An integrated method for the simultaneous determination of alkylphenol ethoxylates and brominated flame retardants in sewage sludge samples by ultrasonic-assisted extraction, solid phase clean-up, and GC-MS analysis

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ABSTRACT

Generally, a major route of alkylphenol ethoxylates (APEs) and brominated flame retardants (BFRs) to enter the environment is via the wastewater treatment works (WWTW) facilities. Consequently, the levels of APEs and BFRs in sewage sludges may give an indication of the general use and exposure of these compounds. The present study was aimed at an integrated method for the analysis and quantification of APEs and BFRs in sewage sludge from selected wastewater treatment plants. The optimization of the extraction procedure included variation of the amount of extracted biomass, the duration, temperature during sonication as well as type of extraction solvent. Chromatographic determinations of APEs and BFRs were carried out with gas chromatography equipped with mass spectrometry detector after derivatization with heptafluorobutyric anhydride (HFBA). The mean percentage recoveries ranged from 39% to 79% (n = 3) for sewage sludge after extracting 5 g biomass sludge with hexane: acetone (4:1) at 55 °C for 45 min in two cycles. The mean concentrations of APEs obtained ranged from <LOQ to 365 ng g^{-1}, <LOQ to 166 ng g^{-1}, <LOQ to 642 ng g^{-1} while the concentration of BFRs obtained range from <LOQ- 17 ng g^{-1}, <LOQ to 163 ng g^{-1}, <LOQ to 14 ng g^{-1} for sludge samples from Leeuwkuil, Rietspruit, and Sebokeng, respectively. All compounds, except for nonylphenol (NP), BDE47, and BDE154, were detected from the Rietspruit WWTW. The presence of these pollutants in Rietspruit WWTW may be attributed by the fact that this treatment plants treat wastewater from domestic as well industrial discharges from the surrounding area.

1. Introduction

Sewage sludge is a very complex environmental solid matrix generated in the wastewater treatment plants. Concerning the disposal practices for sludge, besides incineration and disposal in landfills, the application to agricultural land represents the most important alternative and an economical way to dispose tons of sludge produced in sewage treatment plants [1]. A major route for the treatment and disposal of many chemicals such as alkylphenol ethoxylates (APEs) and brominated flame retardants (BFRs) used in industrial and domestic applications or textiles, furniture, and electronics is via sewage treatment works [2,3]. Biodegradation of APE during wastewater treatment works (WWTW) results in the production of more persistent and estrogenic metabolites such as short chain APEs and alkyl phenols (APs) including nonylphenol, octylphenol. These metabolites are more toxic than the parent compounds, have low water solubility, adsorb to the sludge solids, and they possess the ability to mimick natural hormones by interacting with the estrogen receptor [3,4]. A growing concern for BFRs has risen because of their occurrence and persistence in the environment similar to other halogenated pollutants such as polychlorinated biphenyls (PCBs) [5]. Thus, once the flame retardant enters into the environment, it can be attached to a particle for transport in water or delivery to the sediment or end up on an airborne

dust particle and travel distances far from production and/or emission site. Hence traces of BFRs are found in terrestrial, freshwater, and marine ecosystems at various locations far from where they are produced or used [2,6,7].

Due to the widespread use of APEs and BFRs, an adequate analytical method for their simultaneous quantitation in sewage sludge is needed in order to determine their concentrations in the wastewater treatment systems and derive safe conclusions for their fate and possible disposal threat during final disposal. Up to date, several extraction reports have been published on the analysis of APEs and BFRs from environmental solid samples [8]. Different extraction methods such as microwave-assisted extraction [9,10], Soxhlet extraction [11–15], pressurized liquid extraction [16–20], and ultrasonic-assisted extraction [1,8,21,22] have been employed followed by either liquid or gas chromatographic analysis. These aforementioned reports highlighted the current issues in the development of instrumental technologies related to the detection of these endocrine-disrupting compounds (EDCs). Unfortunately, some of these analytical techniques are either too sophisticated or expensive to allow for the investigation of these compounds in some regions of the world.

