ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/259629083

Polybrominated Diphenyl Ethers and Alternative Flame Retardants in Air and Precipitation Samples from the Northern Lake Victoria Region, East Africa

ARTICLE *in* ENVIRONMENTAL SCIENCE & TECHNOLOGY · JANUARY 2014

Impact Factor: 5.33 · DOI: 10.1021/es403600a · Source: PubMed

CITATIONS
12

READS
65

6 AUTHORS, INCLUDING:

Kenneth Arinaitwe
Makerere University
4 PUBLICATIONS **19** CITATIONS
SEE PROFILE

Bernard Kiremire
Makerere University
46 PUBLICATIONS **339** CITATIONS
SEE PROFILE

Camilla Frances Teixeira
Environment Canada
42 PUBLICATIONS **1,805** CITATIONS
SEE PROFILE

Available from: Kenneth Arinaitwe
Retrieved on: 02 February 2016

Environmental Science & Technology

Article

pubs.acs.org/est

Polybrominated Diphenyl Ethers and Alternative Flame Retardants in Air and Precipitation Samples from the Northern Lake Victoria Region, East Africa

Kenneth Arinaitwe,*[,†] Derek C. G. Muir,[‡] Bernard T. Kiremire,[†] Phil Fellin,[§] Henrik Li,[§] and Camilla Teixeira[‡]

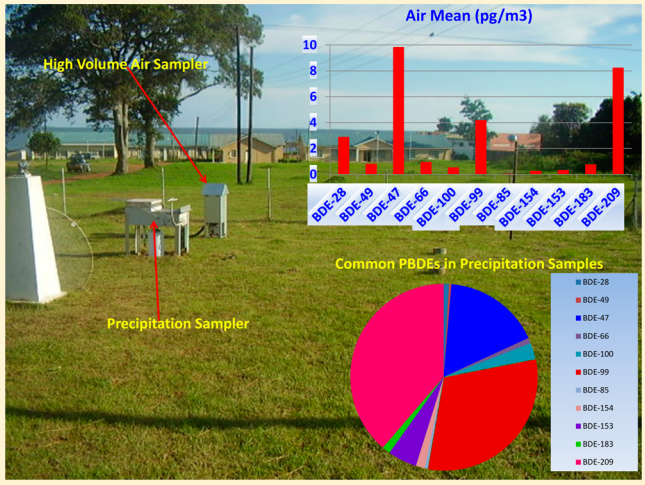
[†]Department of Chemistry, Makerere University, P.O. Box 7062, Kampala, Uganda

[‡]Aquatic Contaminants Research Division, Environment Canada, Burlington, Ontario, Canada

[§]AirZoneOne Inc., Mississauga, Ontario, Canada

Supporting Information

ABSTRACT: High volume air and precipitation samples were collected close to the shore of Lake Victoria at Entebbe, Uganda, between October 2008 and July 2010 inclusive. Polybrominated diphenyl ethers (PBDEs) and alternative flame retardants (AFRs) were analyzed by GC−MS. BDEs 47, 99, and 209 were the predominant PBDEs with mean concentrations (in air) of 9.84, 4.38, 8.27 pg m^{-3} and mean fluxes in precipitation of 3.40, 6.23, and 7.82 ng m^{-2} $sample^{-1}$, respectively. 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), and hexabromocyclododecane (HBCDD), *anti-* and *syn-*Dechlorane plus were detected at levels comparable with those of PBDEs. Both PBDEs and AFRs in air generally increased from 2008 to 2010. Elevated PBDE concentrations in air were associated with slow moving low altitude air masses from the region immediately adjacent to the lake, while low concentrations were mostly associated with fast moving westerly and southwesterly air masses. Analysis of the octa- and nona-BDE profiles suggested photolysis and pyrolytic debromination of BDE-209 in the air samples. The highly halogenated and most abundant PBDEs and AFRs in air also predominated in precipitation samples. This is the first study to report flame retardants in high volume air samples and precipitation in Equatorial Africa.



INTRODUCTION

Flame retardants are added to commercial products such as furniture, electrical equipment, and fabrics to increase fire resistance. Historically, brominated flame retardants (BFRs) were the most used organic flame retardants, especially, polybrominated diphenyl ethers (PBDEs), which were commercially produced, mainly, as penta-BDE, octa-BDE, and deca-BDE mixtures.[1,2] PBDEs exhibit environmental behavior similar to that of the PCBs and other legacy persistent organic pollutants (POPs), characterized by persistence, bioaccumulation, lipophilicity, and semivolatility,[1] and can undergo long-range atmospheric transport (LRAT) from source regions to remote locations. The penta-BDE and octa-BDE mixtures are among the new chemicals whose production and use are banned under the Stockholm Convention on POPs.[3] The atmospheric trends of the congeners in the penta- and octa-BDE products have generally shown a decline while the BDE-209 levels remain elevated, especially in Europe[4] and North America.[2] Although the use of penta- and octa-BDEs in consumer products as fire retardants has been long stopped in most developed countries, these chemicals continue to be frequently detected in atmospheric and other environmental samples in the same countries. This suggests possible current release of these chemicals, through various processes, from the products in which they were applied, as well as LRAT. In Africa, like most developing country regions, the increasing amount of e-waste from old electrical and electronic equipment shipped in from developed countries, coupled with poor recycling and disposal techniques (such as open burning and damping at poorly or nonconstructed landfill sites or even in surface water bodies) represent another major potential source of increased PBDEs and related chemicals in the local environment.[5−8] Recycling in Uganda has been reported for plastics and metals while there is no evidence for formal recycling of BFR containing waste.[9] Uganda passed legislation to regulate the

Received: August 13, 2013
Revised: January 6, 2014
Accepted: January 8, 2014
Published: January 8, 2014

 © 2014 American Chemical Society

importation of ICTs and used electronic materials but has not yet passed any legislation regarding e-waste management.[10] In East Africa, only Kenya has made significant progress toward developing regulations for sustainable e-waste management[11] and also has at least two major e-waste recycling facilities in its capital Nairobi.[12,13]

A wide range of non-PBDE AFRs have been introduced onto the market, attracting interest in their environmental behavior and fate.[14] As is the case with the legacy POPs and other semivolatile lipophilic organic contaminants, many AFRs are globally dispersed by LRAT. For instance, both PBDEs and AFRs have been found in various compartments of the environment in remote locations such as the Arctic,[15,16] the Antarctic environment,[17−20] and alpine environments.[21−24] Atmospheric levels of BFRs rise with ambient temperature[25] underscoring the importance of monitoring ambient levels of these pollutants in the warm tropical environment. Despite the many reports of these chemicals in the environment, there remains an acute lack of related data from measurements in equatorial Africa. Polybromobiphenyls (PBBs) and PBDEs were reported in office dust from South Africa[26] and BFRs were also measured in high volume samples from the Atlantic ocean, on an oceanographic cruise off the western coast of Africa, on a north−south transect.[27] PBDEs have also been investigated in a few passive samples collected under the Global Air Passive Sampling (GAPS) network.[28] Studies of other environmental matrices in Africa have reported FRs for in-land and coastal sediment,[29−32] leachate from landfills,[33] and sludge and effluent from a wastewater treatment plant.[34]

The results reported here constitute the first study to measure the atmospheric prevalence and precipitation of BFRs in the East and Central African region. We measured temporal variation of PBDEs and AFRs in air samples and compared their profiles with PAH profiles for the same sample set[35] to explore any combustion source character in the PBDE data. We analyzed the data for evidence of debromination of deca-BDE. We also estimated the fluxes of the BFRs in precipitation samples.

