ACCELERATED SOLVENT EXTRACTION AND ANALYSIS OF COMMON POLYBROMODIPHENYL ETHERS IN SEDIMENTS FROM JUKSKEI RIVER CATCHMENT

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Introduction

Introduction of new technologies to protect lives and properties has become very attractive and has been embraced globally, thus paving the way for development of new chemicals used in consumer and industrial applications. A good example is the development of synthetic chemicals added to textiles, furniture, TV's, plastics, paints and other electrical and electronic appliances to reduce the incidence of fire. Of all the flame retardants, brominated flame retardants (BFRs) have been used extensively. BFRs are a group of brominated synthetic organic compounds which have been widely used to prevent fire in a variety of consumer polymer products[12]. Out of over 75 brominated organic compounds used as flame retardants, the four common BFRs comprises; polybrominated diphenyl ethers (PBDEs), polybrominated biphenyl ethers (PBBs), hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA). These brominated derivatives have become more popular because of their stability, higher trapping efficiency and lower decomposing temperature[2, 15] thereby giving them the largest share in the flame retardants market of 25%[9]. BFRs have been studied extensively in the last decade for their persistence, bioaccumulation and toxicity (PBT) and they have been found to exhibit similar physical, chemical and toxicological properties to the banned polychlorinated biphenyls (PCBs)[1,3,13]. Levels of BFRs in human samples have been highlighted by Covaci et al. and Xiao et al[2, 20]. These revelations triggered the cessation of industrial production of PBBs in 2000 and two commercial mixtures, Penta and OctaBDE which were banned by the European Union in August 2004[5]. Subsequently the latter have been included in the 9 new POPs listed under the Stockholm Convention[21].

The issue of BFRs as a PBT, emerging and ubiquitous pollutant is still at its infancy in South Africa and information on production and usage of BFRs in Africa is scarce. Few studies, however, have confirmed their presence in the South African environment. For example, levels of BFRs have been reported in landfill leachates[6], river sediment[16], breast milk[18], dust[14] and eggs[4] of some South Africa birds respectively. However, information on levels of BFRs in surface water and sediment in South Africa is still scarce.

The Jukskei River catchment is one of the important river catchments in South Africa. It was chosen as the study area because it receives effluent from industries and run-off in vast amounts from illegal, unmanaged waste dumps and agricultural practices. According to the Department of Water Affairs, the Jukskei River catchments is largely urbanised and industrialised[7]. The land use of the catchment is characterised mainly by agricultural, industrial and urban activities. Therefore, the main objective of this study was to investigate the levels of these ubiquitous pollutants in Jukskei River catchment using the full automated accelerated solvent extraction (ASE) system for extraction and online cleaning of analytes.

Materials and methods

Pure standards (1.2 mL of 50 mg L^{-1}) of each certified standard solutions of 8 PBDE congeners (BDE-28, -47, -77, -99, -100, -153, -154, and -183) were purchased from Wellington Laboratories (Guelph, Ontario, Canada). Copper powder (purity 99.98% from Saarchem (Pty) Ltd., Muldersdrift, South Africa), silica gel (100 - 200 mesh), sodium sulphate (purity 99.9 %), glass wool and HPLC grade solvents: acetone, hexane, dichloromethane, methanol and toluene (products of Sigma Aldrich (Chemie GmbH, Steinheim, Germany), 50 mL of nonane (Purity 99.8%, Sigma Aldrich, product of Switzerland) were purchased from Industrial Analytical Pty. Ltd. Pesticarb was purchased from SMM Instruments (Pty) Africa. Sediment samples were collected between July (winter) 2010 and February (summer) 2011. Samples were collected along the stretch of Jukskei River from the most accessible points using geographical information system GIS. At each point, three samples of sediment were collected; two from the banks and one from the middle of the River.

