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**TARGETED AND NON-TARGET SCREENING OF PERSISTENT ORGANIC POLLUTANTS AND ORGANOPHOSPHORUS FLAME RETARDANTS IN LEACHATE AND SEDIMENT FROM LANDFILL SITES IN GAUTENG PROVINCE, SOUTH AFRICA**

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## **Abstract**

In the present study, target analysis and a non-target screening method were employed to investigate the degree of contamination of landfill sediment and leachate in Gauteng Province, South Africa, by organic contaminants. Polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), organochlorinated pesticides (OCPs) and organophosphorus flame retardants (OPFRs) were extracted from sediment and leachate samples using solid-liquid extraction and liquid-liquid extraction methods, respectively; and analysed by target analysis using gas chromatography mass spectrometry (GC/MS). Targeted PBDEs were all detected but for PCBs, CB 52 and CB 101 were below the quantification limit (LOQ) in the sediment samples. The concentrations of OCPs measured ranged from 0.09 ng/g dw ( $\alpha$ -HCH) to 5.29 ng/g dw (pp-DDE) in Marie Louis, and from 0.14 ng/g dw ( $\alpha$ -HCH) to 11.3 ng/g dw ( $\gamma$ -HCH) in Hatherly, with an average mass fraction of 1.0 ( $\pm$  2.0, SD) ng/g dw in Marie Louis and 2.0 ( $\pm$  3.0, SD) ng/g dw in Hatherly. Among the OPFRs, TnPP, TPTP, T35DMPP and TBPP were below the LOQ in both leachate and sediment samples. Overall, high concentrations of TDCIPP and TCIPP were obtained in both media, ranging from 226-14500 ng/L and 52.0-13800 ng/L and from 19.6-741 ng/g dw and 32.8–1240 ng/g dw in leachate and sediment, respectively. The high concentrations of certain OPFRs suggest that these may have replaced both PCBs and PBDEs in consumer products currently imported into South Africa. Common compounds identified by non-target screening with high-resolution mass spectrometry of leachate were diethyl [2-(1, 3-dioxolan-2-yl) ethyl] malonate (C<sub>12</sub>H<sub>20</sub>O<sub>6</sub>) and 4-(benzyloxy) cyclohexanone (C<sub>13</sub>H<sub>20</sub>O<sub>2</sub>). These compounds are possibly associated with plasticizers used in the production of plastic and plastic coatings.

**Keywords:** GC-MS/MS; LC-Q-TOF-MS; Organophosphorus flame-retardants; PBDEs; OCPs; PCBs

## **1. Introduction**

Persistent organic pollutants (POPs) have been identified as toxic chemicals that adversely affect human health and the environment around the world (EPA, 2017). POPs are characterised by their high persistence in the environment, high resistance to degradation, their capability to bio-accumulate in tissues of living organisms and their potential to undergo long-range atmospheric transport (Jayaraj et al., 2016; Tsai, 2010). Majority of these chemicals exhibit lipophilic properties, leading to their accumulation in the food chain. In aquatic systems, most POPs partition strongly to solids with organic matter than to aqueous media (Jones and de Voogt, 1999). Due to these characteristics, most POPs have been recommended for elimination and restriction from production and use under the Stockholm Convention (Lallas, 2001; Vallack et al., 1998).

Over the past two decades, there has been a gradual decline in the use of PCBs and PBDEs due to concerns related to their environmental persistence, long-range atmospheric transport, bioaccumulation and toxicity (Martin, 2007; Wei et al., 2015), resulting in an increasing demand for alternative FRs. In the past years, the organophosphate tri-esters (OPFRs) have entered the market as replacements of PCBs and PBDEs. However, recent studies have identified several toxicological hazards concerning OPFRs, raising further questions regarding their safety as substitutes for the phased-out commercial Penta- and Octa-BDE formulations because of their toxicity (Wei et al., 2015).

In developing countries, such as South Africa, consumer products are disposed of as general waste into municipal landfill sites when they reach their end of life (Sibiya et al., 2017). Municipal waste landfill sites receive mainly domestic and household waste (foodstuffs, garden waste, packaging materials such as glass, paper and cardboard, plastics, ash, and others). Also business and commercial waste (e.g. glass, paper, plastics, cans from offices, stores, and schools and a limited amount of foodstuffs from hotels and restaurants),

construction rubble, and bulky construction debris from surrounding residential areas are dumped in the landfill sites (CSIR, 2015). About 147 and 127 tonnages of general waste were disposed into landfills in the cities of Pretoria and Johannesburg, respectively in February 2017 (Table S2) (GDARD, 2017). In terms of population figures, both cities have a population of about 3 million inhabitants (DEA, 2008).

In the Province of Gauteng, South Africa there are two types of landfill sites: An engineered landfill referred to as a geomembrane lined landfill and a non-engineered landfill referred to as a geomembrane non-lined landfill site. A typical geomembrane lined landfill comprises four critical elements (Figure S1): a bottom liner, a leachate collection system, a cover, and the natural hydrogeological setting. These settings ensure a minimal hydraulic connection between waste and the surrounding environment, particularly the adjoining groundwater reservoirs (Rapti-Caputo et al., 2006). A geomembrane non-lined landfill site has none of the critical elements mentioned for a geomembrane-lined landfill; becoming one of the sources of pollution in the surrounding environment.

The disposal of products containing POPs in landfill contributes significantly to the environmental load of POPs (Weber et al., 2008). Over time, the waste materials dumped into the landfill may degrade, resulting in the gradual release of these chemicals through leaching, which is known to aggravate during periods of intense precipitation (Anglada et al., 2011). The resultant liquid, otherwise known as leachate and so-called hereafter, may thus contain elevated concentrations of contaminants. In a landfill where there is no leachate collection system, it can easily infiltrate the groundwater reservoirs, or may flow into adjacent rivers, lakes, and dams.

