from the electronic workshop were lower than reported for recycling facilities (Abafe and Martincigh, 2015).

Dust samples from cars in four states in Nigeria presented Σ_7PBDE concentrations from 159 to 736 ng g^{-1} (Olukunle *et al*., 2015b). BDE209 was the main congener contributing up to 47% with a detection frequency of 92%. BDE47 was detected in all samples. Pooled dust samples collected from ten houses and eleven offices in Nigeria showed PBDE detection frequencies between 70 and 100% (Olukunle *et al*., 2015a). BDE209 had mean concentrations of 141 ng g^{-1} in house dust and 180 ng g^{-1} in office dust.

Hassan and Shoeib (2015) investigated PBDE and alt-BFR levels in house, workplace and car dust samples from Egypt. The mean Σ_{14}PBDE concentrations ranged from 248 to 14 993 ng g^{-1} for the investigated areas. BDE209 was reported as the dominant congener with concentrations ranging from 2.20 to 591 ng g^{-1} in the houses, 26 to 72 096 ng g^{-1} in the workplaces and 159 to 36 927 ng g^{-1} in the cars (manufactured between 1999 and 2012) (Hassan and Shoeib, 2015). Eleven alt-BFRs including; ally-2,4,6- tribromophenyl ether (ATE), beta-tetrabromoethylcyclohexane (*β*-TBECH), 2-bromoallyl-2,4,6-tribromophenyl ether (BATE), beta-1,2,5,6 tetrabromocyclooctane (*β*-TBCO), bis (2-ethyl-1-hexyl) tetrabromo phthalate (TBPH), hexabromobenzene (HBB), hexabromocyclododecane (HBCD), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB), 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE) and Dechlorane plus (syn-DP, anti-DP) were also analysed in the respective matrices. ΣHBCD was shown to be the most abundant alt-BFR detected in all three matrices, with mean concentrations ranging from 20.7 to 47.7 ng g^{-1}. EHTBB levels were reported to be 2 to 5-fold lower than the penta-BDE concentrations. The concentrations for ATE, *β*-TBECH, BATE, *β*-TBCO and TBPH were present at higher concentrations in car samples with maximum concentrations ranging from 1.34 to 18.9 ng g^{-1} (Hassan and Shoeib, 2015).

3.2. Soil

Parolini *et al*. (2013) reported background levels for PBDEs in soil from the Mount Meru area in the Arusha district, Tanzania. Surface soil samples were collected at different altitudes at the end of the dry season. The Σ_{13}PBDE ranged from 136.35 to 952.15 pg g^{-1} dry weight (dw) with a mean concentration of 386 pg g^{-1} dw; BDE47 was reported as the main congener followed by BDEs 99, 190 and 100 (Parolini

et al., 2013). PBDE concentrations initially decreased with altitude, followed by a consistent increase with altitude. This effect was previously observed and discussed by Wang *et al*., (2009a). The initial decrease in concentration could be due to a dilution effect as the distance from the anthropogenic influence, or possible source of emission, increases; the subsequent increase in concentration might be due to a condensation or distillation effect as a result of the decreased temperature with altitude. Sun *et al*. (2016) investigated organohalogenated contaminant concentrations in soils from Kenya. Soil samples were collected from three rural areas, a suburban area and at Mount Suswa conservancy surrounding Nairobi. The mean Σ_7PBDE concentrations in the soil samples from the rural areas ranged from 2.54 to 13.65 ng g^{-1} dw, with concentrations in the suburban and conservancy area of 2.19 and 1.03 ng g^{-1}, respectively (Sun *et al*., 2016).

The PBDE concentrations in soil from Tanzania and Kenya were higher than reported for north-eastern China (Wang *et al*., 2009b) and Sweden (Sellström *et al*., 2005). Although the levels for Tanzania were comparable with results reported for background levels in UK (Hassanin *et al*., 2004), levels reported for Kenya were much higher. PBDEs found in soil from pristine mountain areas showed an increase in concentration associated with increased altitude and levels were higher than those reported for the east edge of the Tibetan Plateau (Zheng *et al*., 2012).

