

# Evidence of gross contamination of surface water from Jukskei River, South Africa with hexabromocyclododecane (HBCDD) and tetrabromobisphenol A (TBBPA) flame retardants

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## 1. Introduction

Brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and tetrabromobisphenol A (TBBPA) are important industrial chemicals that have been widely employed for fire retardation purposes in different applications. HBCDD, for instance, consists of three major diastereoisomers, namely:  $\alpha$ ,  $\beta$  and  $\gamma$ , and it is primarily used as additive flame retardant in extruded and expanded polystyrene that is commonly used for thermal insulation in buildings, and sometimes in upholstery textiles [1]. On the other hand, TBBPA is often used either as a reactive or additive flame retardants in polymeric materials during manufacturing processes. Its major area of application is in the electronic circuit boards of electrical and electronic appliances. Regardless of their areas of application, both HBCDD and TBBPA may be released from treated products, thus resulting in the widespread contamination of the environment. Because of its environmental persistence, toxicity, bioaccumulation potential and its propensity to undergo long-range atmospheric transport, like penta- and octa-BDE commercial formulations, the HBCDD technical formulation has been globally restricted. Among the legacy BFRs, only TBBPA and deca-BDE technical formulations are still being produced and used.

In South Africa, there are no information on the production and usage of these BFRs. It is, however, assumed that imported raw materials for local industries and other imported items containing these chemicals are the only means through which these chemicals get into the country [2, 3]. With the growing economic instability within the Southern African region, more immigrants are constantly migrating to South Africa for economic opportunities. The resultant effects of these migration trend include exertion of high pressure on limited infrastructural facilities and the generation of large quantities of waste streams. These problems are particularly exacerbated in informal settlements which are characterized with old-fashioned consumer products such as furniture, carpets, electronic and electrical appliances, which are suspected to contain these chemicals. In particular, the establishment of these informal settlements along the banks of inland rivers within the city is contributing to the declining quality of these freshwater systems because obsolete items and other waste materials are often dumped along the banks of the rivers. It therefore becomes imperative to investigate the potential impacts of these activities with respect to the release of BFRs along the catchment of these inland rivers.

The location of the Jukskei River and its direction of flow provide unique opportunity to assess the impacts of associated activities in informal settlements situated along its banks on its water quality. Besides the contamination of the river by the influx of greywater from the informal settlements, the river also serves as a major conveyance of urban run-off and discharged effluents. During the periods of high precipitation, which coincides with the summer season, large quantities of debris are often transported into the river channel via urban run-off from the adjacent informal settlements. Under these circumstances, it becomes necessary to characterize the surface water of the impacted river during periods of low and high precipitations so that the contributions of the identified sources can be evaluated. For hydrophobic substances such as HBCDD and TBBPA, their presence in surface water at relatively high concentrations may be indicative of fresh release from local sources. Given their strong affinity to solids, these chemicals are expected to significantly accumulate in bottom sediment in aquatic systems. Since previous studies were specifically focused on the assessment of PBDEs concentrations in the investigated river [4, 5], we aimed to assess the degree of contamination of surface water from the Jukskei River with respect to the levels of both HBCDD and TBBPA with a view to identify the potential hotspots of these contaminants along the watercourse of the river.

## 2. Materials and methods

### 2.1. Chemicals and materials

LC-MS grade methanol, LC-MS Ultra CHROMASOLV<sup>®</sup> water and methanol, HPLC grade dichloromethane, and ammonium acetate (eluent additive for LC-MS), and deuterated bisphenol A (BPA-d16) were purchased from Sigma-Aldrich (Aston Manor, South Africa). Unlabeled TBBPA, <sup>13</sup>C-labeled TBBPA as well as native  $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCDD and their corresponding deuterated and <sup>13</sup>C-labeled isomers were purchased in methanol at 50

$\mu\text{g ml}^{-1}$  from Wellington Laboratories (Ontario, Canada). Similarly, Supelco ENVI-18™ SPE cartridges (500 mg, 6 ml) were purchased from Sigma-Aldrich (Aston Manor, South Africa).