Recently, the analysis of POPs has significantly evolved, particularly with the availability and use of sophisticated analytical instruments, which can perform accurate mass-high resolution

mass spectrometry (AM-HRMS) and tandem mass spectrometry (MS–MS). Tandem mass spectrometry is a good tool for target analysis because good sensitivity and selectivity can be achieved for quantification and identification of compounds. However, target analysis neglects the presence of other organic contaminants since it requires analyte specific information and, consequently, it does not give an exhaustive overview of other organic compounds present in the landfill. The use of full spectrum acquisition techniques that provide accurate mass high resolution spectrometry like LC-QTOF-MS is essential to obtain information about a large number of organic compounds present in the landfill. Suspect and/or non-target screening approaches are needed in order to detect the presence of potentially overlooked compounds that could be harmful and present in the landfill sites. This is of high importance since these substances end up in the nearby waterbodies by percolation and in the soil and dust particles during soil erosion; polluting the environment and adversely affecting the health of living organisms.

Reports on POPs in landfill sites in South Africa are still very scarce. Only PBDEs have so far been reported in landfill sites in South Africa (Daso et al., 2013; Odusanya et al., 2009; Olukunle et al., 2015; Sibiyi et al., 2017). Therefore, the present study reports on the concentrations of selected PBDEs, PCBs, OCPs and OPFRs in sediments and leachate, as well as on non-target screening of leachates from the two busiest and largest landfill sites in Pretoria and Johannesburg. OPFRs were also determined for the first time in leachate and sediment samples from four Pretoria and three Johannesburg landfill sites. The results of this study are envisaged to foster an understanding of the current concentrations of the selected POPs in the South African environment.



room. Sediment samples were air-dried, mixed and sieved with a 500  $\mu\text{m}$  sieve prior extraction.

The busiest and largest landfill sites Marie Louis and Hatherly in the two cities Johannesburg and Pretoria were chosen for the analysis of PBDEs, PCBs and OCPs in sediment and for non-target screening in leachate. Sediment was chosen for being known as reservoirs for POPs and leachate was chosen for non-target screening for being known as a liquid that is produced by the process of leaching of compounds from their materials. OPFRs, which are currently in the market as replacements of PBDEs and PCBs, were also targeted in leachate and sediment of all landfill sites in Pretoria and Johannesburg.

### **2.3 Chemicals and Materials**

All chemicals analysed in the present study are listed in Table S1. The PBDE internal standard IS1, was obtained from AccuStandard Inc. (New Haven, CT, USA) and the individual standards of PBDEs were purchased from Wellington Laboratories (Guelph, ON, Canada). Selected individual OCPs, internal standards IS2, IS3 and recovery standard (RS) were purchased from Dr. Ehrenstorfer Laboratories (Augsburg, Germany). OPFRs standards were purchased from Chiron AS (Trondheim, Norway) and Wellington Laboratories, while IS4 was purchased from TCI Europe (Zwijndrecht, Belgium). Labelled internal standards IS5-8 were custom synthesized. The fish reference material was provided by Cambridge Isotope laboratories, Inc. (Tewksbury, USA).

Greiner Bio-one (Belgium) supplied polypropylene-PP tubes (15 mL). The 2  $\mu\text{m}$  filters (Eppendorf) were supplied by VWR (Leuven, Belgium). Dichloromethane (DCM) was analytical grade and ethyl acetate (EtAc) was GC/MS grade they were purchased from Acros Organics (Belgium). All solvents were HPLC grade: *n*-hexane was purchased from Acros



Organics (Belgium); iso-octane, and acetonitrile (SACN) were purchased from Merck (Darmstadt, Germany). All solvents were tested for the investigated analytes contamination before use. Empty polypropylene cartridges (25 mL) were purchased from Grace (Lokeren, Belgium), Florisil<sup>®</sup> cartridges (500 mg, 3 mL) were purchased from Supelco (Bellefonte, PA, USA), while silica gel and concentrated sulphuric acid (H<sub>2</sub>SO<sub>4</sub>, 98 %) were purchased from Merck (Darmstadt, Germany). All chemicals were of analytical grade or equivalent analytical purity. All glassware was washed with detergent, and thereafter, rinsed with MilliQ water, acetone, *n*-hexane and finally oven dried. Prior to use, the clean glassware was rinsed with the extraction solvent.

## **2.4 Sample extraction and clean up**

### **2.4.1 PBDEs, PCBs and OCPs**

Two landfill sites Marie Louis in Johannesburg and Hatherly in Pretoria were considered for sediment analysis of POPs. PBDEs, PCBs and OCPs were extracted from sediment samples using the solid liquid extraction (SLE) method. In a 15 mL PP falcon tube, 0.5 g of dry sediment and 1 g of activated copper (Cu) was weighed and mixed. Each sample was spiked with 50 µL IS (including BDE-77, ε-HCH and CB-143). After spiking, 5 mL of *n*-hexane: DCM (1:1, *v/v*) was added to the samples, capped and ultra-sonicated for 10 min, vortexed for 2 min and centrifuged at 3500 RPM for 5min. The supernatant was transferred to pre-cleaned glass tubes. The same procedure was repeated twice. The combined supernatant was concentrated under gentle nitrogen stream and the solvent was exchanged to 0.5 mL *n*-hexane.

The extract was then loaded onto a 6 mL cartridge packed with 2 g acidic silica (44 %) and 2 g activated copper. The cartridge was pre-conditioned with 6 mL *n*-hexane and the extract

was eluted with 6 mL of *n*-hexane: DCM (1:1, *v/v*) and evaporated to near dryness. Samples were reconstituted with 50  $\mu$ L iso-octane and 50  $\mu$ L RS, the resulting solution was vortexed for 20 s and transferred into amber vials for injection.

#### **2.4.2 OPFRs**

OPFRs were analysed in the sediment and leachate samples from all the selected landfill sites. In a 15 mL PP falcon tube, 0.5 g of dry sediment and 1 g of activated copper (Cu) were weighed and mixed. For leachate samples, 20 mL of leachate was transferred into a 50 mL PP falcon tube. Then 25 ng OPFR IS mix (TAP, TCEP-d12, TPHP-d15, TDCPP-d15, TBOEP) was added to the sample in the falcon tube.