MATERIALS AND METHODS

Sampling. The air samples were collected at the Directorate of Water Resources Management (DWRM) at Entebbe, in Uganda, (Supporting Information, Figure S1a) from October 2008 to July 2010. Details of the site description and sampling are given elsewhere.[35] In brief, air samples were collected weekly with a TE-1000 PUF high volume air sampler (Tisch Environmental Inc., OH, USA) on a weekday rotation basis. Samples were kept at subzero temperatures before shipping them to Canada for analysis. The samples were extracted at AirZoneOne Laboratories, Mississauga, Ontario, for initial analysis of polycyclic aromatic hydrocarbons (PAHs).[35] The samples were thereafter processed for flame retardant analysis in a clean room (positively pressured HEPA and carbon filtered air) at the Environment Canada Centre for Inland Waters (CCIW) in Burlington, Ontario.

The precipitation samples were taken using an MIC type (Meteorological Instruments of Canada) precipitation sampler (Supporting Information, Figure S1b) located at the same Entebbe site described above for air sampling. The sampler consists of a precipitation sensor arm that electronically triggers the opening and closure of a stainless steel chamber (rain-trapping square funnel) that drains into a Teflon column (2 cm internal diameter, 30 cm length) packed with an Amberlite XAD-2 resin. Each column was deployed for about a month, from October 2008 to April 2010, except for a few periods where we could not sample due to sampler failure. The XAD deployment periods and the corresponding total rainfall received at the site are given in Supporting Information, Table S1. The water eluting through the column was collected, and its volume was later measured. However, fluxes for each sample were computed on the basis of the total rainfall received at the sampling site, for the entire sampling period for each column, as determined from daily rain gauge measurement records. This rainfall record was preferred over the total volume of water collected through the XAD column because the high evaporation rates, from the collection can, likely led to an underestimation of water volumes. The daily average temperatures at the sampling site were in the range of 20.5−26.2 °C for all the precipitation sampling periods, the lowest and highest temperatures recorded during sampling being 15.5 and 31.8 °C, respectively. Used columns were kept frozen (−16 °C to −20 °C) before shipping them to Canada for analysis. The samples were extracted and analyzed in the clean room at CCIW.

Sample Preparation and Analysis. The details of sample preparation are given in Meyer et al.[16] (Supporting Information). In brief, for the air samples, (PUF+filter) were extracted by pressurized fluid extraction (ASE 200, Dionex Instruments) with hexane/acetone 70:30 v/v. The extract was then concentrated by nitrogen evaporation. The concentrated extract was eluted over deactivated (10%) silica gel with 5% methanol in dichloromethane (DCM), and the solvent was exchanged to isooctane. The obtained fraction was first analyzed for currently used pesticides (to be reported later) before fractionation on an activated silica column using hexane (fraction A) and hexane/DCM 1:1 v/v (fraction B). Both fractions were concentrated, and the solvent was changed to isooctane and brought to the final volume (200 μL) for analysis. For precipitation samples, the XAD resin was successively eluted with methanol and DCM. The organic layer was separated, following shaking with 3% NaCl solution, dried over anhydrous Na_2SO_4, and concentrated. The concentrated extract was then processed further in the same way as the air sample extracts.

The samples were analyzed for PBDEs and AFRs by GC−MS (Agilent 5975C Series GC−MSD, transfer line at 295 °C) in splitless mode using single ion monitoring (SIM) following negative chemical ionization (NCI). The ions monitored for the SIM program are given in Supporting Information, Table S2a,b. An Rtx-1614 15 m × 0.25 mm × 0.10 μm column (Restek Corporation, Bellfonte, PA) and an HP-5MS 30 m × 0.25 mm × 0.10 μm column (Agilent Technologies, Mississauga, ON) were used for GC analysis. Helium was the carrier gas used in both cases.

Quality Control and Data Analysis. The high volume air samplers were regularly calibrated following the manufacturer's manual. Field PUF/filter and XAD resin column blanks were analyzed along with laboratory procedure blanks. Internal standards (BDE-71 and $^{13}C_{12}$−BDE-209) were spiked to all samples during sample preparation. The average recoveries were 149% and 109%, respectively. Multilevel calibration for the target analytes ($R^2 \geq 0.99$) was used. The method detection limits (MDLs) (Supporting Information, Table S2a,b) for the analytes were calculated as 3 times the standard deviation of the blanks.[36] The MDLs ranged from 0.235−6.4 pg m^{-3} and 0.027−42.6 pg m^{-2} $sample^{-1}$ for PBDEs and AFRs in air and

Table 1. Mean Air Concentrations (pg m^{-3}) for PBDEs and AFRs in Air Samples Collected at Entebbe, Uganda, October 2008 to July 2010. More Detailed Statistics Are Given in Supporting Information, Table S3a−d

	air samples for 2008 (N = 9)				air samples for 2009 (N = 30)				air samples for 2010 (N = 17)			
PBDE	A- mean	G- mean	median	Fd[a] (%)	A- mean	G- mean	median	Fd[a] (%)	A- mean	G- mean	median	Fd[a] (%)
BDE-28	0.86	0.73	0.63	100	1.54	1.15	1.29	90	6.37	2.70	1.59	100
BDE-49	2.43	0.05	bdl	11	0.45	0.06	bdl	23	0.65	0.17	0.21	59
BDE-47	4.79	2.52	bdl	44	8.11	5.37	6.09	87	15.6	11.6	9.75	100
BDE-66	bdl	bdl	bdl	11	1.10	0.17	bdl	37	1.28	0.23	0.21	53
BDE-100	0.62	bdl	bdl	22	0.48	0.35	0.39	53	0.64	0.41	0.42	65
BDE-99	3.38	bdl	bdl	22	2.10	bdl	bdl	43	8.92	2.84	1.86	65
BDE-85	0.21	bdl	bdl	11	bdl	bdl	bdl	20	bdl	bdl	bdl	
BDE-154	0.23	bdl	bdl	33	0.30	0.14	bdl	47	0.31	0.18	0.29	59
BDE-153	0.19	bdl	bdl	11	0.48	0.18	bdl	47	0.27	0.15	bdl	41
BDE-183	0.21	0.12	bdl	44	1.17	0.35	0.26	60	0.55	0.29	0.41	65
BDE-209	2.15	1.79	1.74	67	2.94	1.93	1.84	60	20.9	4.51	3.49	59
BDE-190	bdl	bdl	bdl		0.07	bdl	bdl	23	0.12	0.07	0.07	53
BDE-201	0.92	0.34	0.66	78	0.57	0.19	0.26	70	0.81	0.28	0.27	82
BDE-197	0.92	0.42	0.62	89	0.91	0.50	0.41	97	1.55	0.66	1.27	82
BDE-203	0.74	0.43	0.60	78	0.53	0.29	0.38	77	0.58	0.36	0.28	88
BDE-196	0.37	0.20	0.27	78	0.42	0.26	0.27	83	0.67	0.48	0.59	94
BDE-208	1.71	1.22	1.98	100	1.24	0.34	0.54	63	0.53	0.13	bdl	35
BDE-207	3.17	2.25	3.51	100	2.11	0.52	1.21	63	0.87	0.17	bdl	35
BDE-206	2.19	1.37	2.31	89	1.69	0.60	0.90	77	0.93	0.34	0.45	71
Σtetra BDEs[b]	7.31	2.91	1.12		9.67	6.29	8.11		17.5	13.0	15.0	
Σpenta BDEs[c]	4.00	1.77	1.03		2.58	1.98	1.44		9.56	3.55	2.40	
Σhexa BDEs[d]	0.42	0.18	0.11		0.78	0.37	0.28		0.59	0.39	0.56	
Σ PBDEs[e]	14.9	9.48	6.20		18.7	14.3	15.3		55.5	29.5	22.2	
TBP-AE	0.40	0.06	bdl	33	0.08	bdl	bdl	20	bdl	bdl	bdl	18
PBB	0.28	0.14	0.23	67	0.14	0.07	bdl	47	0.64	0.21	0.64	59
PBT	bdl	bdl	bdl	33	bdl	bdl	bdl	23	1.66	0.33	0.34	88
PBEB	0.06	bdl	bdl	11	bdl	bdl	bdl	10	0.26	0.14	0.17	76
HBB	Bdl	Bdl	bdl		0.09	bdl	bdl	7	0.28	0.10	bdl	29
PBB-Acr	2.65	1.11	1.27	67	3.04	1.17	4.25	60	1.18	0.59	0.54	59
BEH-TEBP	bdl	bdl	bdl		3.39	bdl	bdl	17	18.2	11.0	17.0	88
S-DP	bdl	bdl	bdl		0.21	bdl	bdl	10	0.46	0.05	bdl	18
A-DP	bdl	bdl	bdl		0.10	bdl	bdl	10	0.33	0.18	0.29	76
HBCDD	bdl	bdl	bdl		bdl	bdl	bdl	13	1.47	0.82	1.15	71
BTBPE	2.10	1.04	1.12	89	6.17	1.37	1.11	93	3.21	1.14	1.53	88
DBDPE	bdl	bdl	bdl		bdl	bdl	bdl		17.0	4.58	2.95	18