Control soil sample collected from a rural area far from urban activities was used as blank for method development; analysis of which gave no presence of BDE-77. This was spiked with PBDE standards including BDE-77. The recovery of BDE-77 was used to validate the method. Sediment sample extraction was carried out with Accelerated Solvent Extractor (ASE 350-Dionex, Sunnyvale, CA, USA) equipped with 34-mL stainless-steel cells. The extraction method followed a slightly modified USEPA method 3545A[26]. The instrumental conditions were varied for extraction but two were deemed acceptable at the following conditions; Pre cleaned (with *n*-hexane and heated in an oven @ 200 °C for 1 h) stainless steel cells were loaded by placing a cellulose filter at the bottom of a tightly screwed cell and followed in the order; 5 g washed sand, 4.5 g silica gel, 0.6 g pesticarb (clean up material), mixture of 10 g sample, 10 g washed sand and 5 g sodium sulphate and another cellulose filter was placed at the top. The cells were tightly screwed and loaded into the instrument at120 °C, pressure; 11 MPa, heating time; 5 mins, cycles; 2, flush volume; 90 % and purged for 90 seconds with nitrogen.
For second condition used; clean-up material was 2 g acidic silica, 1 g basic silica and 2 g neutral silica, temperature; 150 °C, pressure; 11-15 MPa, heating time; 7 min, static state; 8 min and 3 cycles for extraction. Solvent used for extraction and clean-up were 60 mL and 100 mL *n*-hexane/acetone (2:1, *v/v*) respectively. The cleaned extract was collected in 100 mL bottles with teflon septa. Sediment samples were spiked with 1 mL of 0.3 ng µL^{-1} of PBDE standards dissolved in acetone. The collected extracts were concentrated to 1 mL under a gentle stream of nitrogen and solvent exchanged to hexane before injecting an aliquot of 1µL into the GC-MS for analysis. Triplicate extract of the sediment was carried out.
Sediment extracts were analysed using Agilent GC 6890 MS 5975 system (serial number: US60532363, made in USA). One micro litre solutions of the extracted sample was injected by Gerstel multipurpose sampler (SN 126377) into split/splitless injection port on DB-5MS column (30 m, 0.25 mm ID, 0.25 µm df). Helium at a flow rate of 1.5 mL min^{-1} as carrier gas, splitless time of 1 min, injection temperature of 290 °C and oven programme of 90 °C for 1 min, ramped by 30 °C min^{-1} to 300 °C for 5 min, 10 °C min^{-1} to 310 °C for 1 min were used. The GC was coupled to an Agilent 5975C inert MSD with triple axis detector, operated in EI mode. Operating conditions were set as follows: ion source; 250 °C and transfer line at 300 °C. Identifications were carried out using full scan, by monitoring the presence of the mass spectra of molecular ion and two qualifier ions of each congener at the elution retention time. Each congener was quantified against four level external standard calibration curves and an internal standard (BDE-77).

Several quality control measures were taken to ensure the correctness and integrity of obtained results. These included the spiking of sediment with BDE-77 as internal standard and each PBDE standard (1 mL of 0.3 ng µL^{-1}) to assess recovery. Three sediment samples collected at each site were homogenised and pre-treated for extraction, followed by triplicate analysis of sediment samples. Duplicate extraction was done for each sample and blank respectively under same condition. Limit of detection (LOD) ranged from 0.025 − 0.038 ng g^{-1}. Chromatographic conditions were monitored to check for variation in retention times, while test standards were run after every five samples and a blank was run after each sample. Results of blank analysis gave values below detection limit for most of the target analytes while retention times showed insignificant deviations of ±0.05 min.

Results and discussion

The procedure described above was applied for the determination of 7 common PBDEs (BDE-28, -47, -99, -100, -154, -153 and -183) in sediment samples collected at different points on Jukskei River namely; Knoppieslaagte, Eastgate, Waterval, Kyalami, Buccleuch and Eastbank. The mean percentage recovery of two of the different instrumental conditions ranged from 74 − 105 % and 51 − 92% respectively for the two acceptable conditions. Condition 1 gave a higher recovery for all tested analytes and was, therefore, applied for extraction and clean-up of all environmental samples, while the extracts from the second condition were subjected to further cleaning. The recoveries obtained were found to be consistent with that of Wang et al[19] and BDE-100 gave the highest level of recovery. Concentrations of PBDEs in the two seasons are shown in Table 1, with high concentrations of