Although these compounds have been detected in solid samples, however, to the best of our knowledge, none of the published studies have reported on the simultaneous determination of APEs and BFRs in sewage sludge using an integrated method that is fast and easy to use. Thus, the main objective of the present work was to develop, optimize, and validate a simple and rapid analytical method for the identification and quantification of APEs and BFRs in sewage sludge using ultrasonic-assisted extraction followed by pre-developed SPE clean-up [23]. Four key parameters in sonication procedure, namely, biomass, the temperature, the duration of sonication, and the type of solvent were carefully studied and optimized. Finally, the developed method was applied to sewage sludge samples collected from different wastewater treatment plants in the Vereeniging region, South Africa, so as to test the applicability of the procedure to real samples.

2. Experimental

2.1. Materials

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

2.2. Sample collection

Sludge samples were collected from three different wastewater treatment works (Sebokeng WWTW, Rietspruit WWTW, and Leeuwkuil WWTW) in the Vereeniging region. The primary sludge was collected before it went through the digestion process from the treatment plant. Collection was carried out in a 1000 mL bottle covered with aluminum foil. The population and capacity of the treatment plants were 127,000, 41 ML/day; 127,000, 36 ML/day, and 352,000, 100 ML/day for Leeuwkuil, Rietspruit, and Sebokeng treatment plants, respectively, in Gauteng Province, South Africa. The sludge samples were characterized for total solids (TS), volatile suspended solids (VSS), pH, conductivity and

alkalinity with the intention of determining whether there is any influence of these parameters with the levels of APEs and BFRs in the sewage sample determined.

2.3. Extraction of analytes from simulated solid sample

To assess the efficiency of the ultrasonic extraction technique employed, different solvents combination (pentane: acetone (4:1), DCM: acetone (4:1), hexane: acetone (4:1) and DCM: hexane: acetone (2:2:1)), biomass (25, 12.5, 10, 5 and 2.5 g), temperature (35, 45, and 55 °C), and time (15, 30, 45 and 60 min) were evaluated. A pre-washed garden sand (n = 3) were spiked with 100 μL of APEs and BFRs standards. The spiked samples were thereafter extracted with 30 mL of the extraction solvent combinations in two cycles. The extracts were then pooled together and 2 g copper added to remove elemental sulfur before being concentrated to near dryness using TurboVap II apparatus. The solvent was exchanged to methanol (MeOH), diluted to 250 mL with MilliQ water, and acidified to pH ~ 3 with acetic acid before clean-up by solid phase extraction (SPE) as described by Chokwe *et al.* (2012). Briefly, the SPE (Strata-X 33 μm; Separations, South Africa) cartridge was conditioned with 6 mL of 30% MeOH in DCM followed by the addition of 6 mL of MeOH. APEs and BFRs were extracted at a flow rate of approximately 10 mL min^{-1}. After passing the sample through the cartridge, the cartridge was dried under vacuum for 1 h. The compounds were eluted with 3×2 mL of mixture of DCM–hexane (4:1). The eluates were evaporated to dryness, under a gentle stream of nitrogen at 40 °C. Finally, the dried residues were subjected to derivatization reaction.

2.4. Extraction and clean-up of sludge samples

Sludge samples were first centrifuged, and the supernatant, discarded. Thereafter, about 5 g of the solid was weighed and mixed with 20 g anhydrous sodium sulfate. The contents were extracted with 30 mL of hexane–acetone mixture (4:1) at 55 °C for 45 min in two consecutive cycles. The extracts were combined, passed through 3 g of acidic silica column, and eluted with 40 mL DCM. Then 2 g of Cu powder was added to remove elemental sulfur before being evaporated to approximately 0.5 mL using TurboVap II apparatus. The extract was then diluted to 250 mL with MilliQ water. MeOH (2.5 mL) was added, acidified to pH 3 with acetic acid and extracted according to the aforementioned procedure during method development.