[a]Frequency of detection. [b]Sum of BDEs 47, 49, and 66. [c]Sum of BDEs 99 and 100. [d]Sum of BDEs 153 and 154. [e]Sum of BDEs 28, 49, 47, 66, 99, 100, 153, 154, 183, 209. A-mean = arithmetic mean, G-mean = geometric mean, bdl = below MDL (or below IDL where the compounds were not detected in the blanks.).

precipitation samples, respectively. All qualified data (i.e., those exceeding the respective MDLs) were then blank corrected using the average blank concentration. For compounds not detected in the blanks, one-half of the instrument detection limit (IDL) was applied. The IDL was determined as the concentration of the target analyte giving rise to a signal/noise ratio in the range of 2.5−5.[36] One half of the MDL (or half of IDL where the blank is zero) was used for nondetect or below-detection-limit values during statistical analyses. Significant correlations (SYSTAT 13, Systat Software Inc., Chicago, IL) were examined using Bonferroni adjusted probabilities (P < 0.05). Principal component analysis (PCA), using SIRIUS 8.1 (Pattern Recognition Systems AS, Bergen, Norway) software, was done on the transformed data to explore relationships within the data. The raw data was $^1/_3$ root transformed in order to remove heteroscedasticity,[37] and the resulting data were standardized prior to PCA. In the PCA, the PBDE data were combined with PAH data previously measured for the same air samples[35] to establish possible combustion source character in the observed PBDE profiles in the air samples. Back trajectory analysis was done using the NOAA HYSPLIT model[38,39] with GDAS meteorological data archives.

RESULTS AND DISCUSSION

PBDEs and AFRs in Air Samples. BDEs 28, 47, 99, and 209 were the predominant PBDEs (Table 1, Supporting Information, Figure S2) in the air samples with overall arithmetic mean concentrations of 2.90, 9.84, 4.38, 8.27, and geometric mean concentrations of 1.38, 6.01, 1.87, and 2.46 pg m^{-3}, respectively (Supporting Information, Table S3a). The high values for BDEs 47, 209, and 99 suggest penta-BDE and deca-BDE mixtures to be the major PBDE contributing formulations in the Lake Victoria regional airshed. The mean concentrations of the aforementioned four PBDEs increase from 2008 to 2010 showing a sharp rise in 2010 where their geometric means increased by 75% (BDE-28), 116% (BDE-47), 81% (BDE-99), and 134% (BDE-209). BDE-47 consistently had the highest mean concentration for the three

dx.doi.org/10.1021/es403600a | Environ. Sci. Technol. 2014, 48, 1458−1466

years. The mean concentrations of BDEs 153, 154, and 183 showed different profiles; BDEs 153 and 183 showed a decrease in mean levels in 2010 after a slight increase in 2009. BDE-154 had a slight increase in its 2010 mean concentration. The geometric mean levels of BDEs 153 and 154 were similar (0.08 and 0.09 for 2008; 0.18 and 0.14 for 2009; 0.15 and 0.18 pg m^{-3} for 2010, respectively). This variation in the profiles of these PBDEs, especially BDE 183, suggests limited contribution of the penta-BDE technical mixtures to the overall PBDE profile in the air samples. With the exception of BDEs 197 and 196, the mean concentrations of the octa- and nona-BDEs decreased with an increase in BDE 209. BDEs 208, 207, and 206 were exceptionally high in 2008 samples reaching levels comparable with the common PBDEs. This indicated possible high degradation of deca-BDE possibly due to increased pyrolysis (in addition to atmospheric photodebromination) of deca-BDE-containing waste locally and/or regionally. Generally, the mean concentrations of the deca-, penta- and tetra-BDEs were very much higher than the hepta- hexa-, octa- and nona-BDEs. Although BDE-47 had the highest overall mean in the sample set, BDE-209 had the highest range (<1.57−168 pg m^{-3}) (Supporting Information, Table S3a).

The predominance of BDEs 47, 99, and 209 in air samples has been reported in several other studies, for example, in the Arctic,[40,41] the European Arctic,[42] the United Kingdom (only BDEs 47 and 99),[4] and the North American Great Lakes region.[2,43−45] The mean levels observed in these studies were lower than levels found in the Entebbe samples, except for levels from the urban centers in Chicago and Cleveland, Ohio.[43,44] The PBDE levels measured at Entebbe were lower than the levels reported for air measurements off the Atlantic coast of Africa by Xie et al.[27] and much lower than the levels reported for most urban and suburban locations in China.[5] The sum of BDEs 47, 99, and 209 ($\Sigma BDE_{47,99,209}$) in samples from Entebbe were higher than those previously measured in passive air samples at three sites in Africa by Pozo et al.[28] One of their three sites, the Kalahari site, had a $\Sigma BDE_{47,99,209}$ value of 6 pg m^{-3} with the other two having levels below detection limits. The Entebbe samples had arithmetic and geometric mean $\Sigma BDE_{47,99,209}$ concentrations of 22.5 and 12.0 (range, 2.69−234) pg m^{-3} (Supporting Information, Table S3a).