3.3. Aquatic environment

Information on PBDE levels in dissolved and suspended phases of water samples is scarce due to the compounds' hydrophobicity, which will cause preferred adsorption to particulate matter and deposition in sediments (Wurl *et al*., 2006). The entire aquatic environment including water, suspended particulate matter, sediments and aquatic organisms analysed in samples from Southern, Central and Western Africa are discussed in this section.

Daso *et al*. (2013a) reported on eight PBDE and BB153 concentrations in river water. Sampling was done at three locations: upstream, at the point where effluent from a wastewater treatment plant (WWTP) enters the river and downstream from the outlet point. Mean Σ_8PBDEs concentrations of 2.60, 4.83 and 4.29 ng L^{-1} were reported for the respective sampling points. The concentration of BB153 was highest at the discharge point (Daso *et al*., 2013a). The Σ_8PBDE levels for sediment taken from two rivers in South Africa ranged from 5.32 to 239 ng g^{-1} dw with BDE209 as the major congener in the first river and BDE47 as the major congener in the second river (Daso *et al*., 2016). River sediment samples

from six rivers were also analysed and Σ_8PBDE concentrations ranged from 0.8 to 44 ng g^{-1} (Olukunle *et al*., 2014). The Σ_8PBDE concentrations (44 ng g^{-1}) reported for one of the rivers was significantly higher than previously reported for the same region (Olukunle *et al*., 2012). La Guardia *et al*. (2013) determined concentrations of eleven PBDEs, EHTBB, TBPH, BTBPE, DBDPE and *α*-, *β*-, *γ*-HBCD in inland and coastal sediment in South Africa and found higher alt-BFR than PBDE levels, with BDE209 and 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB) as the most frequently detected compounds. Levels of up to 46 300 ng g^{-1} total organic carbon (TOC) for Σ_{11}PBDE were reported for inland sediment and the median concentration at the Durban Bay area was 3 240 ng g^{-1} TOC, varying from 1 850 to 25 400 ng g^{-1} TOC (La Guardia *et al*., 2013). These levels were higher than previously reported for San Francisco Bay (Klosterhaus *et al*., 2012) and comparable with the studies from the Pearly River Estuary in China (Mai *et al*., 2005). Wepener *et al*. (2011) assessed the influence of multiple stressors on a river in South Africa by collecting fish at various points and reported a mean concentration for the ΣPBDE that ranged from 5.9 to 43.4 ng g^{-1} lipid weight (lw).

Hellar-Kihampa *et al*. (2013) studied sediments collected during different seasons from the Pangani river basin (PRB) in Tanzania. The most frequently detected PBDEs were BDE99, with concentrations ranging from 38 to 1 097 pg g^{-1}, and BDE47 ranging from 50 to 734 pg g^{-1}. The Σ_6PBDE concentrations ranged from 38 to 920 pg g^{-1} during the dry season, 295 to 2 175 pg g^{-1} before the rainy season and 50 to 940 pg g^{-1} during the rainy season (Hellar-Kihampa *et al*., 2013). PBDE concentrations were determined in sediments and fish from the Murchison Bay of Lake Victoria (Uganda) (Ssebugere *et al*., 2014). The mean Σ_{11}PBDE concentrations for sediment ranged from 60.8 to 179 pg g^{-1} dw and from 48.2 to 177 pg g^{-1} lw for fish samples (Ssebugere *et al*., 2014). Similarly, as with to the sediment samples, BDE47 was the dominant congener followed by BDE99 (BDE209 was not analysed due to analytical limitations). Verhaert *et al*. (2013) reported on PBDE levels in sediments and biota from the Congo River Basin (CRB). The ΣPBDE concentrations ranging from < LOQ to 1.9 ng g^{-1} dw for sediment, < LOQ to 7.9 ng g^{-1} lw for invertebrate and < LOQ to 188 ng g^{-1} lw for fish samples. BDE209 was the major congener in the sediment, with BDE47 and 99 dominant in the biotic samples (Verhaert *et al*., 2013). The presence of halogenated contaminants was also analysed in inland and coastal fish from Ghana and mean Σ_{14}PBDE concentrations for three fish species ranged from 0.89 to 19 ng g^{-1} lw with BDE47 and 99 as the dominant congeners (Asante *et al*., 2013). Polder *et al*. (2014) investigated the levels and patterns of POPs in fish from four different lakes in Tanzania. BDE209 had the highest

concentrations and mean Σ_9PBDE concentrations ranged from 1.5 to 34.3 ng g^{-1} lw for the different lakes. HBCD was found in 78% of the samples from one lake with mean ΣHBCD concentrations of 2.4 ng g^{-1} lw (Polder *et al*., 2014). PBDEs, with BDEs 47 and 99, were irregularly detected at low concentrations in sediment and mollusc samples collected from a delta and a stretch of coast in Senegal (Bodin *et al*., 2011).