2.5. Derivatization

Into a Pyrex test tube containing residues, 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 heated to 50 °C and maintained for 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) were added into the extract, the volume made up to 200 μL. 1 μL was injected into the GC-MS for analysis.

2.6. Instrumentation

An Agilent 6890 GC equipped with 5975 mass selective detector (MSD) was used for GC/MS analysis. The MS was tuned with perfluorotributylamine (PFTBA) using the auto-tune program. The GC was equipped with an Agilent autosampler and separation was 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 s^{-1}; injector temperature, 300 °C; transfer line
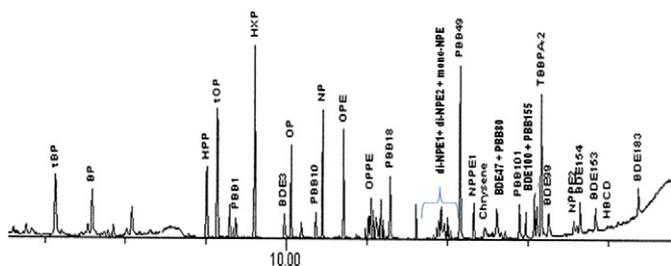
Fig. 1. GC chromatogram of derivatized APEs and TBBPA in the presence of PBBs, PBDEs, and HBCD standard.

temperature, 275 °C; ion source 150 °C. For analysis 1 μL 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 300 °C (held for 2 min) by a temperature ramp of 25 °C min^{-1}.

2.7. Quality assurance

The spiking method was used in the quality assurance process of analytical method due to unavailability of certified reference material for target compounds. Thoroughly washed and filtered sand was spiked with 100 μL of standard mixture of 1.0 μg L^{-1} APs, PBBs, and PBDEs; 5.0 μg L^{-1} HBCD and APEs and was taken through the same extraction and derivatization procedure mentioned above prior to GC analysis. Quality assurance measures observed in this study included running blanks with each sample set and analyzing the sample in triplicates. The mean and standard deviation, expressed as ng g^{-1}, were calculated from the measurements. In addition, a verification standard was analyzed after every five samples.

Statistical analysis was performed using Microsoft excel software (2010 version). The results from validation experiments were determined by one-way analysis of linear regression using peak area abundance while correlation co-efficient was used to test the linear relationship between APEs/BFRs concentration and physicochemical parameters.

3. Results and discussions

Chromatographic analysis achieved after heptafluorobutyric anhydride derivatization of APEs and TBBPA in the presence of PBBs, PBDEs, and HBCD is presented in Fig. 1.

3.1. Optimization of extraction parameter using simulated solid samples

Experiments were initially carried out using 25 g of washed and filtered garden sand spiked with APEs and BFRs standards with the aim of developing an analytical method suitable for the simultaneous analysis of these compounds. The effect of solvents (acetone (Ac), dichloromethane (DCM), pentane (Pent), hexane (Hex), and their

combination), temperature, and the duration of the sonication were studied in details. Finally, the amount of biomass (2.5–25 g) was studied using the best solvent at optimum temperature as well as duration of sonication. All the experiments were performed at least in triplicate, and the optimum value for each parameter was chosen. Furthermore, the optimum conditions were applied to the spiked sludge samples to confirm the extraction efficiency of the selected parameters in the sludge. The results of the optimization experiments are shown in Figs. 2–4.

The effect of solvent on extraction of the analytes was tested first. When these compounds were extracted with the individual solvents at 25 °C for 1 h and 30 min, their recoveries for all the compounds were low (i.e. <50%). However, a slight improvement was achieved with the combination of non-polar solvent with a more polar acetone. Higher ratio of acetone in the binary solvent mixture did not improve the recoveries of these compounds from the garden sand. The optimum ratio of acetone was found to be 10%. The results are presented in Fig. 2 below.

