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A Simplified Analytical Procedure for Simultaneous Determination of Alkylphenol Ethoxylates and Brominated Flame Retardants in Fish Tissue Samples from Vaal River, South Africa

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Abstract

In this study, the concentration of alkylphenol ethoxylates (APEs) and brominated flame retardants (BFRs) were determined in fish samples, *Labeo umbratus* and *Carp*, collected from the Vaal River in South Africa. Ultrasonic-assisted extraction technique was used to extract the organic contaminants from fish samples, and the resulting extract was purified by sulphuric acid lipid removal followed by Strata X-cartridge SPE clean-up. The APEs and BFRs were derivatized using heptafluorobutyric anhydride before analysis with GC-MS. In both types of fish samples, lower oligomers of APEs were more abundant than the higher oligomers, while HBCD, BDE99 and PBB101 were the dominant BFRs. The concentrations of these pollutants ranged from 1.061 ng/g lipids (*t*-BP) in *Labeo umbratus* to 11.860 ng/g lipids (HBCD) in *Carp*.

Keywords

Alkylphenol Ethoxylates, Brominated Flame Retardants, Fish Sample, Heptafluorobutyric Anhydride Derivatization, Vaal River, South Africa

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1. Introduction

Due to high levels of industrial activities in most big cities, the pollution of aquatic systems is generally higher in cities than in rural environment. This is due, in part, to sewage systems receiving effluents from many industrial processes along with domestic wastewater. Such wastewaters, most often, tend to contain a wide range of toxic organic and inorganic substances [1]. Among the chemicals potentially associated with urban wastewater, alkylphenol ethoxylates (APEs) and brominated flame retardants (BFRs) have been identified as one of the nuisance toxic groups. Their presence in aquatic environmental is as a result of their use in several consumer and personal-care products and as flame retardants in electrical and electronic appliances. These organic pollutants, as well as their degradation by-products, are known to be persistent, bio-accumulating and highly toxic, with potential for estrogenic activity [2] [3].

Alkylphenol ethoxylates are one of the most widely used surfactants. They have been used in domestic detergents, pesticide formulations and industrial products [4]. These compounds find their way into the environment in their original form and as natural degradation products of the parent alkylphenol ethoxylates that are popularly used in commerce for their surfactant properties [5]. The levels of these APEs metabolites present in the environment may be well above the threshold necessary to induce endocrine disruption in wildlife. These findings have raised public concern over their environment and human health effects [4]. Brominated flame retardants have shown to be the most effective in the inhibition of fires and are material of choice because of their low cost and lower loading of substrate [6]. Of all the BFRs, PBDEs are the most commonly used compared with polybrominated biphenyls (PBBs), hexabromocyclododecane (HBCD) and tetrabromobisphenol (TBBPA) [2]. Different PBDEs congeners such as decabrominated diphenyl ether (BDE209), are known to be photo-chemically degraded by ultraviolet light resulting in the formation of less brominated PBDEs that are more persistent, bio-accumulative and toxic [7].

Humans can be exposed to these compounds through different sources such as consumption of contaminated foods, inhalation of contaminated particles or direct contact with materials that have been treated with APEs and BFs [8] [9]. Other sources of human exposure included water supply and sewage sludge used as fertilizers. Several studies have confirmed the presence of these pollutants in fish [5] [8]-[13]. So far, the information on the levels of these pollutants in fish samples from around Africa including South Africa is still scarce. Studies conducted to date in some South African environmental samples (waters and sediments) have shown the presence of organochlorinated [14], alkylphenol ethoxylates [15] and PBDEs [16] [17]. With the exception of recent study by Polder *et al.* [18] who reported the presence of HBCD in bird egg in South Africa, the authors are not aware of any report on the simultaneous determination of APEs and BFRs in fish samples. This study describes a simplified method for the simultaneous quantification of alkylphenol ethoxylates and brominated flame retardants in fish matrices using ultrasonic extraction followed by concentrated sulphuric acid fats removal and solid phase extraction clean-up; heptafluorobutyric anhydride derivatization and gas chromatography-mass spectrometry determination.