After spiking, 5 mL of *n*-hexane: acetone (3:1, *v/v*) was added to the samples, capped and ultra-sonicated for 10 min, vortexed for 2 min, then centrifuged at 3500 RPM for 5 min. The supernatant was transferred into a pre-cleaned glass tube. The procedure was repeated twice. The combined supernatant was then concentrated under gentle nitrogen stream and the solvent was exchanged to 0.5 mL *n*-hexane. The extract was further cleaned through elution onto a Florisil cartridge pre-conditioned with 6 mL of EtAc and 6 mL of *n*-hexane. Fractionation was achieved with 12 mL of an *n*-hexane/DCM mixture (4:1, *v/v*) (F1, discarded) and 10 mL of EtAc (F2, containing the target compounds). F2 was evaporated to near dryness, solubilised in a mixture of 50  $\mu$ L iso-octane and 50  $\mu$ L RS (50 pg/ $\mu$ L), and finally transferred into amber vials for injection.

#### **2.4.3 Non-target screening of organic compounds**

Two leachate samples were considered for non-target screening analysis. Twenty millilitres of leachate from Marie Louis (Johannesburg) and Hatherly (Pretoria) were transferred into 50 mL PP falcon tubes, the Marie Louis sample was first diluted 10 times with MilliQ water due

to its heavy contamination. Each sample was extracted twice-using 5 mL EtAc followed by 10 min of ultra-sonication, vortexed for 2 min and centrifuged for 5 min at 3500 rpm. The supernatants were then combined in a clean glass tube after centrifuging and further concentrated under nitrogen stream until dryness. Thereafter, the extract was reconstituted with 150  $\mu$ L of ACN:MilliQ (1:1 v/v), transferred into a 0.2  $\mu$ m filter Eppendorf and centrifuged for 5 min at 5000 rpm. The clean extract was then transferred into an amber injection vial for instrumental analysis.

## **2.5 Instrumental analysis**

### **2.5.1 PBDEs, PCBs and OCPs**

The sediment extracts were analysed using an Agilent 6890 GC (Palo Alto, CA, USA) coupled to an Agilent 5973 MS operated in electron capture negative ionization (ECNI) mode. The targeted compounds were chromatographically separated on a DB-5 capillary column (30 m x 0.25 mm x 0.25  $\mu$ m). The GC system was equipped with electronic pressure control and a programmable-temperature vaporizer (PTV) inlet. The optimised GC-ECNI/MS conditions used were: 92  $^{\circ}$ C, held for 0.03 min, ramped at 70  $^{\circ}$ C/min to 300  $^{\circ}$ C, held 30 min for the injection temperature. One microliter of the sample was injected under a pressure of 10 psi with a purge flow to split vent of 50 mL/min after 1.25 min. The GC oven temperature programme started from 92  $^{\circ}$ C, held for 1.25 min, ramped at 10  $^{\circ}$ C/min to 300  $^{\circ}$ C, held for 1 min, ramped at 40  $^{\circ}$ C/min to 310  $^{\circ}$ C, held for 9.5 min. Helium was used as a carrier gas with a flow rate of 1.0 mL/min until 25 min, then increased to 1.5 mL/min. The ion source and quadrupole temperatures were set at 170  $^{\circ}$ C and 150  $^{\circ}$ C, respectively. The mass spectrometer was operated in selected ion monitoring (SIM) for the quantification of BDE (-47, -100, -99, -154, -153), CB (-153, -138, -180, -170, 118), HCB,  $\alpha$ -,  $\beta$ -,  $\gamma$ -HCH, pp-DDE, pp-DDD and pp-

DDT. BDE-77 was used as an internal standard for all PBDEs,  $\epsilon$ -HCH was used as IS for HCHs and CB-143 was used as IS for the targeted PCBs and remaining OCPs.

### **2.5.2 OPFRs**

Chromatographic analysis was based on the method published by Poma et al. (2017) using an Agilent 7890B gas chromatograph, equipped with an Agilent 7693A autosampler with a multimode inlet (MMI), coupled to a triple quadrupole mass spectrometer (7000C, Agilent Technologies Inc., Palo Alto, CA), with an EI source working in electron impact mode. Briefly, GC separation was performed using a Zebron Semivolatiles column (20 m  $\times$  0.18 mm  $\times$  0.18  $\mu$ m, Phenomenex, Torrance, CA) working at a flow of 1.2 mL of helium/min (99.999%, Air Liquide, Liège, Belgium). The injection of 1  $\mu$ L of sample extracts was performed in splitless mode at 110  $^{\circ}$ C. TAP (IS) corrected for TnPP, TnBP, and TEHP; TCEP-d12 for TCEP and TCIPP; TDCIPP-d15 for TDCIPP and TDBPP; and TPHP-d15 for TPHP, EHDPHP, TOTP, TMTP, TPTP, T2IPPP, and T35DMPP.

### **2.5.3 Non-target screening of organic compounds**

The separation was performed on a Kinetex Biphenyl (150 mm, 2.1 mm, 1.7  $\mu$ m particle size) Phenomenex<sup>®</sup> RP-column, (Utrecht, The Netherlands), connected to an Agilent 1290 Infinity UPLC binary pump (Santa Clara, USA). Mobile phase A was 0.04 % (v/v) of formic acid in water (pH = 2.86), while mobile phase B was composed of 95 % (v/v) acetonitrile and 5 % (v/v) mobile phase A. A gradient was made at a flow rate of 0.3 mL/min starting with 5 % B for 2 min, was increased to 90 % of B at 15 min and 100 % of B at 18 min. The column was rinsed for 6 min and re-equilibrated at starting conditions for 4 min. Column and mobile phases were heated up to 30  $^{\circ}$ C. Injection volume was 3  $\mu$ L. Analytes were detected with an Agilent 6530 Q-TOFMS equipped with an Agilent-Jet-Stream-Electrospray Ionization (AJS-