The results showed that hexane/acetone gave overall best recoveries compared to recoveries from other solvents. Accordingly, hexane: acetone (4: 1) was chosen as the organic solvent of choice for the simultaneous extraction of the target compounds.

Increase of temperature was found to have significant influence on the recoveries of the target compounds (Fig. 3).

For most compounds, an increase in temperature showed a slight increase in recoveries except for NPPE2 (35 °C: 63.24; 45 °C: 40.63; and 55 °C: 56.82). The reason for this phenomenon is unknown at the moment. The RSD for the same compounds was higher at 35 °C and 55 °C (24.64 and 31.32, respectively) indicating the difficulty of the compound to migrate into the solvent phase. Both these experiments (effect of solvent and effect of temperature) were performed by extracting the targeted compounds for 1 h and 30 min. The optimum temperature of 55 °C was chosen as the optimum temperature as most of the compounds were extracted at acceptable recoveries. The effect of time was studied whereby the extraction was done in two consecutives cycles as presented in Fig. 4,

For APEs, extraction time up to 45 min showed a slight improvement of recoveries overall. After 45 min, only mono-NPE that had a sharp increase of recovery after 60 min while the recoveries of other compounds decreased. With the BFRs, an increase in extraction from 15 to 45 min had a positive impact on the recoveries with extraction time of 45 min giving higher recoveries. After 60 min, the recoveries of BFRs dropped. From the result, 45 min was taken as the optimum extraction time for the simultaneous extraction of APEs and BFRs. These conditions (i.e. solvent, temperature, and extraction time) were used to determine the optimum biomass for the extraction of the said compounds. The results for the effect of biomass on the extraction efficiency are presented in Table 1,

The results showed that biomass of 2.5 g had negative effect on the extraction efficiency of the analytes as the recoveries of most compounds were lower except alkylphenol ethoxylates. These results were obtained using the same concentration of the analytes. However, from 5 to 25 g biomass though recoveries did not differ significantly, 5 g biomass gave better recoveries overall for most compounds and
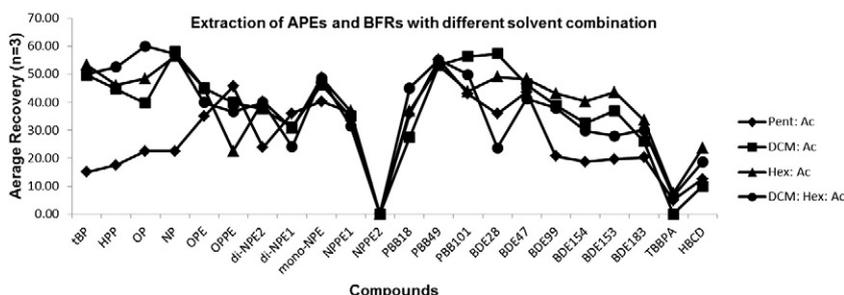

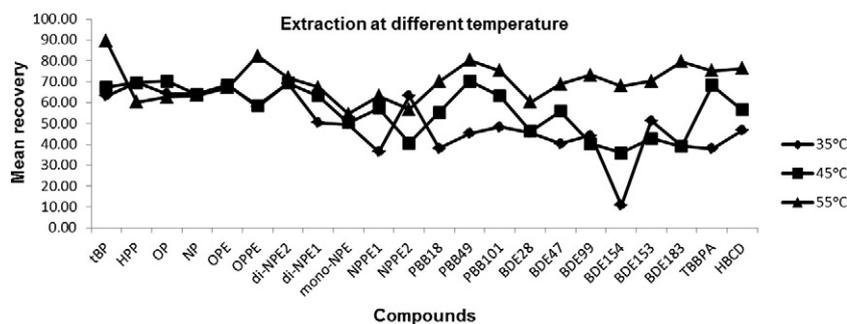Fig. 2. Recoveries of compounds from binary solvent systems at 25 °C.