## 2.2. Sample collection and preparation

Grab surface water samples were collected during two sampling regimes, namely on March 26, 2015 and June 4, 2015 from five (5) sampling sites along the stretch of Jukskei River. The details of the sampling points with specific reference to their geographical coordinates is presented in Table 1. The water samples were collected by dipping a 2.5 L amber glass bottle (previously washed and soaked in acid, rinsed with MilliQ water and finally rinsed with acetone) below the surface of the river. At each sampling site, three samples were collected. Two samples were taken at either side of the river where there was reduced flow and piles of solid wastes were either partially or completely submerged in the river. The other sample was taken near the centre of the river where there high flow and turbulence. Upon collection, the samples were immediately stored in ice containers and were kept cooled *en-route* to the laboratory. Each sample was filtered under vacuum and the resulting filtrate was kept in the refrigerator until further analysis. Two hundred and fifty millilitres of the filtered sample was spiked with known amount of the surrogate standards (500  $\mu\text{l}$  of 100 ng/ml) to monitor the recovery efficiency of the extraction method. The extraction was performed with ENVI-18™ cartridge previously conditioned with 5 mL each of n-hexane, dichloromethane, methanol and MilliQ water in this sequence. The flow rate of approximately one drop per second was maintained throughout the sample extraction. After the extraction, the SPE cartridges were vacuum dried for 45 min. before the elution of the target compounds. TBBPA and the HBCD isomers were eluted with 12 mL of dichloromethane:methanol (4:1, v/v). The extracts were concentrated under a gentle stream of nitrogen to incipient dryness. The dried extracts were then reconstituted with 500  $\mu\text{L}$  of 50 ppb internal standard D- $\alpha,\beta,\gamma$ -HBCDD and 200 ppb of BPA-d16 solution. Ten microliter of the solution was injected for LC-MS/MS analysis.

**Table 1: Geographical coordinates of the sampling sites along the stretch of Jukskei River**

Sampling points	Sample codes	Latitudes (S)	Longitudes (E)
Bucleuch	BUC	-26.0570	28.1040
Eastbank	EAB	-26.1090	28.1140
Eastgate	EAG	-26.0847	28.1088
Knoppieslaagte	KNP	-25.9482	27.9575
Kyalami	KYA	-26.0056	28.0784

## 2.3. Liquid chromatography tandem mass spectrometry

The analyses were performed using a Shimadzu Prominence HPLC system (Shimadzu Corp., Kyoto, Japan) coupled to a Shimadzu LCMS 8030 electrospray triple quadrupole mass spectrometer. The targeted compounds were chromatographically separated on an InertSustain C18 column ((3  $\mu\text{m}$  particle size, 2.1 x 150 mm) (Tokyo, Japan). The mobile phases consist of A (20 mM ammonium acetate) and B (100% methanol) starting at 90:10 A/B for 1 min and increased to 80:20 A/B over 2 min., followed by an increase to 40:60 A/B over 2 min. This was further increased to 5:95 A/B over 37 min and was finally increased to 0:100 A/B over 1 min. The set up was maintained at this gradient for further 2 min. before it was returned to 90:10 A/B over 0.01 min and maintained at this gradient for 10 min. to allow for column equilibration. The flow rate was set at 0.20 ml/min with an injection volume of 10  $\mu\text{l}$ . The oven temperature was maintained at 40°C. The mass spectrometer was equipped with an electrospray ionization source. The source heating block was maintained at 400°C, while the desolvation temperature of 250°C was employed. Nitrogen was used as a drying and nebulizing gases (1.50 L/min), while the collision-induced dissociation (CID) gas was Argon and was maintained at 230 kPa. The resulting fragment ions were monitored in multiple reaction monitoring (MRM) mode with a dwell time of 100 msec. The details of the precursor and product ions obtained in negative electrospray mode and their collision energies as well as cone voltages are presented in Table 2. In all cases, [M-H]<sup>-</sup> ions were monitored for the targeted compounds.

## 2.4. Quality assurance and quality control

To ensure accurate determination of the targeted analytes, isotope dilution method involving the use of deuterated isomers of HBCDD and BPA were employed as internal standards for the native and <sup>13</sup>C-labeled HBCDD and TBBPA, respectively. The possibility of contamination which may arise from glassware and reagents were checked using a total of three procedural blanks. None of the HBCDD isomers were detected in the procedural blanks, although traces of TBBPA were detected and these were subsequently subtracted from the measured values. The limits of quantification (LOQs) of the targeted analytes were governed by the signal to noise (S/N) ratio and were estimated as ten times the background noise in the blank samples. These values were 0.05, 0.12, 0.05 and 0.40 ng/l for  $\alpha$ -HBCDD,  $\beta$ -HBCDD,  $\gamma$ -HBCDD and TBBPA, respectively. The recovery results for the surrogate standards (<sup>13</sup>C-HBCDD isomers and <sup>13</sup>C-TBBPA) ranged from 53-111%, 19-88%, 21-

120%, and 21-129% for  $^{13}\text{C}$ - $\alpha$ -HBCDD,  $^{13}\text{C}$ - $\beta$ -HBCDD,  $^{13}\text{C}$ - $\gamma$ -HBCDD and  $^{13}\text{C}$ -TBBPA, respectively. Because of the wide variations in the recovery of the spiked surrogate standards, the reported results were recovery corrected. For both the surrogate and native standards, six to nine calibration points ranging from 1 to 125 ng/ml were employed. As shown in Table 2, the linearity of the resulting calibration curves generally exceeds 0.9950.