The profiles of BDE-183, 153, and 154 varied from those of other PBDEs and had a close resemblance to the time trend profile of pyrene concentrations (Supporting Information, Figure S3) previously measured in the same samples (EBB2 data set in Arinaitwe et al., 2012).[35] This suggested possible influence of combustion sources on the profiles of the hexa- and hepta-BDEs.

To further explore this possibility, correlations of the common PBDEs for the entire air sample set, with the US EPA priority (unsubstituted) PAHs from the same samples were examined (Supporting Information, Table S4). Of these PBDEs, BDE-183 had the strongest correlations with most PAHs, notably, pyrene, benzo(ghi)perylene, and benzo(e)-pyrene whose correlation coefficients (r = 0.571, 0.667, and 0.603, respectively) with BDE-183 were very significant (Bonferroni adjusted probabilities $p \leq 0.001$ at 95% confidence). This indicated possible combustion source influence on the profile of octa-BDE constituent congeners. BDE-183 also showed significant correlation with BDE-153. The latter also showed significant correlation with BDE-154. BDEs 154 and 153 showed weak correlation with PAHs, suggesting overall limited combustion source influence on the profiles of BDEs 153 and 154 in the octa-BDE group. BDEs 28, 47, 99, 100, and 209 were not significantly correlated with any of octa-BDEs and the priority PAHs suggesting association with sources other than combustion. BDE-47 showed significant correlations with BDEs 99 and 209. BDE-99 also showed significant correlation with BDE-28. This suggests similar atmospheric prevalence and source profiles of these PBDEs for the studied Lake Victoria atmospheric environment.

To understand further these relationships, PCA was performed on the entire PBDE data set along with the PAH data used for the above correlations. Three significant components (p < 0.001) were extracted, explaining 60% of the variance in the combined data set. The extracted loading matrix is shown in Supporting Information, Table S5. The loading plots for the combined PBDEs + PAHs data set are shown in Figure 1. Component 1 shows the highest loading of

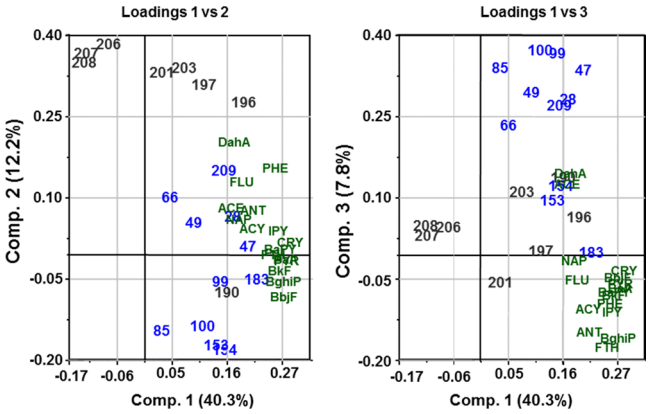


Figure 1. Loading plots of the common PBDEs (blue text), octa- and nona-BDEs (black text), and PAHs (green text) in the air samples on the extracted three components.

PAHs and the highest loadings of BDEs 183, 153, and 154. It also has moderate positive loadings of the octa- and nona-BDEs. This component was designated "combustion sources" and, therefore, suggested that combustion sources were a key contributor of BDEs-183, 153, 154 (major components of the octa-BDE technical mixtures) and lower PBDE congeners in most of the atmospheric samples from Entebbe. The loading of BDE-209 on component 1 is moderate and positive, as is the case with PAHs suggesting emission of BDE-209 from combustion sources. The loadings of BDEs 206, 207, and 208 on component 1 are high and negative suggesting an inverse correlation to the loading of BDE-209 on this component.

Several laboratory and field experiments[46,47] have demonstrated possible photolytic degradation of deca-BDE in the environment producing other highly substituted congeners, notably, the nona-BDEs, octa-BDEs, and some lower congeners. Nona- and octa-BDEs were also reported in emissions from the combustion of flame retarded e-waste.[48] Component 2 had high loadings of BDE-209 and nona-BDEs, consistent with environmental degradation of deca-BDE through processes like photolysis and pyrolysis. This component also had weak to moderate loading of PAHs and the rest of the PBDEs suggesting moderate combustion source influence. Therefore component 2 was designated "photolysis and combustion". This source character was more pronounced in 2008, early 2009, and late 2010 samples. Component 3 had

dx.doi.org/10.1021/es403600a | Environ. Sci. Technol. 2014, 48, 1458−1466

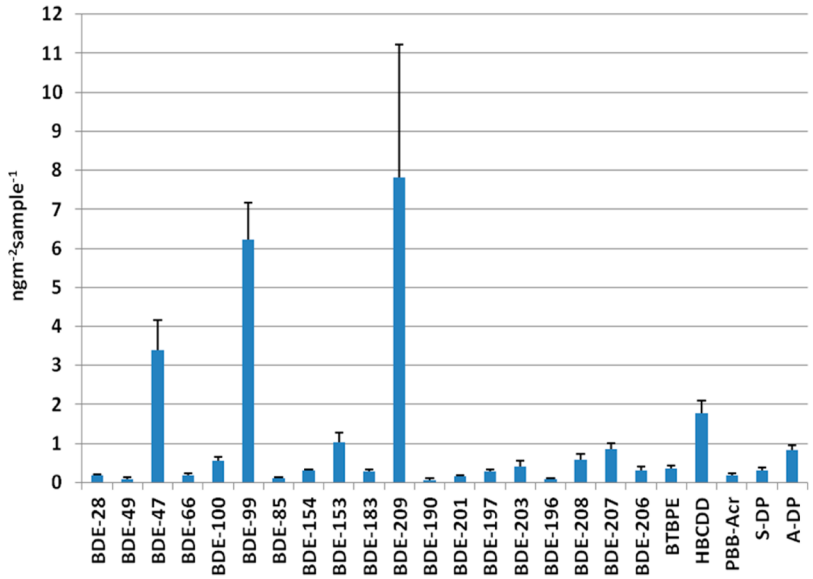


Figure 2. Mean flux (ng m^{-2} $sample^{-1}$) of PBDEs and AFRs in precipitation samples. Error bars represent the positive value of the standard error.

the highest loadings of BDEs 28, 47, 49, 100, 99, 154, 183, and 209 with weak loadings of octa- and nona-BDEs. This component represented mixed sources rich in the major components of the commercial products Penta-, Octa- and Deca-BDE. Component 3 was therefore designated as "volatilization and atmospheric transfer". This source character was the major PBDE contributor throughout the sampling period (Supporting Information, Figure S4a,b). The above PCA results were further reinforced by results of PCA on a combined data set of Entebbe air data and reference profiles from literature (the detailed discussion is in the Supporting Information, pages 16 and 17).