3.4. Eggs

Polder *et al*. (2008) reported on levels of PBDEs and HBCD in eggs of different bird species in South Africa. The mean Σ_8PBDE concentrations for eight species ranged from 2.3 to 396 ng g^{-1} lw. The PBDE congener pattern displayed inconsistencies, imitating diverse trophic levels, migratory behaviour, and exposure distance to different PBDE mixtures (Polder *et al*., 2008). Low BFR levels were reported for eggs collected from terrestrial and aquatic birds in the most northern part of South Africa, with mean Σ_{10}PBDE concentration ranges from < LOQ to 61 ng g^{-1} lw (Bouwman *et al*., 2013). PBDE levels were investigated in eggshells of the population declining Southern Ground-Hornbill (SGH) and Wattled Crane (WC) (Daso *et al*., 2015). The Σ_8PBDE concentrations were 46.63 and 80.77 µg g^{-1} lw for the SGH and WC eggshells. The WC eggs' outer membranes containing possible traces of albumin were separately analysed for the content of PBDEs. The mean Σ_8PBDE concentrations were found to be greater than the concentrations reported for the eggshells (Daso *et al*., 2015). Exposure to environmental PBDE levels was reported to be a possible contributor to the poor breeding success and therefore the decline in population of the WC, but more data is needed to support these findings. The halogenated organic pollutants were also studied in African Penguin and Nile crocodile eggs (Bouwman *et al*., 2015, 2014). The mean Σ_{10}PBDE concentration reported for penguin eggs ranged from 0.14 to 2.3 ng g^{-1} wet weight (ww) and bird species included in the study, reported similar concentrations (Bouwman *et al*., 2015). Nile crocodile eggs collected after an unexpected incident of deaths in June 2008 showed mean Σ_6PBDE concentrations ranging from 0.02 to 0.44 ng g^{-1} ww (Bouwman *et al*., 2014). Although BFR concentrations were irregularly reported at low concentrations, this study presented the first data on BFRs in crocodile eggs.

Bouwman *et al*. (2012) reported on POP levels in marine bird eggs from an oceanic island in the Indian Ocean. The eggs from two species had mean Σ_9PBDE concentrations of 0.7 ng g^{-1} lw with both BDE47 and 100 at quantifiable levels (Bouwman *et al*., 2012). As part of a project to monitor and assess

contaminant risk in Southern Africa, Polder *et al*. (2016) studied the occurrence of POPs (including BFRs) in native free-range chicken eggs from urban transition in Tanzania. Collective egg samples from four villages showed the prevalent occurrence of BFRs, specifically BDE209, HBCD and BTBPE. The mean concentrations of the Σ_{11}PBDE was 40 ng g^{-1} lw ranging from 19 to 81 ng g^{-1} lw with mean HBCD concentrations of 8.4 ng g^{-1} lw (Polder *et al*., 2016). This study reported the occurrence of BTBPE in the African environment for the first time, with mean concentrations of 2.3 ng g^{-1} lw varying from 0.79 to 4 ng g^{-1} lw.