ESI) in positive and negative ionization mode. The drying gas was 250 °C at a flow rate of 10 L/min; the sheath gas was 350 °C at a flow rate of 12 min/L. The pressure on the nebulizer was 45 psi. The voltages of the capillary and the nozzle were 3500 V and 500 V, respectively. The fragmentor voltage was 120 V. For the acquisition of full AM-MS spectra, the MS scan rate was 59 - 1100 m/z with a cycle of 250 ms. Fragmentation spectra were acquired by auto-MS/MS at a scan rate of 125 ms. Precursor ions were selected with a narrow bandwidth ( $m/z = 1.3$ ) and fragmented with a collision energy of 20 V. For each cycle, a maximum of 3 precursors were selected, the threshold was 1000 counts and active exclusion for 4 s was used to increase the coverage of analytes fragmented. A static exclusion list was used to prevent fragmentation of background ions. All data were stored in centroid mode for further data-analysis.

The data were analysed using Mass-Hunter Qualitative analysis (version B.06.00; Agilent Technologies). The method was based on a non-target screening approach: the molecular formulas representing different contaminants were searched by the “*Find by Formula algorithm*” (Agilent Technologies). Parameters were set as follows: match tolerance 10 ppm, expected variation 2 mDa  $\pm$  8 ppm, no match for a score below 90. The algorithm was instructed to look for proton, sodium and ammonium adducts in the positive ionization mode ( $[M + H]^+$ ;  $[M + Na]^+$ ;  $[M + NH_4]^+$ ), and for anionic molecules and formic acid adducts in negative ionization mode ( $[M-H]^-$ ;  $[M+HCOO]^-$ ). Further elimination of possible false positives was performed by blank subtraction and by comparing the mono-isotopic mass accuracies isotope distributions patterns against the theoretical values. The possible names for the formula with a structure that resembles the obtained MS spectra were also checked using Chemspider and PubChem (PubChem, 2018).

## **2.6 Quality assurance and quality control (QA/QC)**

Quality control measures were taken to ensure the accuracy of the analytical methods employed for PBDEs, PCBs, and OCPs. This includes the use of fish reference materials from the 2016 international inter-laboratory study on fish tissue reference materials (CIL, 2016). All measured values were within the certified range ( $\pm 20\%$ ). Mean recoveries of the IS added to the samples ranged from 95-118 % for PBDEs, 78-88 % for PCBs and 79-95 % for OCPs. A procedural blank was analysed every ten samples to check for laboratory contamination. For analytes detected in the blanks, the LOQs were based on the mean blank value + 3SD; and for analytes, which were not detected in the blanks, the LOQs were calculated based on the signal/noise ratio for a standard of known concentration. LOQs for PBDEs ranged from 0.02 to 0.04 ng/g dw, for PCBs it was 0.20 ng/g dw and for OCPs they ranged from 0.05 to 0.2 ng/g dw.

The method validation for the OPFRs was performed using the fish oil previously used in the first worldwide inter-laboratory study on OPFRs (Brandsma et al., 2013). The measured values were within the range of the consensus concentrations ( $\pm 15\%$ ), while mean recoveries of the IS spiked samples ranged from 60 to 120 %. A procedural blank was analysed every ten samples to check for laboratory contamination. If analytes were detected in the procedural blanks, the blank mean concentrations were subtracted from the values found in the samples. The limit of quantification (LOQ) was ten times the signal to noise ratio of each peak for compounds not detected in the procedural blanks or it was calculated as average blank values plus three times the standard deviation of the blanks for compounds present in the blanks. LOQs ranged from 0.40 to 2.00 ng/g dw for sediment and from 2.00 to 10.0 ng/L for leachate.

To guarantee correct extraction and identification of the features for the non-target screening, the workflow has been optimised using an in-house standard mix as reported (Poma et al.,

2017). To provide transparency of the identification confidence, the quality of identification during the non-target screening analysis was evaluated according to Schymanski et al. (2014).

The identification of contaminants with known molecular formula, but without an MS/MS spectrum is considered of low quality and receives a score of 4. When MS/MS patterns are available to suggest a chemical class, but an unequivocal confirmation is not possible, the compound receives a score of 3. When the MS/MS spectrum is of good quality and the fragments match libraries and can be explained, the identification quality would then be classified as level 2. If standards are available, they would be injected to confirm the identity of the compounds, and such compounds would be classified as level 1.

### **3. Results and Discussion**

#### **3.1 Concentrations of POPs**

Reports on the concentrations of PBDEs, PCBs and OCPs in sediment samples from landfill sites are generally scarce, compared to reports on landfill leachates. In South Africa, the Department of Environmental Affairs (DEA), in fulfilling its Stockholm Convention commitments, encourages phasing out the formulation and use of POPs in products that end up in landfills (DEA, 2012). The concentrations of PBDEs, PCBs and OCPs (HCHs and DDTs) in sediments from the largest landfill sites in Pretoria and Johannesburg are shown in Table 1.

All targeted BDE congeners were detected in Marie Louis and Hatherly landfill sediment. The congener with the highest concentration is BDE 99 in Marie Louis at 0.33 ng/g dw, followed by BDE 47 at 0.28 ng/g dw. In Hatherly, BDE 47 had the highest concentration at 0.65 ng/g dw, followed by BDE 99 at 0.33 ng/g dw. Congeners with the lowest concentrations in Marie Louis were BDE 100 and BDE 154 at 0.06 ng/g dw and 0.05 ng/g dw. In Hatherly, they were BDE 154 and BDE 100 at 0.11 ng/g dw and 0.04 ng/g dw. Marie Louis is 28 years-old and has a geomembrane liner, while Hatherly is 15 years old without a geomembrane liner. Therefore, the observed low concentrations in Marie Louis could be attributed to the age or geomembrane lining of the landfill site. The older the landfill the more the micro-organisms that break down the organic compounds, reducing their concentrations (Christenson and Cozzarelli, 2003). The low PBDE concentrations could be due to the dilution effect of the rainy southern hemisphere during the summer season in February 2017 in which the samples were collected. No guideline values exist to allow a comparison of BDE results against allowable limits for PBDEs. PBDE sediment concentrations in the current study ranged from 0.04-0.65 ng/g dw and were very low compared to those reported in other studies in Table S3. The concentrations were far lower



than concentrations reported in our previous study (Sibiya et al. 2017), which ranged between 2.50-3.87 ng/g dw. This is the first study reporting BDE concentrations in landfill sediment in South Africa during summer season.