The most frequently detected AFR in the air samples was BTBPE with arithmetic and geometric mean concentrations of 4.62 and 1.24 pg m^{-3} for the entire data set and arithmetic mean concentrations of 2.10, 6.17, and 3.21 pg m^{-3} for the samples collected in the years 2008, 2009, and 2010, respectively (Supporting Information, Table S3a–d). The BTBPE profile was not significantly correlated either with profiles of the common major PBDEs or with the priority PAHs (Supporting Information, Table S4) suggesting a unique source. The mean concentrations of the AFRs show a general increase from 2008 to 2010. A notable example is BEH-TEBP which is not detected in 2008 but is seen in 2009 (arithmetic mean 3.39 pg m^{-3}, detected in 16% of the samples) and is the most abundant in 2010 (mean 18.2 pg m^{-3}, detected in 88% of the samples). PBT was also detected in a significant number of samples from each of the three years, but it had a relatively constant arithmetic mean concentration for 2008 and 2009 (0.05 pg m^{-3}) before increasing to 1.66 pg m^{-3} in 2010. Pearson correlations between the profiles of individual AFRs and the common PBDEs in the 2008 and 2009 did not show any significant coefficients, except for BTBPE which had significant correlation with BDE-206 (r = 0.787, p < 0.001) as well as moderate correlations with BDEs 207 and 208 (r = 0.695 and 0.671; p = 0.006 and 0.014, respectively) in the 2009 samples. For the 2010 air samples, two AFRs, PBT and PBEB had the highest significant intercorrelations (r > 0.900, Bonferroni probabilities p < 0.001) (Supporting Information, Table S6). These two AFRs, along with BTBPE, were the only ones to show a significant correlation with a common PBDE with correlation coefficients of 0.890 (BTBPE vs BDE-100), 0.940 and 0.865 (BDE-99 vs PBT and PBEB, respectively). Selected physical-chemical parameters estimated for BTBPE, PBT, and PBEB (Supporting Information, Table S7) (Estimation Program Interface (EPI) Suite, US EPA) show that BTBPE has higher potential to adsorb onto airborne particulate matter than the penta-BDEs (e.g., BDE-99). PBT and PBEB have a very much lower predicted adsorption but similar vapor pressures to that of BDE-99. Therefore, the PCA results, coupled with a significant correlation between the three AFRs and the penta-BDEs in the 2010 samples, suggest similar emission sources such as combustion of old and recently manufactured flame retarded consumer products. BTBPE was most likely concentrated in the particulate phase while PBT and PBEB were more likely to be in the gas phase, thereby susceptible to long-range atmospheric transfer as seen with the high loading of BDE-99 on component 3. The only other significant correlation involving AFRs was the one between *syn*-DP and *anti*-DP (r = 0.838, p < 0.001) which are isomeric forms of the same compound. S-DP and A-DP had no significant correlation with any of the common PBDEs or the AFRs.

The air mass movements associated with the samples were investigated by backward air trajectory analysis using the NOAA HYSPLIT model.[38,39] A total of eight dates representing samples with relatively high (December 30, 2008; October 12, 2009; November 29, 2009; June 11, 2010) and low (November 30, 2008; January 25, 2009; July 18, 2009; April 25, 2010) levels of key PBDEs were selected for this analysis, and the computed trajectories are shown in Supporting Information, Figures S5 and S6, respectively. The samples with high levels of PBDEs in 2008 and 2009 were found to be largely associated with slow moving low altitude air masses originating within the watershed of Lake Victoria (trajectory models A, B, and C in Figure S5). The 2010 high levels were associated with fast low altitude southeasterly air masses from East African coast sweeping in over the relatively highly urbanized region of the watershed (trajectory model D in Figure S5). The samples with low levels of PBDEs were associated with either high altitude fast moving South Easterly air masses (trajectory models G and H in Figure S6) or very slow low altitude air

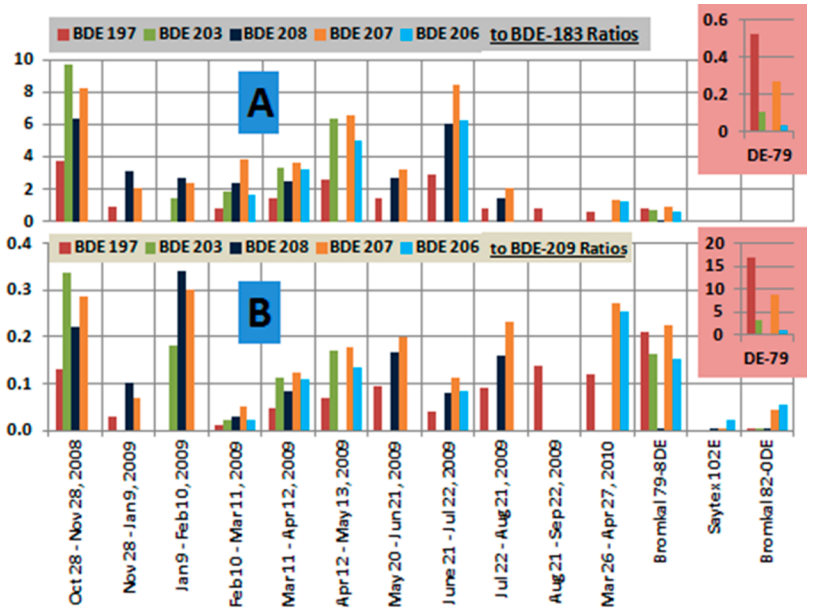


Figure 3. Ratios of the detected octa- and nona-BDEs to BDE-183 (A) and BDEs-209 (B) in the precipitation samples and in the octa-and deca-BDE technical mixtures.[56]

masses originating from less urbanized parts of the watershed (trajectory models E and F in Figure S6). These observations suggest that processes and activities (such as combustion and e-waste recycling and disposal) in the watershed of Lake Victoria and urbanized centers in the East African region as the most probable sources of PBDEs in the air samples. The PBDE and AFR concentrations in the air samples were varied despite the air masses associated with samples sweeping over similar geographical areas. This suggested varied emission sources and patterns. According to the wind rise computed for all air samples at this sampling station, which is given elsewhere,[35] any combustion and e-waste handling sources occurring in urbanized Entebbe and Kampala areas were likely to influence FR profiles of incoming regional air masses and consequently, the measured FR profiles of the samples. Kampala is the most densely populated and most urbanized region of Uganda with a population of more than one million people. More details on the demographic characteristics of Kampala have been previously reported elsewhere.[35]

PBDEs and AFRs in Precipitation Samples. Of all the PBDEs measured, BDEs 209, 99, 47, and 153 had the highest average fluxes of 7.82, 6.23, 3.40, and 1.02 ng m^{-2} $sample^{-1}$ (Figure 2 and Supporting Information, Table S8a). The same congeners had the highest average daily fluxes (Supporting Information, Table S8b) and the highest fractions of total PBDEs in all the samples (Supporting Information, Figure S7). The overall average proportions of these four congeners in all the samples analyzed (for the 11 common PBDEs shown in Figure 2) were 32% (range, 17−65%) for BDE-209, 35% (15−44%) for BDE-99, 18% (10−29%) for BDE-47 and 5% (2−8%) for BDE-153. This shows that the most abundant PBDEs in the atmosphere (penta-BDEs and deca-BDE) happen to be the most scavenged compounds during precipitation. The high fluxes of BDE-209 are most probably due to the efficient washout by precipitation since it is bound to atmospheric particulates.[44,45,49] The high fluxes of BDEs 47 and 99 could be due to extensive use and release in the Lake Victoria region combined with prevailing warm temperatures which favor volatilization from products. The low flux of BDE-183 relative to penta-BDEs and deca-BDE, as seen in the air samples, suggests low use and release of the octa-BDE in the study region. In spite of BDEs 154 and 153 having similar low abundances in the air samples, the latter exhibited higher wet deposition fluxes.