2. Materials and Methods

2.1. Materials

2.1.1. Standards and Reagents

Derivatizing agents (heptafluorobutyric anhydride (HFBA)) was of analytical grade purchased from Sigma-Aldrich, South Africa. The solvents, acetone and hexane used in the study were of GC grade and were used without further purification. The APEs and PBBs were purchased from Laboratories Dr Ehrenstorfer-Schäfers, Augsburg, Germany. Only the NPE, NPPE and OPPE were of technical grade and the remaining APEs, PBBs and PBDEs were of analytical grade. Tetrabromobisphenol A of technical grade as Firemaster BP4A and hexabromocyclododecane of technical grade were purchased from AccuStandard, USA. Helium as He 5.5 pure was purchased from Air Product South Africa, Vereeniging.

2.1.2. Fish Sample Collection

Seven bottom feeders, *Labeo umbratus*, and nine predatory fish, *Carp*, were collected from the Vaal River. The selected fishes were caught using a fishing rod. Fish selected for analysis were killed by a blow to the head and were identified as males. The length and weight of each fish was recorded. The fish were individually wrapped

in aluminum foil, placed in plastic bags packed with ice for transport to the laboratory where the samples were frozen pending preparation of the tissue samples. Fish tissue samples were prepared following the guidance in EPA [19]. Techniques to minimize potential for sample contamination were used. During sample preparation, non-talc nitrile gloves were worn and heavy-duty aluminum foil cutting board was used. The gloves and foil were changed between samples and the cutting board cleaned between samples. The fish were thawed enough to remove the foil wrapper and rinsed with tap water, then deionized water to remove any adhering debris. Before use, the skins were removed and the sample, muscle tissues, collected.

2.2. Methods

2.2.1. Muscle Tissue Sample Preparation: Homogenization, Extraction and Clean-Up

About 5 g of the tissue was weighed and mixed with 20 g anhydrous sodium sulphate and grounded to free flowing. The contents were extracted with 20 ml of hexane/acetone mixture (4:1) at 55˚C for 45 min in two cycles. After the ultrasonic extraction, the extracts were combined and placed in separating funnel. Roughly 10 ml of concentrated sulphuric acid was added, the mixture shaken for 5 min and phase separated. The acid layer was washed once with 25 ml of hexane. The hexane extracts were combined and washed with 40% (v/v) sulphuric acid for further removal of residual lipids. The phases were separated and the organic phase evaporated to dryness using TurboVap II instrument. The residue was re-constituted with 2.5 ml of MeOH, diluted to 250 ml with MilliQ water and acidified to pH 3 with acetic acid. The mixture was then passed through an SPE cartridge conditioned with 6 ml of 30% MeOH in DCM, followed by 6 ml DCM. After passing the mixture through the cartridge, the cartridge was dried for 1 h and APEs and BFRs eluted with DCM:hexane (4:1) mixture. The eluates were then concentrated under a gentle stream of nitrogen to dryness and placed under derivatization conditions as described in our previous report [20]. Briefly, to the residue containing APEs and BFRs, 0.1 ml hexane; 70 µl of 0.1 M triethylamine (TEA) and 7 µl HFBA were added. The test tubes were closed and completely mixed for 1 min using a vortex system. The contents were gradually heated to 50˚C and the derivatization was achieved within 30 min. Thereafter, the contents were cooled, quenched with 0.3 mL of 5% aqueous solution of K_2CO_3. The organic phase was then drawn off. The aqueous phase was washed twice with 0.5 mL of hexane to recover some organic fractions. After separation, the organic phase extracts were concentrated to 100 µl. Thereafter, the internal standards (Chrysene and PBB80, 20 µl of 2 ppm each) were added into the extract, the volume made up to 200 µl and 1 µl of a mixture of extracts and internal standards injected into the GC-MS.