All targeted PCBs were detected with the exception of CB 52 and CB 101 in samples obtained from Hatherly. The order of congener concentrations was observed as follows CB 153 > CB180 > CB 170 at 1.78 ng/g dw > 1.36 ng/g dw > 0.89 ng/g dw and 0.65 ng/g dw > 0.64 ng/g dw > 0.35 ng/g dw in Marie Louis and Hatherly, respectively. The lowest concentrations obtained in Marie Louis were CB 101 and CB 52 at 0.75 ng/g dw and 0.45 ng/g dw and in Hatherly, they were CB 138 and CB 118 at 0.34 ng/g dw and 0.26 ng/g dw after CB 52 and CB 101 which were detected <LOQ. The observed low concentrations in Hatherly may be due to the absence of PCB containing waste in the reported household waste in Pretoria (Table S2). According to the United States Agency for Toxic Substances and Disease Register (USA TSDR), a screening level of 0.05 ng/g dw for soils and sediments warrants further investigation (Bouwman, 2005). All detected PCBs in Table 1 were > 0.05 ng/g dw, and the most dominant congeners in Marie Louis, CB 153 and CB 180, were measured at 1.80 ng/g dw and 1.40 ng/g dw respectively. Higher concentrations of PCBs were measured in Marie Louis than in Hatherly. In comparison to other studies, PCB concentrations obtained in this study were very low and the low levels could be due to the current South African government initiative to eliminate the presence of PCBs and other POP chemicals from its environment, particularly water systems (DEA, 2012). Table S4 shows the higher concentrations reported by other researchers in sediment other than landfill media.

For OCPs, the targeted compounds were HCHs ( $\alpha$ -,  $\beta$ - and  $\gamma$ -), DDT metabolites (pp-DDE, pp-DDD and pp-DDT), nonachlor (*cis*- and *trans*-), chlordane (*cis*-, *trans*- and *oxy*-), and hexachlorobenzene (HCB). Targeted HCHs ( $\alpha$ -,  $\beta$ - and  $\gamma$ -) were detected in Marie Louis and Hatherly. The highest detected isomer was  $\beta$ -HCH at 0.78 ng/g dw in Marie Louis and  $\gamma$ -

HCH at 11.3 ng/g dw in Hatherly. The isomer with the lowest concentration between the two-landfill sites was  $\alpha$ -HCHs in Marie Louis at 0.09 ng/g dw and 0.14 ng/g dw in Hatherly. The targeted DDT metabolites were detected in Marie Louis but in Hatherly, pp-DDE and pp-DDD were detected below the LOQ. In Marie Louis, pp-DDE had the highest concentration of 5.29 ng/g dw followed by pp-DDT at 2.66 ng/g dw. In addition, the nonachlor (*cis*- and *trans*-) (CN and TN) and chlordane (*cis*- and *trans*-) (CC and TC) targeted isomers were all detected, except *oxy*-chlordane (OxC) which was below the LOQ in both sites. Low concentrations in Marie Louis were obtained for CN and TN at 0.24 ng/g and 0.70 ng/g dw. TC had higher concentrations at 1.38 ng/g dw in Marie Louis and 3.45 ng/g dw in Hatherly. CC had a higher concentration of 2.55 ng/g dw in Hatherly as well. According to the Interim Sediment Quality Guideline (ISQC) set by the Canadian Government, the benchmark values that were selected for OCPs are as follows: pp-DDE < 1.42 ng/g dw, pp-DDD < 3.54 ng/g dw, pp-DDT < 1.19 ng/g dw, CC < 4.50 ng/g dw and  $\gamma$ -HCH < 0.940 ng/g dw (CEQG, 2000). Only  $\gamma$ -HCH in Hatherly exceeds the ISQC value at 11.3 ng/g dw, and in Marie Louis pp-DDT and pp-DDE exceeded the ISQC at 2.70 ng/g dw and 5.30 ng/g dw, respectively. In Table 1, the sum of DDTs obtained in this study ranged from <LOQ-9.00 ng/g dw, which is comparable to other studies (Table S6).

OCP concentrations ranged from 0.09 ng/g dw ( $\alpha$ -HCH) to 5.30 ng/g dw (pp-DDE) in Marie Louis and in Hatherly from 0.14 ng/g dw ( $\alpha$ -HCH) to 11.3 ng/g dw ( $\gamma$ -HCH). Among OCPs, the HCH concentrations in the present study were the highest ranging from 0.09 ng/g dw ( $\alpha$ -HCH) in Marie Louis to 11.3 ng/g dw ( $\gamma$ -HCH) in Hatherly. The OCP concentrations in this study were the second highest when compared to other studies (Table S5 and S6).

Figure S2 shows the POPs profile in sediment of the two-landfill sites. Hatherly comprises 65% of the total PBDEs and 62% of the total OCPs, thus implying that Hatherly is more contaminated by PBDEs and OCPs compared to Marie Louis. About 75% PCBs was

observed in Marie Louis landfill site. The findings agree with the concentrations of PBDE, PCBs and OCPs obtained in this study. Furthermore, Marie Louis is in the Johannesburg city centre, and Hatherly is in a township on the north-eastern side of Pretoria. The informal settlements near Hatherly landfill site and the use of various pesticides by inhabitants to kill pests followed by indiscriminate disposal of pesticides' containers is a cause for concern. As a consequence, there is the possibility that the indiscriminate disposal of pesticide containers into domestic waste bins, eventually get disposed into the landfill site and may have contributed to the observed concentrations of OCPs.