**Table 2: Optimum MRM parameters employed for the targeted BFRs**

Target compound	Acquisition time (min.)	$R^2$	Quantitation ion	Collision energy (eV)	Confirmation ion	Collision energy (eV)
<i>Native HBCDD</i>						
$\alpha$ -HBCDD	33.00-37.00	0.9959	640.70→80.95	15	640.70→78.90	17
$\beta$ -HBCDD	34.50-39.50	0.9993	640.70→79.10	42	640.70→81.00	27
$\gamma$ -HBCDD	36.00-40.00	0.9989	640.70→81.00	22	640.70→78.85	18
<i><math>^{13}\text{C}</math>-HBCDD</i>						
$\alpha$ -HBCDD	33.00-37.00	0.9970	652.90→78.85	13	652.90→80.95	17
$\beta$ -HBCDD	34.50-39.50	0.9979	652.60→78.90	21	652.60→81.00	22
$\gamma$ -HBCDD	36.00-40.00	0.9966	652.60→81.00	16	652.60→79.00	13
<i>Deuterated HBCDD-d18</i>						
$\alpha$ -HBCDD	33.00-37.00	-	657.60→81.05	13	657.60→78.80	15
$\beta$ -HBCDD	34.50-39.50	-	657.80→81.05	21	657.80→79.00	15
$\gamma$ -HBCDD	36.00-40.00	-	657.80→80.85	21	657.80→78.90	26
<i>Native TBBPA</i>						
TBBPA	22.00-28.00	0.9992	542.75→445.70	35	542.75→419.75	43
					542.75→80.90	53
<i><math>^{13}\text{C}</math>-TBBPA</i>						
MTBBPA	22.00-28.00	0.9993	554.90→78.85	44	554.90→459.75	34
					554.90→428.60	46
<i>Deuterated BPA</i>						
BPA-d16	11.40-17.40	-	241.20→223.15	22	241.20→142.20	29

### 3. Results and discussions

#### *Levels of targeted BFRs in surface water samples*

The observed concentrations of the targeted BFRs during the first and second sampling campaigns are presented in Table 3. Overall, the measured concentrations of these analytes ranged from ND-1.72 ng/l, ND-0.88 ng/l, ND-3.33 ng/l and 1.53-775.05 ng/l for  $\alpha$ -HBCDD,  $\beta$ -HBCDD,  $\gamma$ -HBCDD and TBBPA, respectively. The highest concentrations of the HBCDD isomers were found at the BUC sampling site. Among the HBCDD isomers,  $\gamma$ -HBCDD had the highest overall concentration (3.33 ng/l). The highest concentrations of  $\alpha$ - and  $\beta$ -HBCDD in the analysed samples were found in the sample group from the first sampling campaign, whereas  $\gamma$ -HBCDD was highest in the sample group from the second sampling campaign. Interestingly, the highest concentrations of the HBCDD isomers were detected in samples collected from near the mid-point of the river. In line with our initial speculations that the sample taken from the mid-point of the river may be representative of important point sources such as wastewater treatment plant (WWTP) discharges or industrial discharges which are usually characterized with high volumes. Despite the dilution effects of the river water, the highest concentrations of the HBCDD isomers were generally obtained at near the mid-point sampling points across the sampling sites. Based on these observations, we conclude that WWTP discharges may be contributing to the surface water contamination of the Jukskei River with respect to the observed levels of HBCDD in the analysed samples.

With respect to the occurrence of TBBPA in the investigated water sample, a completely different pattern was observed. First, TBBPA had 100% detection frequency across all the sampling sites during the two sampling campaigns. Furthermore, the observed concentrations of TBBPA were generally higher than those observed for the HBCDD isomers, although with a much higher variation across the sampling sites than the HBCDD isomers. The highest concentration (775 ng/l) was observed at a sampling site (EAG), which is in close proximity to an informal settlement situated along the catchment of the investigated river. It is worth mentioning that majority of the housing units within most informal settlements in South Africa are poorly constructed without any adherence to physical and town planning procedures. Majority of these households are also known to be important repositories of old and non-functional electronic and electrical appliances. Due to the economic hardships and non-availability of jobs, these informal settlements are often heavily congested with the influx of immigrants and migrants from the rural communities of the country. As a result of these congestion problems, the provision of essential services such as waste collection and disposal by appropriate municipalities become a problem [6]. Consequently, obsolete waste materials are often discarded and dumped at any open space, including the Jukskei River bank. During the reconnaissance survey visit to the sampling sites, submerged waste materials were visibly seen along the banks of the river. With regard to the observed levels of TBBPA, it is