2.2.2. Instrumentation and GC/MS Conditions

An Agilent 6890 GC equipped with 5975 mass selective detector (MSD) was used for analysis. The GC was equipped with a Gerstel autosampler and separation performed on a capillary column (Restek RTx-1614, film thickness 0.10 µm, 15 m × 0.25 mm I.D. (Chromspec cc South Africa)). The GC/MS conditions used for analysis were as follows: carrier gas He; linear velocity, 40 $cm \cdot s^{-1}$; injector temperature, 275˚C; transfer line temperature, 280˚C; ion source 150˚C. For analysis 1µl splitless injection were carried out by autosampler. The GC temperature program conditions were as follows: initial temperature 50˚C, heated to 120˚C by a temperature ramp of 7.5˚C/min then 275˚C by a temperature ramp of 15˚C/min then finally heated to 280˚C (held for 1 min) by a temperature ramp of $25^{\circ}C \cdot min^{-1}$.

2.2.3. Quality Assurance

Several quality control measures were taken to ensure the correctness and integrity of the results. These include the use of pre-extracted tissue samples spiked with pure APEs and BFRs standard (16 ng/g and 80 ng/g) to assess recovery. The recoveries ranged from 50.02 ± 14.63 (NPPE2) - 90.88 ± 6.32 (BDE47) with six values below 60%. Several other quality assurance measures were also routinely observed in this study and included running blanks in between samples, analyzing samples in triplicates as well as analyzing test standard after every five samples.

3. Results and Discussion

A total of seven APEs isomers (*tert*-butylphenol (*t*-BP), *tert*-nonylphenol (*t*-NP), octylphenol ethoxylate (OPE), nonylphenol ethoxylate (mono-NPE), nonylphenol di-ethoxylates isomers (di-NPE1 and di-NPE2), octylphenol penta ethoxylates (OPPE), nonylphenol penta ethoxylates isomers (NPPE1 and NPPE2)); seven PBDEs congen-

ers (BDE28, BDE47, BDE100, BDE99, BDE154, BDE153, BDE183) together with pentabromobiphenyl (PBB101) and hexabromocyclododecane (HBCD) were determined and quantified fish samples from the Vaal River, South Africa.

Recovery Test

Different methods were tested for lipid removal (2.92% lipids, n = 9, predatory; 2.44%, n = 7, bottom feeder) and recovery of APEs and BFRs from tissue samples. The following lipids removal methods, aminopropyl cartridge, destruction with concentrated sulphuric acid, silica gel stirring and/or their combinations were tested. With the aminopropyl cartridges, the lipids removal was ~80% (n = 4), while silica gel stirring gave a lipid removal of 65% (n = 4). The combination of aminopropyl cartridge with silica gel column gave 98.3% lipid removal with recoveries of 10% - 78.7% (n = 5). This combination for lipid removal was found to be inadequate in removing lipids from the *Carp* species were 75% lipids removal was recorded. Concentrated sulphuric acid wash was used and ~80% lipid was removed. However, by washing the post-extract with concentrated acid, followed by a dilute sulphuric acid (40% (v/v)), ~97% lipids (n = 16) was removed and the recovery after lipids removal and SPE clean up ranged between 50.02 ± 14.63 (NPPE2) - 90.88 ± 6.32 (BDE47) as presented in **Figure 1**.

The developed method was applied to determine the concentration of sixteen (16) fish samples collected from the Vaal River. The composition of the fish were seven (7) bottom feeders, *Labeo umbratus*, and nine (9) predatory fish, *Carp*. The concentrations of APEs and BFRs from the samples are shown in **Figure 2**.

