INFLUENCE OF LOCAL GEOLOGY ON TRANSPORT OF POLYBROMINATED DIPHENYL ETHERS IN GROUNDWATER AND LANDFILL LEACHATES

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Introduction

The soil, dust, surface water and groundwater have become the immediate environmental reservoirs for recalcitrant pollutants[1-3]. Polybrominated diphenyl ethers (PBDEs) are among the environmental pollutants that have attracted much attention in recent times. These have been produced since 1970s and were first reported as environmental contaminants in River Viskan, in early 1980s[4]. Since then, they have been found in most environmental matrices[5-6]. South Africa generates about 42 million metric tons of domestic waste per annum. It is highly likely that large quantities of these wastes are products that may contain brominated flame retardants, particularly PBDEs. The placement and compaction of municipal wastes into landfills and the infiltration of rain result in the production of leachates. Since some BFRs such as PBDEs are additives, they may be released more readily into the landfill environment and from there can infiltrate into groundwater, especially from old and poorly designed landfills. Therefore, the determination of PBDEs in landfill leachates and surrounding water system, particularly groundwater facilities is deemed important. The present study was undertaken to investigate the extent of groundwater contamination within the study area with a view to evaluate the extent of the impact of the local geology on the transport of the contaminants. When seen in this light, an investigation was, therefore, deemed necessary in order to evaluate the current status of the South African environment with emphasis on groundwater.

Materials and methods

All chemicals used were of analytical grade and were purchased from Sigma-Aldrich. Fifteen common PBDEs. The study area consists of boreholes located within the vicinity of landfill sites in and around Pretoria in the Gauteng Province of South Africa. The study area is bound by the latitudes 25° 25' S and 26° 00' S and longitudes 28° 00' E and 28° 30' E. Pretoria lies in a warm, well sheltered, fertile valley, surrounded by the hills of the Magaliesburg range, 1,370 m above sea level. The average range of monthly rainfalls and temperatures for summer and winter are: (22-136 mm) and (25-38 °C) and (6 and 51 mm) and (22-30 °C) respectively. The location of the study area is shown in Figure. 1. congeners were identified for investigation. Mixture of PBDEs standards were donated by Dr. Jacob de Boer of Animal Sciences Group, Institute for Fisheries Research, Netherlands and Drs Per Ola Darnerud and M Aune, of National Food Administration, Uppsala, Sweden. Other experimental details are as described[7].

Results and discussion

The limit of detection ranged from 0.2-5.0 pg L^{-1}.The mean percentage recoveries of the congeners, BDE-47 and BDE-99 ranged from 93.0 ± 6.7-102.9 ± 7.1. The mean concentrations of triplicate measurements of common PBDEs congener in groundwater and leachate samples are shown in Tables 1 and 2 respectively. As can be seen in Table 1, the following PBDEs were detected in the groundwater samples in significant concentrations: BDE-47>BDE-100>BDE-154>BDE-183. Also from Table 1, the predominate PBDEs congeners in the entire groundwater samples were BDE-47, BDE-100 and BDE-154. This observation is similar to most of the reports for environmental samples[8]. However, samples obtained near Garankuwa and Onderstepoort landfill sites recorded the highest concentration values of 1445 pg L^{-1} and 1334 pg L^{-1} for BDE-47 respectively. Onderstepoort and Derdepoort exhibited the highest concentrations of 1597 pg l^{-1} and 1379 pg l^{-1} for BDE-100 respectively. The lowest concentration (nd-4 pg L^{-1}) was observed from samples collected near Temba landfill site. From Table 1, the ∑BDEs/congener in the groundwater samples analysed, BDE-47 accounted for 50% of the ∑BDEs; while BDE-100 and BDE-154 ranked second and third with 42 % and 4 % respectively. The rest of the ∑BDEs add up to 4 %. With respect to ∑BDEs/site, the trend was as follows: 24 %, 23 %, 16 %, 13 %, 10 %, 10 %, 2 %, 1 % and 0.06% for Onderspoort, Derdepoort, Garankuwa, Kwaaggasrand, Valhalla, Hatherley, Garstkloof, Soshanguve and Temba respectively.