possible that treated materials containing TBBPA which are disposed into the river banks are slowly releasing it into the water column. The observed levels of the targeted BFRs, particularly the TBBPA has a gruesome implication for both aquatic organisms and other wildlife. In particular, avian species are known to depend on water from this river and would probably drink from the banks of the river. Considering the high levels of TBBPA measured in the present study, it becomes necessary to focus further studies on investigating the mechanisms of release of this pollutant from the submerged waste materials and to characterize other potential sources of these BFRs into the investigated river.

**Table 3: Measured concentrations of the targeted BFRs in surface water samples from the Jukskei River**

Sampling sites	1 <sup>st</sup> sampling regime						2 <sup>nd</sup> sampling regime					
	a	b	c	Mean	SD	DF (%)	a	b	c	Mean	SD	DF (%)
<b>BUC</b>												
<i>α</i> HBCDD	ND	1.72	ND	0.57	0.81	33.33	ND	ND	ND	-	-	0
<i>β</i> HBCDD	ND	0.39	0.26	0.22	0.16	66.67	ND	ND	ND	-	-	0
<i>γ</i> HBCDD	ND	0.88	0.09	0.32	0.40	66.67	0.62	3.33	ND	1.32	1.45	66.67
TBBPA	114.10	140.22	114.31	122.88	12.26	100	30.27	286.73	718.39	345.13	283.94	100
<b>EAG</b>												
<i>α</i> HBCDD	0.36	0.81	0.57	0.58	0.18	100	0.33	0.50	0.61	0.48	0.12	100
<i>β</i> HBCDD	ND	ND	ND	-	-	0	ND	ND	ND	-	-	0
<i>γ</i> HBCDD	ND	0.21	0.12	0.11	0.09	66.67	0.05	0.08	ND	0.04	0.03	66.67
TBBPA	775.05	8.00	9.08	264.04	361.34	100	96.74	136.08	79.38	104.07	23.72	100
<b>EAB</b>												
<i>α</i> HBCDD	ND	ND	ND	-	-	0	ND	0.50	ND	0.17	0.24	33.33
<i>β</i> HBCDD	ND	ND	ND	-	-	0	0.18	0.19	ND	0.12	0.09	66.67
<i>γ</i> HBCDD	ND	ND	ND	-	-	0	0.08	0.39	ND	0.16	0.17	66.67
TBBPA	28.63	259.15	69.61	119.13	100.41	100	55.31	13.61	10.22	26.38	20.50	100
<b>KYA</b>												
<i>α</i> HBCDD	ND	ND	ND	-	-	0	ND	ND	ND	-	-	0
<i>β</i> HBCDD	ND	ND	ND	-	-	0	ND	ND	ND	-	-	0
<i>γ</i> HBCDD	ND	ND	ND	-	-	0	ND	ND	ND	-	-	0
TBBPA	21.24	14.34	50.65	28.74	15.74	100	260.36	1.53	50.54	104.14	112.26	100
<b>KNP</b>												
<i>α</i> HBCDD	ND	0.50	ND	0.17	0.24	33.33	ND	ND	ND	-	-	0
<i>β</i> HBCDD	ND	ND	ND	-	-	0	ND	ND	ND	-	-	0
<i>γ</i> HBCDD	ND	ND	ND	-	-	0	ND	ND	ND	-	-	0
TBBPA	477.16	61.22	390.82	309.73	179.23	100	69.12	7.75	91.27	56.05	35.33	100

ND – not detectable; SD – standard deviation; DF – detection frequency; a – sampling point with reduced flow rate at the bank of the river; b – sampling point at near the mid-point of the river with increased flow rate and turbulence; c – sampling point at the other side of the river bank with reduced flow rate and turbulence.

## Conclusions

The occurrence of HBCDD isomers and TBBPA were investigated in surface water samples collected from the Jukskei River. The findings from this pilot study suggest that the detection of these contaminants might be associated with WWTP discharges. However, the widespread contamination of the surface water samples with TBBPA implies that sources other than effluent discharges may be contributing to the contamination of the investigated river. Based on our findings, we speculate that the influx of obsolete waste materials through urban run-off from adjoining informal settlements may be contributing to the contamination of the river. Further studies are required to establish these possibilities and to investigate the occurrence of these BFRs in other potential point sources along the river.

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