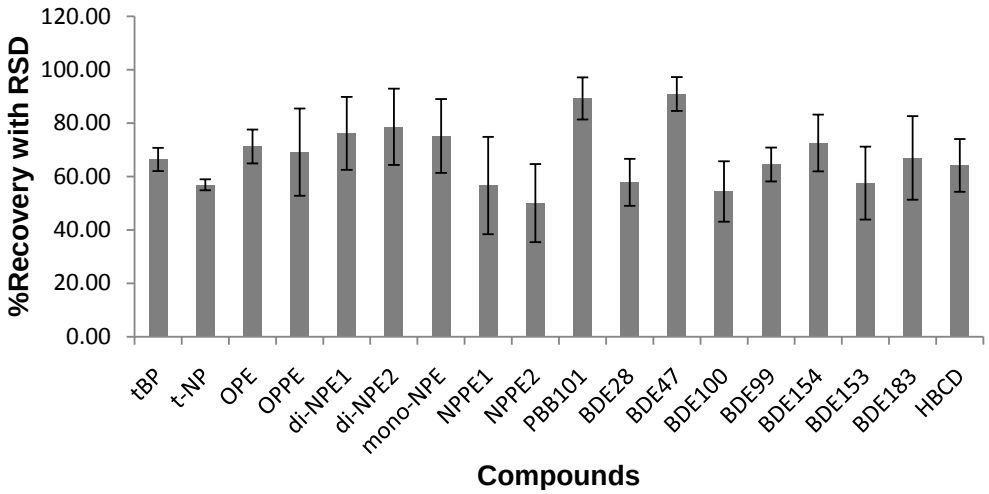

Figure 1. Recoveries of APEs and BFRs from tissue.

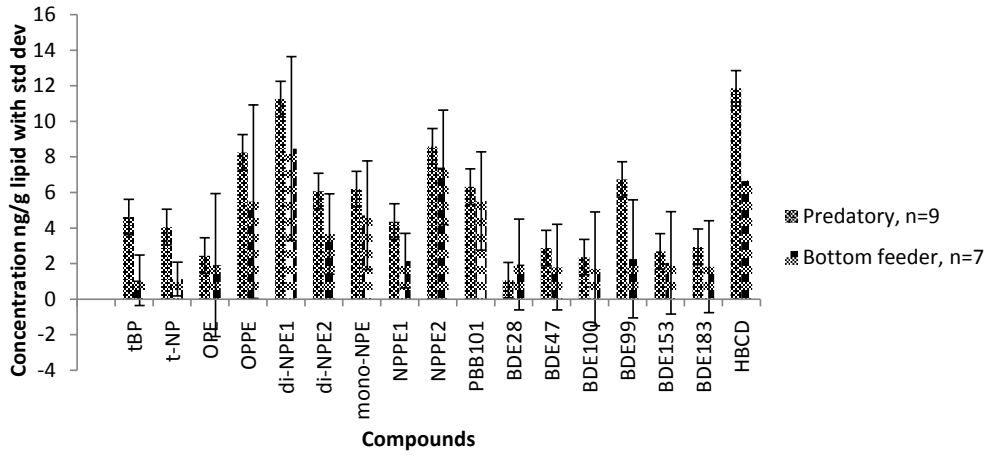

Figure 2. Levels of APEs and BFRs in fish samples from Vaal River.

The concentrations of APEs from *Carp* fish followed the following pattern: di-NPE1 > OPPE/NPPE2 > di-NPE2/mono-NPE > *t*-BP/*t*-NP/NPPE1 > OPE. The same pattern was also observed from *Labeo umbratus*. The BFRs concentrations pattern was as follows: HBCD > BDE99 > PBB101 > BDE47/BDE183 > BDE153/BDE100 > BDE28 in both types of fish samples. It can also be observed in **Figure 2** that higher concentrations of the organic contaminants were found in the predator than in the bottom feeder. The observed higher concentrations can be attributed to intake of already contaminated fish by the predator fish. The same pattern is observed in the sum concentrations of the analytes presented in **Figure 3**.

The results as presented in **Figure 3** show that APEs are the major contaminants found in fish as compared to BFRs. With APEs, the lower ethoxy, *i.e.*, di-NPE and mono-NPE, were found to be the most abundant at 23.52 ng/g lipids vs 12 ng/g lipids for NPPE with the remainder (10.6 ng/g lipids) being the sum of OPE and OPPE. These ratios were also observed by Schmitz-Afonso *et al.* [3], Rice *et al.* [5] and Datta *et al.* [8]. However, the concentrations obtained in this study were lower than the concentrations reported in those reports as shown in **Table 1**. With the BFRs, the PBB101 was detected in almost the same concentration in both fish while HBCD was slightly higher in *Carp* than in *Labeo umbratus* species. When compared to the results reported by Hiebl & Vetter [21] as presented in **Table 1**, the concentration of HBCD was lower in this study. With the PBDEs, congener BDE99 was more abundant in *Carp* than in *Labeo umbratus*. This predominance of the penta congeners is