∑PBDEs observed in winter compared to summer. The values obtained ranged from 4.66 ng g^{-1} (S1) to 53.09 ng g^{-1} (S3) for sum PBDEs in the winter sediment while a range of 2.32 ng g^{-1} (S1) − 20.86 ng g^{-1} (S4) ∑PBDEs was observed in summer sediment samples. The result showed negative correlation with a statistical significance ($r = -0.21$, $p = 0.045$) between concentrations of PBDEs detected at different sites in the two seasons. This seasonal difference may be attributed to the impact of dilution during the summer period, caused by heavy rainfall in the catchment area. During this period, it was observed that the river level rose. Furthermore, inputs from storm water run-offs may have also contributed to the observed lower concentration in summer compared to the dry winter months. This is also supported by the corresponding high and low median concentration of PBDEs 39.87 ng g^{-1} d.w and 8.05 ng g^{-1} d.w for winter and summer, respectively.

Table 1: Mean PBDE concentrations (ng g^{-1} d.w) in winter and summer (in bracket) sediment samples

PBDEs	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
BDE-28	0.66 (O.47)	21.55(11.95)	10.95 (0.41)	4.89 (4.16)	n.d (0.79)	n.d (0.93)
BDE-47	0.38 (0.15)	1.83 (0.43)	32.15 (0.29)	0.49 (8.78)	n.d (0.24)	15.07 (0.17)
BDE-100	0.73 (0.37)	0.08 (0.42)	5.12 (0.28)	0.37 (0.26)	n.d (n.d)	16.57 (0.23)
BDE-99	0.69 (0.35)	0.08 (0.4)	4.87 (0.26)	0.35 (0.25)	n.d (n.d)	15.78 (0.22)
BDE-154	n.d (n.d)	1.52 (1.64)	n.d (2.23)	1.86 (1.66)	30.14 (2.43)	n.d (1.15)
BDE-153	0.78 (0.98)	1.33 (0.62)	n.d (2.46)	1.36 (n.d)	2.29 (n.d)	n.d (0.85)
BDE-183	1.42 (n.d)	5.92 (2.22)	n.d (6.63)	0.91 (5.75)	16.26 (n.d)	n.d (n.d)
∑PBDE	4.66 (2.32)	32.31(17.66)	53.09 (12.56)	10.24(20.86)	48.7 (3.46)	47.42 (3.54)

N.B: n.d = below detection, S1= Knoppieslaagte, S2= Eastgate, S3= Waterval, S4= Kyalami, S5= Buccleuch and S6= Eastbank

PBDE concentrations in rivers have been measured in several regions and reported in the literature. The results of the present study were, therefore, compared with those found in the literature. The $\sum_7$PBDE in the present study ranged from 2.32 − 53.09 ng g^{-1}d.w. and a total PBDE of 347.51 ng g^{-1}d.w. was recorded. However, ∑PBDE concentrations in sediments measured in our study are comparable to those reported in Saginaw River, USA[23] and marine waters, Hong Kong[24], but lower than Fuhe River, China[11], Spanish coast[8], Niagara River[10] and sewage sludge in Switzerland being the highest with several order of magnitude. This may be attributed to more pronounced industrial activities in the catchments of the waste water treatment plant. It is important however, to note that accurate and direct comparison of PBDE concentration levels are impossible as a result of different regulations of BFRs, usage in different countries and difference in time and measurement. This study covered two seasons, winter and summer to observe seasonal variation.

The accelerated solvent extractor is a robust instrument that combines the ability of time saving extraction with online cleaning; it uses less solvent than the classical Soxhlet method, while the high temperature weakens interaction between analytes and matrix, the high pressure ensures the solvents remain liquid even at temperatures far above their boiling points. The present study has shown the attenuating impact of rainfall on concentration of PBDEs in Jukskei River sediment. Relatively, the highest concentration was detected at Waterval. It is believed that pollution source of the river comes largely from sewage effluent discharge, storm water run-off from agricultural activities around the catchment and illegal unmanaged dumping of refuse. The two instrumental conditions with different cleaning materials gave good and acceptable recoveries; however, condition 1 was applied for the environmental samples because it gave a higher recovery.

Acknowledgements

This work was conducted in the Organic Chemistry Laboratory of Resource Quality Services (RQS) of the Department of Water Affairs (DWA), Roodeplat, Pretoria, South Africa. The authors would like to thank

Tshwane University of Technology for the bursary given to Mr Olubiyi Olukunle towards his Masters degree in Environmental Management.

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