### **3.1.1 Influence of the geomembrane liner and waste on the concentrations of the targeted POPs**

Table 1 shows concentrations of PCBs, OCPs, PBDEs, and Table S2 shows general waste in tonnages per month of February 2017, that has been disposed into landfill sites in the cities of Pretoria and Johannesburg. Total PCB concentrations of 6.86 ng/g dw in the geomembrane lined Marie Louis landfill and 2.25 ng/g dw in the geomembrane non-lined Hatherly landfill were obtained. The higher PCB concentrations in the sediment at the geomembrane lined landfill site could be due to the 7.60 tons of household waste and the 12.7 tons of commercial waste being disposed at Johannesburg landfill sites. The lower PCB concentrations at the geomembrane non-lined landfill site could be due to low PCB containing waste sources such as insulating material used in electric equipment, surface coatings, plasticizers, paints, inks and adhesives dumped on the landfill sites (IWG, 2016).

OCPs and PBDEs total concentrations were almost the same with a factor less than 5 for OCPs and a factor less than 2 for PBDEs, with Hatherly at 20.8 ng/g dw and 1.44 ng/g dw and Marie Louis at 13.8 ng/g dw and 0.81 ng/g dw. The higher concentrations of OCPs and PBDEs at Hatherly could possibly be because of the geology of the non-lined landfill sites,



known to be persistent in the environment, and its observed high concentrations in the present study could be attributed to its persistent characteristic (Leung et al., 2006).

TCEP is the third most abundant compound detected in all sites and in both media ranging from 12.0 ng/L (Robinson Deep) to 3470 ng/L (Ennerdale) in leachate and from 0.759 ng/g dw (Ennerdale) to 15.2 ng/g dw (Onderstepoort) in sediment. TCEP is mainly used in polyurethane foam, furniture and plastic housing of electronics and it is considered as non-biodegradable by the European Union. Consequently, its production within the EU states has been discontinued (EU, 2009). TCIPP is now used as a replacement of TCEP, and its frequent detection at elevated concentrations may be related to its increased usage in consumer products (Stapleton et al., 2011).

T21PPP had the lowest concentrations in the analysed leachate and sediment samples after the four compounds (TnPP, TPTP, T35DMPP and TBPP), and it was mainly detected below the LOQ. The measured concentrations for T21PPP range from <LOQ-17.0 ng/L (Marie Louis) in leachate and in sediment from <LOQ to 6.89 ng/g dw (Robinson Deep). In Robinson Deep TOTP was detected at 418 ng/g dw in sediment, while it was below the LOQ in the leachate and TCP was detected at 3.70 ng/g dw in sediment and at 47.0 ng/L in leachate. In Onderstepoort TCP was not detected in sediment, but was found to be 9.00 ng/L in the leachate. The detection of TOTP in the analysed sediment samples from Robinson Deep could be due to its strong affinity to solids, whereas the low detection of TCP in leachate samples could be due to having a few materials disposed that can leach into the leachate (WHO, 1990). TnBP was detected below the LOQ in both leachate and sediment samples from Garankuwa and Soshanguve landfill sites. TnBP is extensively used in materials like aircraft hydraulic fluids, construction materials, paint, plaques, varnishes, among others, and its non-detection in the investigated matrices suggest the possibility that such waste items are not disposed into the landfill sites (Zhou et al., 2017).

TnBP was also below LOQ in sediment collected from the Ennerdale landfill; however, it was detected in the leachate at 58.0 ng/L. The presence of TnBP in the leachate rather than in sediment sample at this site could indicate a recent leaching event from treated waste material. Furthermore, TnBP was detected in sediment samples from the Robinson Deep at 4.98 ng/g dw, but was below LOQ in the leachate. TPHP, EHDHP and TEHP were below LOQ in Ennerdale leachate also, TPHP and EHDHP in Soshanguve leachate. In addition, other compounds that were below the LOQ in leachate samples include TPHP in Garankuwa and TEHP in Hatherly and Robinson Deep.

Most OPFRs (TnBP, TBEP, TCIPP, TCP, TBPP, TDCIPP, T21PPP, TPHP, amongst others etc) have very low water solubility and some (TXP, IDPP and TPP) are immiscible with water which may explain why most of these compounds were below the LOQ (Van der Veen and de Boer, 2012).

Due to lack of information about OPFR concentrations in landfill leachate, the measured concentrations in the present study were mainly compared with contaminants reported in river water and other environmental waters, such as landfill-impacted groundwater. The details of these comparisons are presented in Table S7. In general, the range of OPFR concentrations in the present study (556-17200 ng/L) was much higher than those previously reported in other studies (Table S7), but second highest after the study in Yorkshire, UK that ranged between 300-26500 ng/L in River Aire (Bollmann et al., 2012).

Few studies have reported on OPFR concentrations in sediment (AbouDonia, 2016). However, the sediment samples studied were from lakes, rivers and marine environments, and not from leachate ponds. Table S8 shows the comparison between the measured OPFR concentrations in the present study and those reported in other studies. The concentrations obtained in this study (113-571 ng/g dw) are lower than those reported by Kawagoshi et al. (1999) (180-21300 ng/g dw) from a marine waste disposal site. However, the reported OPFR



Table S9, S10 and S11 present the list of compounds detected in positive and negative ionization of leachate from Marie Louis and Hatherly landfill sites. The overall co-elution or overlapping score > 90% was used and there were no compounds detected in blanks. Furthermore, five levels of identification and confirmation described by Schymanski et al. (2014) was used to communicate the level of confidence for identification purpose.