3.5. Landfills

Leachates and sediment from landfills are complex environmental matrices containing organic and inorganic compounds mainly determined by the composition and solubility of the waste constituents. BFRs were only analysed in leachate samples from South Africa. Odusanya *et al*. (2009) found PBDEs in leachate samples collected from five landfills. The mean Σ_{13}PBDEs (excluding BDE209) concentrations ranged from 8 392 to 54 761 pg L^{-1} with BDE47 as the major congener at three of the sites (Odusanya *et al*., 2009). Olukunle *et al*. (2014) analysed PBDEs in landfill leachate and sediment samples from six operational landfills and high detection frequency for BDE47, 99, 100, 153, 154, 183 and 209 was reported. The concentrations for the Σ_7PBDEs for the leachates range from 127 to 3703 pg L^{-1}, with BDE209 concentrations up to 1 930 pg L^{-1} (Olukunle *et al*., 2014). The levels for two of the landfills were lower than reported by Odusanya *et al*. (2009), collected from the same sites. Landfill sediment samples reportedly contained Σ_7PBDE concentrations ranging from 0.8 to 8.4 ng g^{-1} dw (Olukunle *et al*., 2014). Leachate samples, collected from three landfills over a one year period showed increased BDE concentrations for the period with a high frequency of rainfall (Daso *et al*., 2013b). The mean concentration for Σ_8PBDEs ranged from 0.28 to 2 240 ng L^{-1} and BDE209 was reported as the major congener followed by BDE153 and 183. BB153 concentrations ranged from 7.14 to 70.4 ng L^{-1} (Daso *et al*., 2013b). In the only study targeting alt-BFRs in leachate and sediment samples from six landfill sites, EHTBB, Bis-(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEHTEBP), BTBPE, DBDPE and ΣHBCD were analysed (Olukunle and Okonkwo, 2015). Concentrations in the leachate samples ranged from 8.7 to 142 pg L^{-1} for EHTBB, 4.8 to 40 pg L^{-1} for ΣHBCD and 4.4 to 15 pg L^{-1} for BTBPE. The sediment samples showed a detection frequency from < 20% to 50% for the alt-BFRs and DBDPE was not detected in any of the samples (Olukunle and Okonkwo, 2015).

3.6. Wastewater treatment plants

Daso *et al*. (2012) collected effluent and sludge samples over a one year period at different purification process stages of a WWTP in South Africa. For effluent samples, BDE28, 47, 99 and 209 were reported as the dominant congeners. The mean Σ_8PBDEs concentrations range from 369 to 4 370 ng L^{-1} for the raw water, 19.2 to 2 640 ng L^{-1} for the secondary effluent and 90.4 to 15 100 ng L^{-1} for the final effluent (Daso *et al*., 2012). The authors concluded that WWTPs might be seen as a source for PBDE exposure to aquatic environments. Sludge collected from the dewatering unit had mean Σ_8PBDE concentrations from 2.09 to 48.4 ng g^{-1} dw with BDE47, 153, 183 and 209 as the dominant congeners (Daso *et al*., 2012). Alt-BFRs were also analysed in sludge samples collected prior to the digestion process from three different WWTPs in South Africa and showed irregular detection of TBBPA and ΣHBCD (Chokwe *et al*., 2015c). One of the investigated sites reported concentrations of 19.24 ng g^{-1} for TBBPA and 133.16 ng g^{-1} for ΣHBCD. (Chokwe *et al*., 2015c).

3.7. Breast milk and serum

Human breast milk and blood/ serum are used as markers to assess human exposure to POPs and BFRs and provide information on contaminant transfer to infants. Four studies reported on BFR levels in breast milk collected from South Africa, Tunisia, Ghana and Tanzania. Darnerud *et al*. (2011) investigated non-occupational exposure to BFRs by collecting breast milk samples from mothers residing in a rural district in South Africa. Mean Σ_8PBDE concentrations were reported as 1.7 ng g^{-1} lw ranging from 0.7 to 6.3 ng g^{-1} lw. BDE47, 99, 153 and 183 were the dominant congeners, and one of the analysed samples reported a BDE183 level of 4.5 ng g^{-1} lw. Hassine *et al*. (2012) determined PBDE concentrations in breast milk collected in Tunisia; the Σ_8PBDE ranged from 2.49 to 22.62 ng g^{-1} lw with a mean concentration of 10.74 ng g^{-1} lw. BDE183 was the dominant congener with a concentration of 2.49 ng g^{-1} lw followed by BDE47 and 153 (Hassine *et al*., 2012). Asante *et al*. (2011) analysed breast milk samples collected in Ghana during 2004 and 2009 to evaluate human exposure to BFRs. The mean Σ_{16}PBDE concentrations (excluding BDE209) for the samples collected in 2004 were reported as 2.2 ng g^{-1} lw and the Σ_{17}PBDE (including BDE209) in 2009 were reported as 4.5 ng g^{-1} lw. BDE47, 209, 99, 100, and 153 were reported as the dominant congeners. Higher PBDE levels were reported for milk collected from urban areas as compared to rural areas. The ΣHBCD concentrations ranged between 0.01 and 3.2 ng g^{-1} lw with a mean concentration of 0.54 ng g^{-1} lw (Asante *et al*., 2011). This is in good agreement with the concentration for ΣHBCD (0.55 ng g^{-1} lw) reported for South Africa (Darnerud *et al*.,