The predominance of penta-BDE and deca-BDE in precipitation has previously been observed in other measurements, for example, in Sweden,[50,51] the Baltic Sea,[52] and the Great Lakes region.[43,53] In a study of the influence of urban areas on wet deposition of POPs to Lake Ontario, the average compositions of BDE 209, 99, and 47 for all three sampling sites were >70%, 10%, and 9%, respectively.[53] These three congeners were also predominant in samples obtained from the North American Great Lakes region by Venier and Hites.[54] The fluxes reported for a study site in the Baltic Sea and the urban sites from Sweden, including those from a rural site,[51] were much higher than the fluxes observed in the Entebbe samples. The average daily fluxes of BDEs 47 and 99 reported for a number of sites in the North American Great Lakes region for the period 2004−2010 by Robson et al.[55] were similar to those estimated for the Entebbe samples, but the BDE-209 average daily fluxes were several orders of magnitude above the one for Entebbe samples.

There was no significant correlation between the precipitation profiles of PBDEs and total rainfall received at the sampling during the collection of each precipitation sample (Supporting Information, Table S9). In general all the PBDEs showed correlations with at least one other PBDE. The interestingly notable exception was BDE-154 which had no significant correlation with any other PBDE. The strongest and most significant relationships were between BDEs 47, 99, and 100 suggesting similar prevalence factors for the penta-BDEs in the precipitation samples. BDE-209 and 49 had a significant correlation, but it was not informative enough given that the latter was detected in about half of the precipitation samples. The correlation of the flux profiles of BDEs 209 and 153 (r = 0.9111) suggests a possibility of similar emission sources or

dx.doi.org/10.1021/es403600a | Environ. Sci. Technol. 2014, 48, 1458−1466

even atmospheric photolysis of the former to the latter[47] and has been discussed for the air data above. The mean fluxes of the BDEs 207, 208, 206, and 197 were the highest among the octa- and nona-BDEs (Figure 2 and Supporting Information, Table S8a,b).

The ratios of octa- and nona-BDEs to BDE-209 (Figure 3B) in the precipitation samples were generally higher than their respective values in the technical deca-BDE mixtures (Saytex 102E and Bromkal 82-0DE). The BDE-208:209 ratio measured in the precipitation samples was much higher than its corresponding values in the technical mixtures. This indicated significant environmental degradation of BDE-209 to BDE 208. The ratios of the other high congeners measured in the precipitation samples were generally similar to their respective values in one of the octa-BDE mixtures (Bromkal 79-8DE) but significantly lower than their corresponding values in the second octa-BDE mixture (DE-79) (Figure 3B,inset). This scenario would normally suggest significant contribution of higher PBDE congeners from octa-BDE sources, but this is not the case with these precipitation samples. This is because the ratios of octa- and nona-BDEs to BDE-183 (the major congener in the octa-BDE technical mixtures) were considerably higher than their corresponding values for the octa-BDE technical mixtures (Figure 3A). This further suggests significantly more contribution of the higher PBDEs, in the precipitation samples, from deca-BDE sources than the octa-BDE sources. This is in agreement with the predictions from the analysis of the air samples which showed association of octa-, nona-, and deca-BDEs with photolytic and pyrolytic sources. The high abundance of the higher PBDE congeners in the precipitation samples may also be attributed to high adsorption to airborne particulate matter and therefore easy wash-out by rain. BDEs 190, 202, 204, 205, 194, and 195 were not detected in any of the precipitation samples. Very low or nondetect levels were observed for the same PBDEs in the air samples as well.

The mean fluxes (ng m^{-2} $sample^{-1}$) determined for the most frequently detected AFRs in precipitation samples were 0.37 (range, 0.14−0.79) for BTBPE, 1.77 (range, 0.58−4.56) for HBCDD, 0.18 (range, bdl−0.71) for PBB-Acr, 0.30 (range, 0.07−0.85) for S-DP, and 0.82 (range, 0.21−1.74) for A-DP (Supporting Information, Figure S8 and Table S8). These AFRs were detected in all samples except PBB-Acr which was above its detection limit in 64% of the samples. The mean concentration and average daily flux of HBCDD were only exceeded by BDEs 47, 99, and 209. Although A-DP was consistently higher than S-DP, both AFRs showed a general decline during the sampling period with peak levels seen in late 2008 (for S-DP) and early 2009 (for A-DP). As expected given their common source, both stereoisomers had a strong correlation (r = 0.832, p = 0.001) (Supporting Information, Table S10) and an overall average A-DP/S-DP ratio of 3.3 which is similar to the one in technical DP. [57] There were no significant correlations between individual AFRs and the common PBDEs, suggesting different sources of these FRs in the precipitation samples. In addition, there was no significant correlation between individual AFR profiles and the one for total rainfall received at the sampling station during the collection of each precipitation sample.

Wind roses corresponding to each of the monthly precipitation samples (Supporting Information, Figure S9a−c) were computed to investigate possible influence of local sources on ambient atmospheric prevalence and wet deposition of the FRs at the sampling station. The samples were found to be largely associated with Northerly and Easterly local winds, except ER1 which was associated with Northerly and Westerly winds. This allows the possible influence of local activities in Entebbe and Kampala city, located north of the sampling site,[35] on the FR profiles observed in the samples.

In this study, we have established a reference data set for future studies of atmospheric prevalence of PBDEs and AFRs. The abundance of BDEs 47, 99, and 209 in both the air and precipitation samples shows the predominance of legacy penta-BDE and currently used deca-BDE residues in the environment. The temporal profiles show elevated levels of the PBDEs in the atmospheric samples collected in 2010. The significant correlation of BDEs 183 with priority PAHs measured in the same air samples and the results of PCA suggest significant combustion sources involving PBDE containing consumer products. As part of the assessment of impacts of chemicals in the Lake Victoria region, it is important to monitor the trends of these FRs given the prevalent exposure risk factors. These factors include; the equatorial climate (elevated temperature, precipitation and sunlight which favor atmospheric pathways) and poor e-waste management. In the East African region, Uganda in particular, there is an acute lack of high temperature incineration facilities. Consequently, dumping at poorly designed waste sites and low-temperature open burning of waste are the common disposal methods, both of which may release BFRs into the environment through leachate and combustion emissions, respectively.

■ ASSOCIATED CONTENT

Supporting Information

A descriptive image of the precipitation sampler and additional descriptive statistics; graphics for PCA (scores plots), backward air trajectory, and wind rose computations for the air and precipitation data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +256772858394; e-mail: ken.arina@gmail.com.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was funded in part by the Swedish International Development Cooperation Agency (Sida) through Makerere University and the International Foundation for Science (IFS). We thank Moses Tumusiime, Gabriel Achema, Stephen Mulinda, and Christopher Bitainensha for their field and technical assistance throughout the sampling period.

■ REFERENCES

(1) De Wit, C. A. An overview of brominated flame retardants in the environment. *Chemosphere* **2002**, *46* (5), 583−624.

(2) Venier, M.; Hites, R. A. Flame retardants in the atmosphere near the great lakes. *Environ. Sci. Technol.* **2008**, *42* (13), 4745−4751.

(3) UNEP. *Risk Profile for Pentabromodiphenyl Ether*; United Nations Environment Program, Stockholm Convention on Persistent Organic Pollutants Geneva, Switzerland, 2006; p 46.