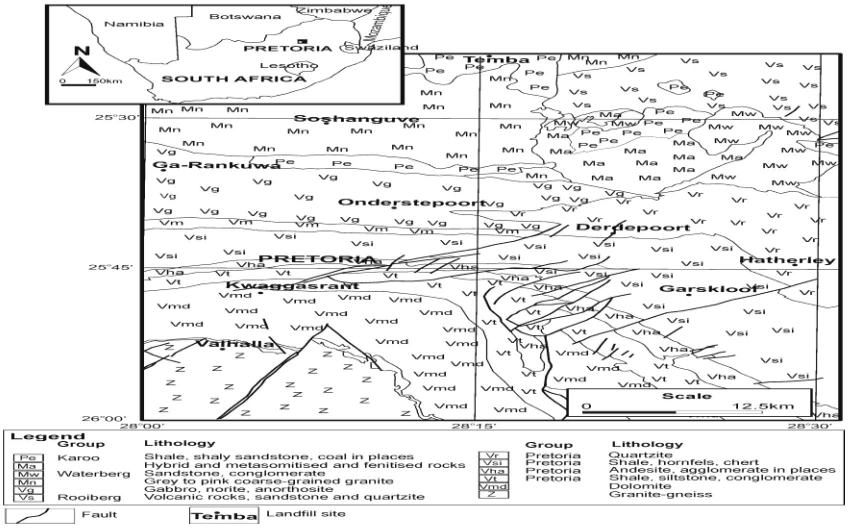

Figure 1. A sketch map of South Africa (top right) and the geology of the study area.

Table 1 Concentrations of BDEs in groundwater samples (mean ± SD pg l^{-1}).

BDEs	Tem	Sos	Hat	Kwa	Ga	Val	Ond	Gar	Der	∑BDE
BDE-28	nd	nd	1±0.5	3±1.2	3±0.8	1±0.5	5±1.2	nd	5±0.9	18
BDE-47	nd	51±6.4	877±25.5	784±12.8	1445±25.3	764±12.4	1334±30.4	79±4.5	1204±20.2	6538
BDE-66	nd	nd	nd	nd	nd	nd	nd	1±0.2	nd	1
BDE-71	nd	nd	nd	6±1.5	nd	2±0.7	4±0.9	6±1.5	4± 0.7	22
BDE-75	2±0.7	1±0.5	4±1.5	32±4.5	5±1.3	32±2.5	74±9.8	2±0.5	73±7.2	18
BDE-77	nd	2±0.7	4±1.7	nd	8±2.1	nd	nd	3±0.1	nd	17
BDE-85	nd	7±1.1	23±6.5	nd	32±5.1	nd	nd	2±0.2	nd	64
BDE-99	nd	nd	nd	nd	nd	3±0.6	nd	nd	nd	3
BDE-100	nd	10±2.5	298±12.3	850±15.2	516±10.2	524±11.5	1597±.51.2	158±2.5	1379±25.5	5332
BDE-119	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BDE-138	nd	98±9.9	12±3.3	10±3.2	7±1.5	nd	1±0.4	4±0.7	1±0.7	133
BDE-153	1±0.2	nd	nd	nd	nd	nd	3±0.9	1±0.4	3±0.8	8
BDE -154	4±1.0	nd	118±9.6	43±5.2	3±1.1	2±0.9	166±7.5	4±1.2	156±7.4	496
BDE-183	2±0.5	nd	nd	17±3.2	76±8.4	6±1.6	45±5.5	2±0.8	43±4.6	191
BDE-190	nd	nd	nd	nd	nd.	4±1.2	nd	2±1.0	nd	6
∑BDE/site	9	169	1337	1745	2095	1338	3229	264	3168	

nd = not detected, Tem =Temba, Sos =Soshanguve, Hat = Hatherley, Kwa =Kwaggasrand, Ga =Garankuwa, Va = Valhalla, Ond = Onderstepoort; Gar = Garstkloof, Der = Derdepoort.