2011). Linderholm *et al*. (2010) investigated serum collected from adult men between 1990 and 2007 in Guinea-Bissau. Low PBDE levels were reported with BDE209 and 153 as the major congeners. No temporal trend was observed for BDE209 while BDE153 levels increased over time. Müller *et al*. (2016) assessed BFR levels in breast milk from mothers in the northern part of Tanzania. The median concentrations for the Σ_7PBDE were 19.8 ng g^{-1} lw and ranged from <LOD to 785.8 ng g^{-1} lw with BDE47, 99, 100 and 153 detected in more than 80% of the samples. BDE28, 154, 183 and HBCD reported detection frequencies of > 40% and HBB, PBEB, 2,3,4,5,6-pentabromotoluene (PBT), BTBPE and (2,3-Dibromopropyl) (2,4,6-tribromophenyl) ether (DPTE) were not detected. Higher levels for BDE47 were reported for samples collected from mothers living in urban areas compared to rural areas (Müller *et al*., 2016). In this study, mothers consuming a clay product, used as a mineral supplement and anti-emetic for pregnancy related nausea, had higher BDE47, 99, 100 and 153 levels than individuals who did not take the product during pregnancy (Müller *et al*., 2016). The PBDE levels reported for Tanzanian breast milk samples were higher than previously reported for Europe and Asia (Frederiksen *et al*., 2009). The BDE congener profiles were dominated by BDE99 and 47 in samples collected from Tanzania and Ghana (Asante *et al*., 2011; Müller *et al*., 2016), and BDE183 in South Africa and Tunisia (Darnerud *et al*., 2011; Hassine *et al*., 2012).

The Secretariat of the SC, the United Nations Environment Programme (UNEP) and the World Health Organization (WHO) implemented a global monitoring plan to provide a consistent framework to present global differences for POPs listed in the Stockholm Convention in human breast milk (UNEP, 2013). Results from the survey showed large variations in global POP contamination; contamination associated with dioxin-like compounds was among the highest for certain African countries (UNEP, 2013). Results pertaining to PBDEs showed their ubiquitous presence with high levels reported for pooled samples from industrialised countries, such as USA and Australia, the Pacific Islands and countries in Latin American and the Caribbean (UNEP, 2013).

Since 2008, an increased number of reports on the presence of BFRs in the African environment is being produced. Most of the reports contain valuable information on the manifestation of these compounds in all environmental compartments and differences in concentrations may reflect differences in exposure routes. Recent publications provide information indicating an increase in BFR concentrations reported for dust, sediment and breast. Indoor dust samples also showed that work environments contain HBCD and levels reported for banned penta-BDE formulations were higher than

for BFR replacements. The redistribution of BFRs to aquatic environments was mostly associated with more industrialised cities with high PBDE concentrations reported for sediment. Although data on landfills and WWTPs were only available for South Africa, this was seen as a major source. Limited information is however available on the usage of BFRs in Africa and it is likely that these compounds enter the African environment through the use and disposal of manufactured and imported BFR-containing products, and from non-point sources such as atmospheric fallout and urban runoff. The redistribution of these compounds to landfills, WWTPs, sediment and eventually to food (fish and chicken eggs) and humans (breast milk) underlines the need for ongoing investigation in support of continuous environmental and human monitoring to understand the origin, fate and impact of these chemicals. Despite the scarcity of systematic monitoring studies on BFR levels in the African environment, exposure to the general population seems to be highly variable between different geographical areas and even within countries.