(4) Birgul, A.; Katsoyiannis, A.; Gioia, R.; Crosse, J.; Earnshaw, M.; Ratola, N.; Jones, K. C.; Sweetman, A. J. Atmospheric polybrominated diphenyl ethers (PBDEs) in the United Kingdom. *Environ. Pollut.* **2012**, *169*, 105−111.

(5) Ma, J.; Qiu, X.; Zhang, J.; Duan, X.; Zhu, T. State of polybrominated diphenyl ethers in China: An overview. *Chemosphere* **2012**, *88* (7), 769−778.
(6) Nnorom, I. C.; Osibanjo, O. Overview of electronic waste (e-waste) management practices and legislations, and their poor applications in the developing countries. *Resour., Conserv. Recycl.* **2008**, *52* (6), 843−858.
(7) Robinson, B. H. E-waste: An assessment of global production and environmental impacts. *Sci. Total Environ.* **2009**, *408* (2), 183−191.
(8) Schluep, M.; Manhart, A.; Osibanjo, O.; Rochat, D.; Isarin, N.; Mueller, E. *Where are WEEE in Africa. Findings from the Basel Convention E-Waste Africa Programme*; Secretariat of the Basel Convention: 2011.
(9) E-waste generation and management in Uganda. http://www.ucpc.co.ug/index.php?option=com_content&view=article&id=99:e-waste-generation-and-management-in-uganda&catid=47:ucpc-publications-&Itemid=99 (accessed December 30, 2013).
(10) E-waste Management in East African Community. http://www.igi-global.com/chapter/waste-management-east-african-community/64858 (accessed December 30, 2013).
(11) UNEP backs action on e-waste in East Africa. http://www.unep.org/environmentalgovernance/News/PressRelease/tabid/427/language/en-US/Default.aspx?DocumentID=647&ArticleID=6744&Lang=en (accessed December 19, 2013).
(12) WEEE Centre homepage. http://www.weeecentre.com/index.html (accessed December 19, 2013).
(13) East African Compliant Recycling homepage. http://www.eastafricancompliantrecycling.net/ (accessed December 19, 2013).
(14) Covaci, A.; Harrad, S.; Abdallah, M. A. E.; Ali, N.; Law, R. J.; Herzke, D.; de Wit, C. A. Novel brominated flame retardants: A review of their analysis, environmental fate, and behaviour. *Environ. Int.* **2011**, *37* (2), 532−556.
(15) de Wit, C. A.; Herzke, D.; Vorkamp, K. Brominated flame retardants in the Arctic environment—Trends and new candidates. *Sci. Total Environ.* **2010**, *408* (15), 2885−2918.
(16) Meyer, T.; Muir, D. C. G.; Teixeira, C.; Wang, X.; Young, T.; Wania, F. Deposition of brominated flame retardants to the Devon Ice Cap, Nunavut, Canada. *Environ. Sci. Technol.* **2012**, *46* (2), 826−833.
(17) Dickhut, R. M.; Cincinelli, A.; Cochran, M.; Kylin, H. Aerosol-mediated transport and deposition of brominated diphenyl ethers to Antarctica. *Environ. Sci. Technol.* **2012**, *46* (6), 3135−3140.
(18) Möller, A.; Xie, Z.; Cai, M.; Sturm, R.; Ebinghaus, R. Brominated flame retardants and dechlorane plus in the marine atmosphere from Southeast Asia toward Antarctica. *Environ. Sci. Technol.* **2012**, *46* (6), 3141−3148.
(19) Wang, P.; Zhang, Q. H.; Wang, T.; Chen, W. H.; Ren, D. W.; Li, Y. M.; Jiang, G. B. PCBs and PBDEs in environmental samples from King George Island and Ardley Island, Antarctica. *RSC Adv.* **2012**, *2* (4), 1350−1355.
(20) Yogui, G. T.; Sericano, J. L.; Montone, R. C. Accumulation of semivolatile organic compounds in Antarctic vegetation: A case study of polybrominated diphenyl ethers. *Sci. Total Environ.* **2011**, *409* (19), 3902−3908.
(21) Usenko, S.; Landers, D. H.; Appleby, P. G.; Simonich, S. L. Current and historical deposition of PBDEs, pesticides, PCBs, and PAHs to Rocky Mountain National Park. *Environ. Sci. Technol.* **2007**, *41* (21), 7235−7241.
(22) Xiao, H.; Shen, L.; Su, Y.; Barresi, E.; Dejong, M.; Hung, H.; Lei, Y. D.; Wania, F.; Reiner, E. J.; Sverko, E.; Kang, S. C. Atmospheric concentrations of halogenated flame retardants at two remote locations: The Canadian High Arctic and the Tibetan Plateau. *Environ. Pollut.* **2012**, *161*, 154−161.
(23) Arellano, L.; Fernández, P.; Tatosova, J.; Stuchlik, E.; Grimalt, J. O. Long-range transported atmospheric pollutants in snowpacks accumulated at different altitudes in the Tatra Mountains (Slovakia). *Environ. Sci. Technol.* **2011**, *45* (21), 9268−9275.
(24) Bartrons, M.; Grimalt, J. O.; Catalan, J. Altitudinal distributions of BDE-209 and other polybromodiphenyl ethers in high mountain lakes. *Environ. Pollut.* **2011**, *159* (7), 1816−1822.
(25) Wania, F.; Dugani, C. B. Assessing the long-range transport potential of polybrominated diphenyl ethers: A comparison of four multimedia models. *Environ. Toxicol. Chem.* **2003**, *22* (6), 1252−1261.
(26) Kefeni, K. K.; Okonkwo, J. O. Analysis of major congeners of polybromobiphenyls and polybromodiphenyl ethers in office dust using high resolution gas chromatography−mass spectrometry. *Chemosphere* **2012**, *87* (9), 1070−1075.
(27) Xie, Z.; Möller, A.; Ahrens, L.; Sturm, R.; Ebinghaus, R. Brominated flame retardants in seawater and atmosphere of the Atlantic and the southern ocean. *Environ. Sci. Technol.* **2011**, *45* (5), 1820−1826.
(28) Pozo, K.; Harner, T.; Lee, S. C.; Wania, F.; Muir, D. C. G.; Jones, K. C. Seasonally resolved concentrations of persistent organic pollutants in the global atmosphere from the first year of the GAPS Study. *Environ. Sci. Technol.* **2009**, *43* (3), 796−803.
(29) Bodin, N.; N'Gom Ka, R.; Le Loc'h, F.; Raffray, J.; Budzinski, H.; Peluhet, L.; Tito de Morais, L. Are exploited mangrove molluscs exposed to persistent organic pollutant contamination in Senegal, West Africa? *Chemosphere* **2011**, *84* (3), 318−327.
(30) Verhaert, V.; Covaci, A.; Bouillon, S.; Abrantes, K.; Musibono, D.; Bervoets, L.; Verheyen, E.; Blust, R. Baseline levels and trophic transfer of persistent organic pollutants in sediments and biota from the Congo River Basin (DR Congo). *Environ. Int.* **2013**, *59*, 290−302.
(31) La Guardia, M. J.; Hale, R. C.; Newman, B. Brominated flame-retardants in sub-Saharan Africa: Burdens in inland and coastal sediments in the eThekwini metropolitan municipality, South Africa. *Environ. Sci. Technol.* **2013**, *47* (17), 9643−9650.
(32) Olukunle, O.; Okonkwo, J.; Kefeni, K.; Lupankwa, M. Concentrations of polybrominated diphenyl ethers in sediments from Jukskei River, Gauteng, South Africa. *Bull. Environ. Contam. Toxicol.* **2012**, *88* (3), 461−466.
(33) Daso, A. P.; Fatoki, O. S.; Odendaal, J. P.; Olujimi, O. O. Polybrominated diphenyl ethers (PBDEs) and 2,2′,4,4′,5, 5′-hexabromobiphenyl (BB-153) in landfill leachate in Cape Town, South Africa. *Environ. Monit. Assess.* **2013**, *185* (1), 431−439.
(34) Daso, A. P.; Fatoki, O. S.; Odendaal, J. P.; Olujimi, O. O. Occurrence of selected polybrominated diphenyl ethers and 2,2′,4,4′,5,5′-hexabromobiphenyl (BB-153) in sewage sludge and effluent samples of a wastewater-treatment plant in Cape Town, South Africa. *Arch. Environ. Contam. Toxicol.* **2012**, *62* (3), 391−402.
(35) Arinaitwe, K.; Kiremire, B. T.; Muir, D. C. G.; Fellin, P.; Li, H.; Teixeira, C.; Mubiru, D. N. Atmospheric concentrations of polycyclic aromatic hydrocarbons in the watershed of Lake Victoria, East Africa. *Environ. Sci. Technol.* **2012**, *46* (21), 11524−11531.
(36) EPA, Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11. In *Code of Federal Regulations*, 2011.
(37) Zar, J. H. *Biostatistical Analysis*, 4th ed.; Prentice Hall: Upper Saddle River, NJ, 1999.
(38) Draxler, R. R.; Rolph, G. D., *HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model*; NOAA Air Resources Laboratory: Silver Spring, MD, 2011; access via NOAA ARL READY Website http://ready.arl.noaa.gov/HYSPLIT.php.
(39) Rolph, G. D., *Real-time Environmental Applications and Display sYstem (READY)*; NOAA Air Resources Laboratory: Silver Spring, MD; 2011; http://ready.arl.noaa.gov.
(40) Hung, H.; Kallenborn, R.; Breivik, K.; Su, Y.; Brorström-Lundén, E.; Olafsdottir, K.; Thorlacius, J. M.; Leppänen, S.; Bossi, R.; Skov, H.; Manø, S.; Patton, G. W.; Stern, G.; Sverko, E.; Fellin, P. Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993−2006. *Sci. Total Environ.* **2010**, *408* (15), 2854−2873.
(41) Su, Y.; Hung, H.; Sverko, E.; Fellin, P.; Li, H. Multi-year measurements of polybrominated diphenyl ethers (PBDEs) in the Arctic atmosphere. *Atmos. Environ.* **2007**, *41* (38), 8725−8735.
(42) Möller, A.; Xie, Z.; Sturm, R.; Ebinghaus, R. Polybrominated diphenyl ethers (PBDEs) and alternative brominated flame retardants in air and seawater of the European Arctic. *Environ. Pollut.* **2011**, *159* (6), 1577−1583.