Fig. 3. Effect of temperature on the extraction of APEs and BFRs.

was therefore chosen as the optimum biomass for the simultaneous extraction of APEs and BFRs because of slightly overall better RSD for most compounds. The recoveries from the 5 g biomass range from 44.93% (HPP) to 100.88% (BDE183). Though the recovery of HPP was low, it should be accepted because of its low RSD (5.77).

3.2. Method performance

The instrumental performance was evaluated through the estimation of linearity, repeatability, limit of detection, and quantification as well as recoveries of the target compounds from the sludge. The results on linearity, limit of detection, and limit of quantification are presented in Table 2.

For quantification, five-point calibration curves were constructed, from the GC-MS analysis of standard solutions of APEs and BFRs in hexane at concentration ranging from 8 to 40 ng g^{-1} for APs, PBBs, PBDEs, and 40 to 200 ng g^{-1} for APEs, TBBPA, and HBCD. From the results as presented in Table 6, the calibration curves had good linear relationships using the internal standard method at these five different concentration levels. The limit of detection and quantification of the method were estimated by linear regression using the peak area abundance. As shown in Table 2, the LOD obtained ranged from 0.12 ng g^{-1} (t-BP) to 5 ng g^{-1} (di-NPE2) and LOQ ranged between 0.72 ng g^{-1} (t-BP) and 16.40 ng g^{-1} (di-NPE2).

In order to evaluate trueness of the method used in this study, recovery experiments were performed on the sewage sludge. To accomplish this, the three sludges were spiked with a standard mixture of the compounds and taken through the whole procedure as described earlier. However, during the concentration of the post-ultrasonic extracts, 2 g of Cu was added in order to remove elemental sulfur. The percentage recovery of the compounds is presented in Fig. 5.

The recoveries in spiked sludge samples range from 38.65 ± 8.24 (for HPP) to 78.63 ± 6.53 (for BDE154) with adequate repeatability (RSD < 20) except for nonylphenol di-ethoxylates (di-NPE1 and di-NPE2 which had RSD of 27 and 23, respectively). The relative standard deviations (RSD) of below 20% for these compounds indicate the good precision of the developed extraction method for simultaneous determination. The recoveries of NP (61%), di-NPE (78.08% and 63.45%),

mono-NPE (71.32%) were comparable to results from other studies reported in the literature. For the APs and APEs recoveries, Gatidou et al. [8] reported recoveries for NP of 62.7%, mono-NPE of 106%, and di-NPE of 101%. In another study, Fountoulakis et al. [9] reported recoveries of above 70% for both NP and NPEO while Andreu et al. [18] reported the recovery range of 89–94% for OP, NP, and APEs. A study by Rice et al. [16] reported recoveries of between 70% and 115% for NP and NPEs, and recoveries of 65–106% for OPEs including OP. With the BFRs recoveries, several studies reported recoveries range from 41.7% to 130% [1,15,19, 22]. The results indicated that the developed method can be applied successfully for the determination of the targeted compounds from solid matrix samples, having the advantage of one integrated method for the simultaneous analysis of APEs and BFRs in solid samples. The proposed method in this study gave comparable recoveries with those reported in the literature; however, the proposed method used cheaper instrument and is much easier and faster for analyzing these compounds simultaneously.

3.3. Levels in environmental samples

The developed method was used to determine the presence of the targeted compounds in sludge samples collected from different sewage treatment plants and to evaluate the fate of these compounds at those treatment plants. Table 3 lists the concentration of the APEs and BFRs in primary sludge obtained from different treatment plants.