4. Conclusion

Until recently, BFR analyses in Africa were effectively only carried out in South Africa. Although information on BFR contamination in other parts of Africa was available, this was often acquired through outsourced analyses in non-African countries or South Africa. Clearly, further development of analytical methodology, including sufficient QA/QC in the entire continent is needed.

Brominated flame retardant levels pertaining to indoor dust were limited to PBDEs and PBBs in South Africa and Nigeria, with information on the prevalence of PBDEs and alt-BFRs in Egypt. Recent publications from South Africa indicated that PBDE levels are comparable with the rest of the world. Dust PBDE levels from South Africa are higher than reported for Nigeria and Egypt. Limited information on the occurrence of alt-BFRs in indoor dust are available, with only one study for Egypt where ΣHBCD was shown to be the major alt-BFR. PBDEs found in soil from pristine mountain areas show an increase in concentration associated with increased altitude and levels are higher than reported for similar environments in central Asia. South Africa had higher PBDE levels in river sediment than reported for the rest of Africa. These were shown to be affected by seasonal rainfall. Sediment PBDE levels reported for Durban Bay are comparable and higher than reported for renowned contaminated areas in the USA and China. PBDE levels in fish from South Africa are comparable with levels reported for fish from different lakes in Tanzania. The prevalence and occurrence for BFRs in wild bird, and penguin eggs in

South Africa is dependent on the geographic area and dietary habits. Brominated flame retardants were commonly detected at low concentrations, with the highest levels reported for the African sacred ibis. Although at low levels, PBDEs were also reported in bird eggs collected from a remote island in the Indian Ocean. Chicken eggs from Tanzania reported high BFR levels indicating that the environment is exposed to commercial BDE mixtures and banned BFR replacements. BFRs in Landfills were only analysed in South Africa and showed irregular detection of PBDEs, with BDE209 as the major congener and regular presence of the tetra-, penta- and tri-BDE congeners. PBDE levels analysed in WWTP compartments in South Africa are lower than reported for river sediment. BFR levels were reported in human breast milk for South Africa, Tunisia, Ghana and Tanzania. The highest levels are reported for Tanzania, compared to South Africa, Tunisia and Ghana and countries in Europe and Asia.

The majority of countries in Africa, as signatories of the Stockholm Convention (SC), have the responsibility to undertake appropriate research, development, monitoring and cooperation pertaining to persistent organic pollutants including PBDEs. Due to lack of established monitoring programmes, Africa exclusively depended on global surveys such as programs implemented by the UNEP and WHO. Developing countries in Africa have limited facilities that specialise in BFR analysis and this has required the development of alternative approaches influenced by ease of operation, low cost and availability in most laboratories. In cases where BFR analyses were performed in Africa, liquid sample preparation was generally limited to LLE. Solid sample preparation included Soxhlet extraction which remains the default method for exhaustive extraction, with ultrasound-assisted extraction (UAE) increasingly being used. Clean-up and fractionation of BFRs mainly involved the use of miniaturised multi-layer silica columns. These sample preparation approaches were generally implemented from conventional methods developed for POPs and/ or BFR analysis. Considering instrumental techniques, analyses were limited to GC-ECD and GC-LR-EI-MS for the qualitative analysis of BFRs at low concentration levels with GC-TOFMS employed for structural confirmation. The inclusion of alt-BFRs and emerging contaminants in monitoring protocols highlights the need for commercially available reference standards (labelled and un-labelled) and appropriate matrix matched CRMs.

This study has shown that low BFR levels were mostly found in the studies reported for African environmental matrices. This raises the question whether the standard deviation related to repeated measurements, in several cases at or near the LOD, can realistically be used for the determination of uncertainty values. The calculation of uncertainty, for the analysis of organic contaminants in

environmental matrices is a complex process. Practical uncertainty contributions may include measurement reproducibility, the error associated with the concentration estimate (specifically if a concentration near or at the LOQ is reported) and the contribution as a result of bias (where matrix matched CRMs were analysed). To perform a realistic estimation of the measurement uncertainty for an analytical method, the parameters influencing the measurement result, as well as the magnitude of their effect, needs to be determined as fit for the intended purpose of the data being generated.

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