(43) Salamova, A.; Hites, R. A. Discontinued and alternative brominated flame retardants in the atmosphere and precipitation from the great lakes basin. *Environ. Sci. Technol.* **2011**, *45* (20), 8698−8706.
(44) Strandberg, B.; Dodder, N. G.; Basu, I.; Hites, R. A. Concentrations and spatial variations of polybrominated diphenyl ethers and other organohalogen compounds in Great Lakes air. *Environ. Sci. Technol.* **2001**, *35* (6), 1078−1083.
(45) Su, Y.; Hung, H.; Brice, K. A.; Su, K.; Alexandrou, N.; Blanchard, P.; Chan, E.; Sverko, E.; Fellin, P. Air concentrations of polybrominated diphenyl ethers (PBDEs) in 2002−2004 at a rural site in the Great Lakes. *Atmos. Environ.* **2009**, *43* (39), 6230−6237.
(46) Stapleton, H. M.; Dodder, N. G. Photodegradation of decabromodiphenyl ether in house dust by natural sunlight. *Environ. Toxicol. Chem.* **2008**, *27* (2), 306−312.
(47) Söderström, G.; Sellström, U.; De Wit, C. A.; Tysklind, M. Photolytic debromination of decabromodiphenyl ether (BDE 209). *Environ. Sci. Technol.* **2004**, *38* (1), 127−132.
(48) Wyrzykowska-Ceradini, B.; Gullett, B. K.; Tabor, D.; Touati, A. Waste combustion as a source of ambient air polybrominated diphenylethers (PBDEs). *Atmos. Environ.* **2011**, *45* (24), 4008−4014.
(49) Chen, L. G.; Mai, B. X.; Bi, X. H.; Chen, S. J.; Wang, X. M.; Ran, Y.; Luo, X. J.; Sheng, G. Y.; Fu, J. M.; Zeng, E. Y. Concentration levels, compositional profiles, and gas-particle partitioning of polybrominated diphenyl ethers in the atmosphere of an urban city in South China. *Environ. Sci. Technol.* **2006**, *40* (4), 1190−1196.
(50) Ter Schure, A. F. H.; Larsson, P. Polybrominated diphenyl ethers in precipitation in Southern Sweden (Skåne, Lund). *Atmos. Environ.* **2002**, *36* (25), 4015−4022.
(51) Ter Schure, A. F. H.; Agrell, C.; Bokenstrand, A.; Sveder, J.; Larsson, P.; Zegers, B. N. Polybrominated diphenyl ethers at a solid waste incineration plant II: Atmospheric deposition. *Atmos. Environ.* **2004**, *38* (30), 5149−5155.
(52) Ter Schure, A. F. H.; Larsson, P.; Agrell, C.; Boon, J. P. Atmospheric transport of polybrominated diphenyl ethers and polychlorinated biphenyls to the baltic sea. *Environ. Sci. Technol.* **2004**, *38* (5), 1282−1287.
(53) Melymuk, L.; Robson, M.; Diamond, M. L.; Bradley, L. E.; Backus, S. Wet deposition loadings of organic contaminants to Lake Ontario: Assessing the influence of precipitation from urban and rural sites. *Atmos. Environ.* **2011**, *45* (28), 5042−5049.
(54) Venier, M.; Hites, R. A. Atmospheric deposition of PBDEs to the great lakes featuring a Monte Carlo analysis of errors. *Environ. Sci. Technol.* **2008**, *42* (24), 9058−9064.
(55) Robson, M.; Melymuk, L.; Bradley, L.; Treen, B.; Backus, S. Wet deposition of brominated flame retardants to the Great Lakes basin—Status and trends. *Environ. Pollut.* **2013**, *182* (0), 299−306.
(56) La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environ. Sci. Technol.* **2006**, *40* (20), 6247−6254.
(57) Sverko, E.; Tomy, G. T.; Reiner, E. J.; Li, Y. F.; McCarry, B. E.; Arnot, J. A.; Law, R. J.; Hites, R. A. Dechlorane plus and related compounds in the environment: A review. *Environ. Sci. Technol.* **2011**, *45* (12), 5088−5098.

■ NOTE ADDED AFTER ASAP PUBLICATION

Figure 1 was modified, and minor text corrections made to the version of this paper published January 15, 2014. The correct version published January 21, 2014.