Results in Table 2 show the measured values of PBDEs in leachate samples from the selected landfill sites. The concentrations of PBDEs in the leachate samples range from nd-9793 pg L^{-1}. This concentration range is significantly ($p<0.05$) higher than the values of nd-4000 pg L^{-1} and 29-248 pg L^{-1} reported for BDE-28, BDE-77, BDE-77, BDE-100, BDE-154 and BDE-185 in landfill leachates[1]. As can be seen from Table 2, BDE-47>BDE-71=BDE-75>BDE-28=BDE-99>BDE-100=BDE-119 were the predominant congeners detected. In the ∑BDEs/congener, BDE-47 was the most predominant congener with approximately 22 % followed by BDE-71 and BDE-75 with 17 % each. BDE-28 and BDE-85 accounted for 8 %, while 5 % was observed for BDE-66, BDE-100 and BDE-119. The other congeners make up the remaining 13 %. It can also be seen in Table 2 that all the congeners with the exception of BDE-138 and BDE-190 were detected at high concentrations (90-9793 pg l^{-1}) in the leachate samples from Temba landfill site. The ∑BDEs/site showed Temba with approximately 43 % followed by Kwaggasrand, Hatherley, Soshanguve and Garankuwa with approximately 15 %, 13%, 13 % and 7

% respectively. Onderspoort, Valhalla and Derdepoort accounted for 6 %, 1.2 % and 0.1 % respectively. This is completely the opposite as observed in Table 1 for BDEs concentration in groundwater samples.

Table 2 Concentrations of BDEs in leachate samples (mean ± SD pg l^{-1}).

BDEs	Tem	Sos	Hat	Kwa	Ga	Val	Ond	Gar	Der	∑BDE
BDE-28	3333±0.8	2830±0.2	1167±1.6	2670±2.0	100±1.2	17±1.25	28±2.45	15±1.46	6±0.35	10166
BDE-47	9793±1.5	1469±0.1	6638±2.0	2720±1.1	2670±2.1	605±6.5	2796±20.5	261±2.65	16±0.1	26968
BDE-66	4000±2.5	1373±0.5	nd	nd	290±1.7	8±0.5	24±3.32	74±1.75	5±0.25	5774
BDE-71	9459±1.9	4009±0.8	1667±1.2	3650±1.0	2430±1.4	9±0.7	14±1.05	nd	12±1.8	21250
BDE-75	7426±0.7	743±1.5	4455±0.9	230±2.3	941±2.2	4±0.5	30±3.48	9±0.58	55±1.40	20893
BDE-77	4257±1.5	396±2.5	119±1.5	nd	nd	nd	nd	nd	nd	4772
BDE-85	587±2.6	41±1.50	nd	223±1.1	1240±1.8	18±1.5	21±1.45	nd	nd	2130
BDE-99	5191±2.0	2295±0.4	1585±2.2	nd	437±0.9	40±1.20	41±1.72	5±0.3	12±1.3	9606
BDE-100	2162±1.1	264±0.2	237±2.1	nd	nd	320±1.7	2383±4.32	384±1.6	11±1.04	5761
BDE-119	5392±2.2	588±2.0.	nd	nd	196±2.5	nd	28±1.42	nd	nd	6204
BDE-138	nd	nd	nd	nd	nd	30±0.7	100±1.3	6±0.05	nd	136
BDE-153	875±1.2	nd	450±1.7	nd	88±1.1	23±1.05	58±1.5	nd	9±0.7	1503
BDE -154	2176±0.9	139±0.2	nd	1340±2.4	nd	25±0.55	214±1.7	36±0.5	4±0.22	3934
BDE-183	90±2.1	263±0.5	177±1.3	nd	nd	75±1.15	317±2.6	9±0.5	6±0.48	937
BDE-190	nd	nd	nd	nd	nd.	180±2.4	1350±2.5	nd	19±1.4	1549
∑BDE/site	5006914410	14663		17833	8392	1354	7404	799	155	

nd = not detected, Tem =Temba, Sos =Soshanguve, Hat = Hatherley, Kwa =Kwaggasrand, Ga =Garankuwa, Va = Valhalla, Ond = Onderstepoort, Gar = Garstkloof, Der = Derdepoort.