The concentration of these compounds in sludges depends on various factors, such as discharge from industrial wastewater into the inlet of treatment plant, the population size of the area being served by the treatment plant, and type of sludge. For the purpose of the study, only the primary sludge was sampled because this sludge contains particulate organics that serve well as matrix for the retention of adsorbed xenobiotics, especially the hydrophobic ones [9]. As can be observed from the results, almost all the compounds were detected in Rietspruit sewage sludge sample. The highest concentration of alkylphenols detected was for t-BP (38.58 ng g^{-1}) which was detected at Rietspruit sewage sample, the alkylphenol ethoxylates (APEs) was for di-NPE1 (642 ng g^{-1}) detected at Sebokeng sewage sample. With the BFRs, it was only PBB101 that was detected in all the sewage sludge
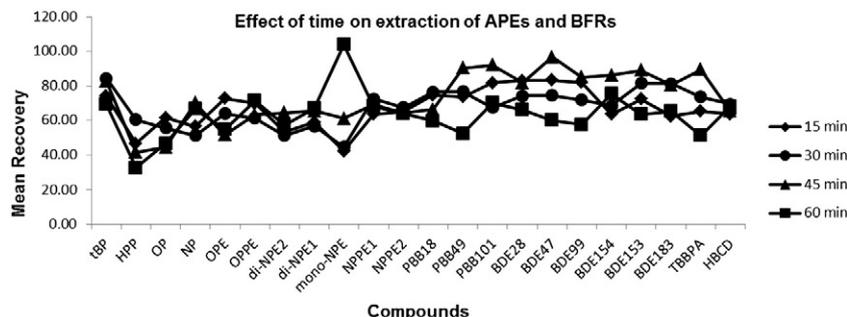

Fig. 4. Effect of time during the extraction of APEs and BFRs.

Table 1
Effect of biomass on the extraction efficiency of APEs and BFRs.

Compound	25 g % Recovery	12.5 g % Recovery	10 g % Recovery	7.5 g % Recovery	5 g % Recovery	2.5 g % Recovery
t-BP	82.65	70.15	53.60	61.58	79.35	45.80
HPP	41.60	63.23	55.08	58.33	44.93	46.68
OP	44.30	66.68	53.93	54.98	68.65	48.28
NP	70.05	73.52	75.08	61.85	61.32	55.08
OPE	51.60	74.88	98.53	64.98	80.98	58.00
OPPE	63.21	68.10	117.24	60.63	78.73	57.95
di-NPE2	64.32	70.02	53.93	60.18	78.08	59.80
di-NPE1	65.39	71.02	55.32	60.98	63.45	88.33
mono-NPE	61.00	97.50	98.53	73.98	71.32	66.21
NPPE1	69.30	63.24	71.12	60.97	82.04	90.21
NPPE2	64.30	66.98	63.32	69.36	69.32	84.32
PBB18	66.25	63.20	70.20	72.35	72.32	76.98
PBB-49	90.25	61.34	108.02	76.08	82.60	83.20
PBB-101	92.10	75.11	74.69	81.32	90.32	72.20
BDE28	81.65	71.32	88.20	63.24	76.32	66.30
BDE-47	96.60	63.32	72.35	80.32	96.60	51.32
BDE99	85.00	58.65	49.03	55.95	85.00	40.60
BDE154	84.10	85.30	70.28	100.88	86.10	84.95
BDE153	89.00	59.63	78.32	71.00	91.00	60.32
BDE183	80.35	77.05	69.80	75.68	100.35	63.32
TBBPA	89.35	96.97	86.60	67.32	80.35	77.03
HBCD	65.32	54.91	65.32	67.10	69.32	40.75

samples from all the treatment plants with Rietspruit detected at higher concentration than both the Leeuwkuil and Sebokeng treatment plants. The highest concentration of the PBDEs was for BDE183 of 163 ng g^{-1} at Rietspruit sewage sludge sample. The high concentration from Rietspruit can be suspected from the more industrial activities around the treatment work compared to industries around both Sebokeng and Leeuwkuil treatment works.

Although there are numerous reviews and research articles that have reported concentrations of BFRs in different environmental samples such as water, sediments, or soils, little is reported about their occurrence in sewage sludge. In the few articles that reported the presence of APs and APEs in sewage sludge, the level of these compounds in this study was detected at lower concentration levels compared to those reports. Fountoulakis et al. [9] reported NP and NPEO concentration of 93 and 234 mg kg^{-1} from the primary sludge at Heraklion WWTP in Greece. Gatidou et al. [8] reported NP, NP1EO, and NP2EO concentration of 110, 1010, and 2890 ng g^{-1}, respectively from Mytilene City WWTP, Greece.