Most of the compounds in positive and negative ionisation mode are classified as level 4 because only the formula was identified, resulting in a wide range of unconfirmed possible compounds. Compounds detected at level 3 in positive ionisation of leachate from Marie Louis and Hatherly include isomers of the formula  $C_{10}H_{15}NO_2S$ ,  $C_{24}H_{26}O_2$ ,  $C_5H_{12}O_2$  and  $C_{27}H_{52}O_4$ ,  $C_{28}H_{46}O_4$ ,  $C_6H_{12}O_3$ ,  $C_{24}H_{42}O_7$ . Contaminants from the first suggested isomer name of the compound (Table S9 & S10) for a level 3 formula such as N-butylbenzenesulfonamide ( $C_{10}H_{15}NO_2S$ ) and diisodecyl phthalate ( $C_{28}H_{46}O_4$ ) are used as plasticizers, while propylene glycol dilaurate ( $C_{27}H_{52}O_4$ ) is used as a cosmetic ingredient, and ascorbyl stearate ( $C_{24}H_{42}O_7$ ) is used as a food additives. Compounds in the negative ionisation mode detected at level 3 for Hatherly and Marie Louis include isomers of the formula  $C_{18}H_{28}O_3$ ,  $C_{18}H_{34}O_2$ ,  $C_{22}H_{30}O_2S$ ,  $C_{18}H_{30}O_3S$ . The latter mentioned contaminants are as per the first suggested compound name on Table S11 and they are applied as emulsifying agents, emollients, antioxidants (for synthetic and natural rubber) and surfactants.

In the positive ionisation mode, only two formulae were found to match between Marie Louis and Hatherly, and they were  $C_{13}H_{16}O_2$  and  $C_{12}H_{20}O_6$ . The formula  $C_{13}H_{16}O_2$  is associated with the contaminant 4-(benzyloxy) cyclohexanone used as a drug ingredient for medication such as contraceptives, antiasthmatics, bronchodialators, anti-tissue agents etc, and the formula  $C_{12}H_{20}O_6$  is associated with the contaminant diethyl [2-(1,3-dioxolan-2-yl) ethyl]-malonate which is used in perfumes and to synthesise other compounds such as Vitamin B<sub>1</sub>, artificial flavourings and Vitamin B<sub>6</sub>.



There are more compounds detected in Hatherly compared to Marie Louis in positive ionisation mode, this could be an indication that Hatherly has a diverse number of contaminants than Marie Louis. Contaminants with Level 4 identification as per first suggested compound name of the molecular formula in positive ionisation of Hatherly leachate indicate that the source of the contaminants are: surfactants, preservatives (of detergents, paints, pesticides etc), fragrances, drugs, rubber components, lubricants, plasticizer, flame retardants, additives, adhesive, sealants and components of pesticide formulations. Supplementary Table S2 reports general waste in tonnages disposed into Pretoria (Hatherly) and Johannesburg (Marie Louis) landfill sites. Monthly, household waste is 16.9 tons in Pretoria and 7.60 tons in Johannesburg, confirming that Hatherly is potentially more contaminated than the Johannesburg landfill site, Marie Louis. Furthermore, the possible source of contamination of the detected compound formula could be arising from the specific type of waste disposed at the landfill site, which is the household waste.

In Marie Louis, there are more compounds identified in the negative ionisation compared to the positive ionisation mode. Contaminants identified as level 4 as per first suggested compound of the molecular formula in the negative ionisation mode of Marie Louis leachate, suggest that the source of contamination could be: co-monomers of polymers, paint and coating additives, agents for manufacturing plastic and epoxy resins, drugs, surfactants and fragrant ingredients, thickening agent (in lotions), hardening agent (in soaps and candles) and compounds used as part of caulking ship ingredients. The landfill site location could also be a contributing factor on the type of contaminants detected in Marie Louis. Johannesburg (Marie Louis) receives more of commercial waste at 12.7 tons than household waste (7.60 tons) since it is located in the city centre surrounded by different industries and most of the detected compound formulas link the possible contaminants to the commercial waste, which is more dominant than the household waste.

#### **4. Conclusions**

Target analysis of POPs and OPFRs in landfill leachate and sediment was effective in confirming the concentrations and degree of landfill contamination by the selected compounds. Non-target screening using LC-QTOF-MS proved to be an effective tool in identifying the presence of possible organic contaminants in landfill leachate. Non-target screening is a qualitative method of analysis, although possible contaminants detected include plasticizers, cosmetic ingredients, surfactants and drugs; target screening is recommended for quantification. The investigated POPs concentrations in sediment decreased in the order OCPs > PCBs > PBDEs in the Pretoria and Johannesburg landfill sites. The low PCB and PBDE concentrations were potentially due to a dilution effect caused by high precipitation during the summer season.

The high OPFR concentrations of TDCIPP, TCIPP, TCEP and TCP confirm their use as replacements of PCBs/PBDEs in the South-African waste materials. Targeted OPFRs in landfill leachate and sediment are reported for the first time in South Africa, using GC-MS/MS. Generally, there is a lack of information regarding OPFRs in landfill leachate and sediment and the concentrations obtained in the city of Pretoria and Johannesburg were similar in this study.