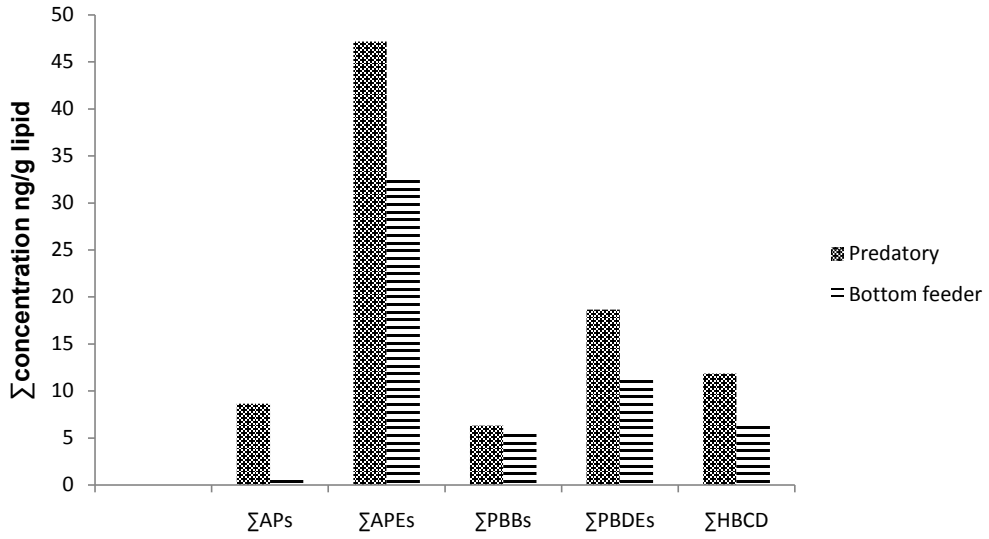

Figure 3. Sum concentration of APEs and BFRs in fish.

Table 1. Concentration of APEs and BFRs of fish samples from other studies (ng/g lipid).

Area	Sample	∑PBDE	∑PBBs	∑APE	HBCD	Ref
Canada	*Mussel*	n/a	n/a	177 - 12,440	n/a	[1]
USA	*Trout*	n/a	n/a	18 - 2075	n/a	[8]
USA	*Carp*	n/a	n/a	32 - 920	n/a	[5]
USA	*Carp*; *Walleye*	n/a	n/a	4900 - 8200	n/a	[3]
USA	*Small mouth bass*	800 - 29,000	n/a	n/a	n/a	[9]
Taiwan	Fish	2.85 - 1243	n/a	n/a	n/a	[13]
Germany	*Coregonus* sp.	n/a	n/a	n/a	40 - 60	[21]
Australia	Fish	6.4 - 115.4	n/a	n/a	n/a	[25]
Spain	*Trout*	0.024 - 11.48	n/a	n/a	n/a	[23]
South Africa	*Carp*; *Labeo umbratus*	11.58 - 18.68	5.52 - 6.33	32.57 - 47.18	6.64 - 11.86	***This study***

n/a: not applicable.

consistent with previous studies, which indicated that BDE47 and BDE99, in particular, bio-accumulate and bio-magnify up the food chain [9] [13] [22] [23]. Another factor that might be important is debromination of the higher substituted congeners resulting in increasing concentration of lower substituted BDEs over time [24]. The reported concentration of BFRs, are slightly lower than the results reported by des Jardins Anderson & MacRae [9], Peng *et al.* [13] and Losada *et al*. [25] but similar with concentrations reported by Lacorte *et al*. [23]. Some of the key activities along the river include flows from wastewater treatment works, stock farming, irrigation agricultural activities as well as the overall increase in human population around the sub-catchment area. These activities may be responsible for the observed levels of the analytes determined.

4. Conclusion

Using a simplified derivatization approach as described in this study, the presence and levels of APEs and BFRs in fish samples collected from the Vaal River in Gauteng, South Africa, were determined simultaneously. The large variation in the concentrations of APEs and BFRs found in the fish may be attributed to feeding habit of the fish and the exposure levels of contamination in the river. In comparison to other reported concentrations, our finding indicated a moderate contamination level for both types of compounds; however, owing to lack of specific regulations for APEs and BFRs in environmental samples in South Africa at present, further studies on determining the source of these pollutants in the environment are needed.

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