Table 2
Calibration range, linearity, limit of detection, and quantification results.

Compound	Range (ng g^{-1})	Linearity	LOD (ng g^{-1})	LOQ (ng g^{-1})
t-BP	8.0–40.0	0.992	0.12	0.72
HPP	8.0–40.0	0.995	0.40	1.32
OP	8.0–40.0	0.994	0.40	1.34
NP	8.0–40.0	0.992	0.40	1.40
OPE	8.0–40.0	0.993	4.00	10.40
OPPE	40.0–200.0	0.990	4.60	13.80
di-NPE2	40.0–200.0	0.993	5.00	16.40
di-NPE1	40.0–200.0	0.994	3.50	11.60
mono-NPE	40.0–200.0	0.990	3.00	10.10
NPPE1	40.0–200.0	0.997	4.80	13.60
NPPE2	40.0–200.0	0.986	4.30	12.80
PBB18	8.0–40.0	0.991	0.30	1.20
PBB-49	8.0–40.0	0.993	0.80	2.64
PBB-101	8.0–40.0	0.996	0.90	2.97
BDE28	8.0–40.0	0.976	1.60	5.28
BDE-47	8.0–40.0	0.990	1.60	5.32
BDE99	8.0–40.0	0.993	1.45	5.06
BDE154	8.0–40.0	0.985	1.52	5.02
BDE153	8.0–40.0	0.993	1.30	4.29
BDE183	8.0–40.0	0.992	1.40	4.86
TBBPA	40.0–200.0	0.990	4.50	9.84
HBCD	40.0–200.0	0.963	2.82	4.40

LOD: limit of detection; LOQ: limit of quantification.

3.4. Correlation of APEs and BFRs in sludges with physicochemical parameters

As shown in Table 4, sludge samples from different WWTW were characterized for TS, VSS, pH, conductivity as well as alkalinity. The mean pH value for the three WWTW sludge ranged from 4.68 to 6.20, generally indicating an acidic characteristic. Conductivity ranged from 175.35 to 264.3 mS m^{-1}, alkalinity ranged from 265.07 to 605.60 mg L^{-1} while the TS and VSS ranged from 30.35 to 44.15 g L^{-1} and 22.68 to 33.35 g L^{-1}, respectively.

The correlation analysis between APEs and BFRs concentrations and physicochemical parameters of the sludge samples was performed. Correlation values for $\sum$ APEs versus TS ($r = 0.88$), VSS ($r = 0.57$), conductivity ($r = -0.30$), alkalinity ($r = -0.81$), and pH ($r = -0.58$) were observed. The results showed a positive correlation between TS and VSS indicating a possible influence of TS and VSS on concentration of APEs in sludge. The other parameter (pH, conductivity, and alkalinity) gave a negative correlation. The correlation analysis between $\sum$ BFRs and physicochemical properties were performed. The analysis indicated a negative correlation between concentrations of BFRs with TS ($r = -1.00$), VSS ($r = -0.92$), and conductivity ($r = -0.24$). Only the alkalinity ($r = 0.39$) and pH ($r = 0.07$) exhibited a positive correlation. A positive correlation of PBDEs, type of BFRs, with pH has been reported [24]. According to the above evidence, our data suggested that the concentration of APEs in sewage sludge is influenced by water quality parameters especially TS and VSS while the concentration of BFRs is influenced by pH and alkalinity.