#### **5. Acknowledgements**

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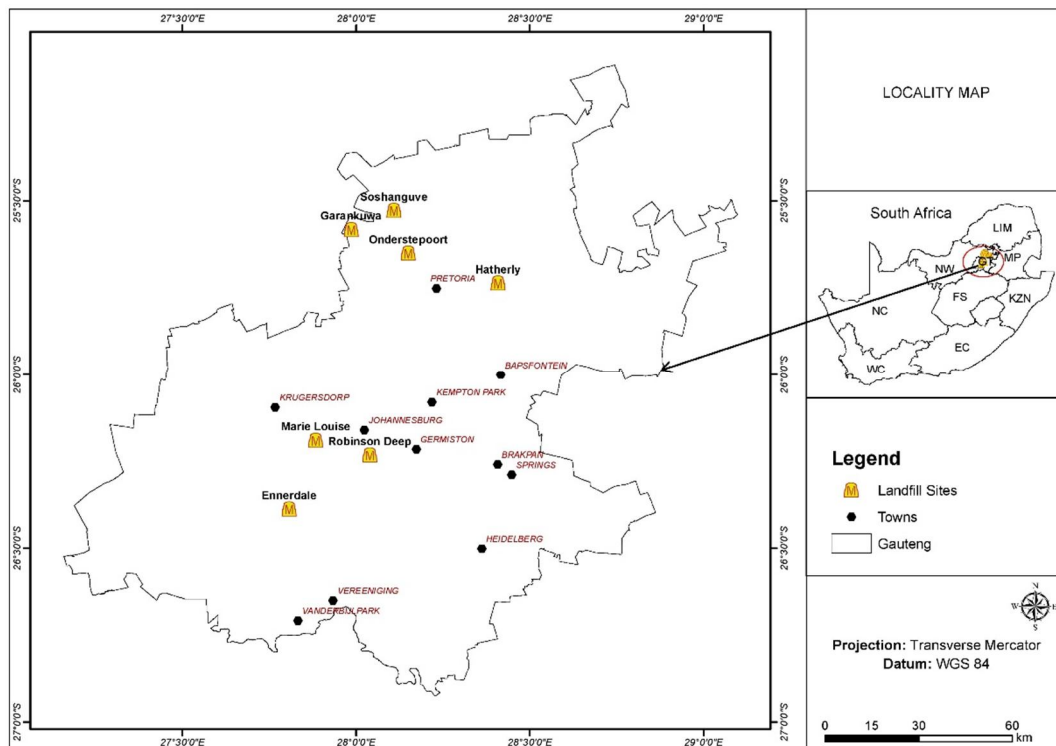
Table 1. Concentrations of PCBs, OCPs and PBDEs in sediments (ng/g dw) from Pretoria (Hatherly) and Johannesburg (Marie Louis)

<b>Sediment (ng/g dw)</b>	<b>LOQ</b>	<b>Marie Louis</b>	<b>Hatherly</b>
<b>PBDEs</b>			
BDE 47	0.02	0.28	0.65
BDE 100	0.02	0.06	0.04
BDE 99	0.02	0.33	0.33
BDE 154	0.04	0.05	0.11
BDE 153	0.04	0.09	0.31
Total		0.81	1.44
<b>PCBs</b>			
CB 52	0.20	0.45	<LOQ
CB 101	0.20	0.75	<LOQ
CB 118	0.20	0.76	0.26
CB 153	0.20	1.78	0.65
CB 138	0.20	0.86	0.34
CB 180	0.20	1.36	0.64
CB 170	0.20	0.89	0.35
Total		6.86	2.25
<b>OCPs</b>			
$\alpha$ -HCH	0.05	0.09	0.14
$\beta$ -HCH	0.10	0.78	0.22
$\gamma$ -HCH	0.05	0.32	11.3
pp-DDE	0.50	5.29	<LOQ
pp-DDD	0.50	1.26	<LOQ
pp-DDT	0.20	2.66	0.47
CN	0.10	0.24	0.65
TN	0.10	0.70	2.03
CC	0.10	1.12	2.55
TC	0.10	1.38	3.45
OxC	0.10	<LOQ	<LOQ
HCB	0.05	0.05	0.16
Total		13.8	20.8

Table 2: OPFR concentrations in leachate (ng/L) and sediment (ng/g dw) from seven selected landfill sites.

		TnPP	TnBP	TCEP	TCIPP	TDCIPP	TPHP	EHDHP	TEHP	TOTP	TCP	T2IPPP	TPTP	T35DMPP	TBPP	Total
Sediment	LOQ	2.00	0.50	0.50	0.50	0.50	0.50	0.40	0.80	0.50	0.50	0.50	0.50	0.50	0.50	
(ng/g dw)	Ond*	<LOQ	0.928	15.2	316	19.6	0.81	1.90	9.56	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	364
	Gar	<LOQ	<LOQ	9.65	32.8	65.7	1.43	0.771	8.80	<LOQ	<LOQ	0.740	<LOQ	<LOQ	<LOQ	120
	Sosh	<LOQ	<LOQ	3.37	43.8	741	3.43	0.499	6.67	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	132
	Hat	<LOQ	1.18	3.05	1240	391	7.65	5.06	13.2	<LOQ	<LOQ	0.601	<LOQ	<LOQ	<LOQ	1660
	Enn	<LOQ	<LOQ	0.759	51.5	516	1.41	0.41	0.845	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	571
	Rob	<LOQ	4.98	2.21	426	192	33.8	8.41	36.5	418	3.70	6.89	<LOQ	<LOQ	<LOQ	1132
	Mar	<LOQ	2.93	3.42	270	147	3.49	8.49	6.50	<LOQ	<LOQ	0.747	<LOQ	<LOQ	<LOQ	443
Leachate	LOQ	10.0	10.0	2.00	2.00	2.00	2.00	2.00	3.00	5.00	5.00	5.00	5.00	5.00	5.00	
(ng/L)	Ond	<LOQ	29.0	394	570	14500	22.0	8.00	27.0	<LOQ	9.00	<LOQ	<LOQ	<LOQ	<LOQ	15500
	Gar	<LOQ	<LOQ	36.0	232	8950	17.0	<LOQ	12.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	9250
	Sosh	<LOQ	<LOQ	39.0	287	226	<LOQ	<LOQ	3.00	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	556
	Hat	<LOQ	130	164	1440	1210	14.0	26.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2990
	Enn	<LOQ	58.0	3470	3990	7300	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	14800
	Rob	<LOQ	<LOQ	12.0	52.0	7570	12.0	12.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	7660
	Mar	<LOQ	817	770	13800	885	128	519	195	<LOQ	47.0	17.0	<LOQ	<LOQ	<LOQ	17200

\*Ond = Onderstepoort, Gar = Garankuwa, Sosh = Soshanguve, Hat = Hatherly, Enn = Ennerdale, Rob = Robinson Deep, Mar = Marie Louis



1  
 2 Figure 1. Map of South Africa (top right) and Gauteng Province (centre) showing the  
 3 selected landfill sites.  
 4