4. Conclusion

A quantitation method for the simultaneous determination of APEs and BFRs in sewage sludge was developed and optimized. The method combined ultrasonic-assisted extraction followed by solid phase extraction enrichment step prior to GC-MS analysis. Various conditions were tested in order to obtain the maximum sensitivity and selectivity. When the optimized conditions were applied to the determination of these compounds in primary sewage sludge samples from different treatment plants, the concentration of these compounds ranged from <LOQ to 642 ng g^{-1} for the APEs while the BFRs concentrations ranged from <LOQ to 161 ng g^{-1}. Of the three treatment sludge samples, almost all the compounds were detected from Rietspruit sludge
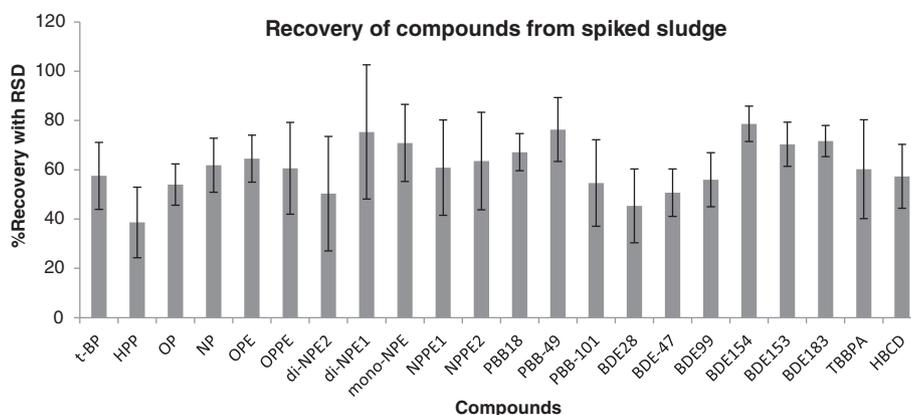
Fig. 5. Recoveries of targeted compounds from spiked sludge.

samples. This may be due to high industrial activities around the treatment works as the plant treats both domestic and industrial wastewater.

There is cause for concern about the levels of APEs and BFRs obtained in the present study. Considering the fact that sludge can be used as fertilizer in agriculture, contamination of sludge poses the foremost concern as the farmers who depend very much on sludge for their farming activities will, therefore, be exposed to these endocrine-disrupting compounds. Further investigation on more wastewater treatment plants should be conducted in order to estimate the extent to which the burden from these sources contribute to the total amount of APEs and BFRs into the South African environment.

Table 3
Levels of APEs and BFRs from environmental sludge samples (n = 3).

Compounds	Leeuwkuil ng g^{-1}	Rietspruit ng g^{-1}	Sebokeng ng g^{-1}
t-BP	<LOQ	38.58	<LOQ
HPP	9.05	5.73	2.009
OP	<LOQ	8.403	<LOQ
NP	<LOQ	<LoQ	<LOQ
OPE	<LOQ	10.66	<LOQ
OPPE	93.70	101.22	78.86
di-NPE2	182.82	96.89	348.51
di-NPE1	16.52	165.56	642.07
mono-NPE	329.61	78.92	364.46
NPPE1	11.78	13.64	<LoQ
NPPE2	365.01	104.36	59.16
PBB18	<LOQ	14.717	<LOQ
PBB-49	3.94	15.32	<LOQ
PBB-101	17.34	87.96	14.01
BDE28	<LOQ	17.820	<LOQ
BDE-47	<LOQ	<LOQ	<LOQ
BDE99	6.22	46.42	<LOQ
BDE154	<LOQ	<LOQ	<LOQ
BDE153	<LOQ	10.32	<LOQ
BDE183	<LOQ	162.70	<LOQ
TBBPA	<LOQ	19.24	<LOQ
HBCD	10.69	133.16	<LOQ

Table 4
Characterization of sludge samples from different WWTW.

Parameter	Leeuwkuil	Rietspruit	Sebokeng
TS, g L^{-1}	42.57	30.35	44.15
VSS, g L^{-1}	33.35	22.68	29.44
Conductivity, mS m^{-1}	264.30	197.20	175.35
Alkalinity, mg L^{-1}	605.60	544.20	265.07
pH	6.20	5.47	4.68

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