In order to establish the influence of the type of wastes dumped in the landfill sites located within the vicinity of the groundwater sampling sites, a plot of percentage industrial and other wastes against landfill sites were carried out and this is shown in Figure 2. The highest concentration of BDE-47 and BDE-100 was exhibited by the groundwater sampling points close to Onderspoort and Derdepoort landfill sites. These sites receive approximately 20% industrial wastes in addition to domestic and other types of waste. Conversely, Temba landfill site which receives high household waste showed high concentrations of BDE-47 and BDE-100 among others in the landfill leachate samples. The high industrial wastes may have contributed to the observed high concentrations of BDE47 and BDE-100 observed, although the quantity of household waste is relatively small in the case of Derdepoort. The high levels of all the congeners in the leachate samples (except BDE-138 and BDE-190) detected from Temba landfill site may suggest that at the time of sampling that the landfill site was at the peak of leachate generation.

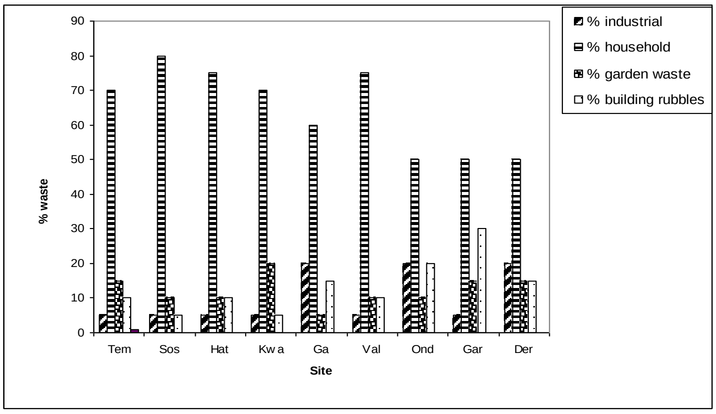

Figure 2. Percentage wastes disposed in the landfill sites.

A significant correlation between the most common PBDEs in groundwater and landfill leachate for the following sites was observed: Onderstepoort (r, 0.99-0.89), Valhalla (r, 0.77-0.98), Derdedepoort, (r, 0.49-0.66), Hatherley (r, 0.94-0.96), Garstkloof (r, 0.97-0.99), Kwaggaastrand (r, 0.77-0.99) and Garankuwa (r, 0.97-0.99). This may suggest similar source, most probably landfill sites within the vicinity of the groundwater sampling points. However, no significant correlation was found between PBDEs in groundwater and landfill leachate samples from Temba (r, 0.50-0.86) and Soshanguve (r, 0.49-0.97). This may indicate different sources. In South Africa and other developing countries, wastes are not given any form of treatment except crushing and compaction before finally disposing into landfill sites. It is possible that the leachates from the landfill sites may have infiltrated into the groundwater over a period of time, particularly in the case of Onderstepoort and Derdepoort sites. Although PBDEs are not readily soluble in water, it is possible that the soil pH may have enhanced their mobility from landfill sites to the groundwater.

It is generally accepted in South Africa among the groundwater experts that approximately 88 % of the groundwater in South Africa occurs in secondary aquifers, that is, faults, fractures, contact planes and cavities. Though the general movement of groundwater in the study area is in the direction of the topographic decline (north-east), the direction of movement of groundwater is locally influenced by geological conditions. The yield range and the weathering range of the different rock types are summarized in Table 3. The higher the value of the yield range the easier it is for groundwater to flow through that rock. The weathering depth gives an indication of the amount of water that is stored in the rock type.

Table 3 Hydrogeological properties of rocks in the in the study area, Pretoria

Group lithology	Symbols	Yield range(l/s)	Weathering depth (m)
Gabbro, norites, anorthosite	Vg	0.1-4	20-50
Quartzite	Vr	0.1-4	20-60
Shale, hornfels and chert	Vsi	0.1-7	20-80
Andesite, agglomerates	Vha	0.05-2	10-30
Shale, siltsone, conglomerate	Vt	0.05-1	10-40
Dolomite	Vmd	1-180	20-150
Granite-gneiss	Z	0-1	10-40

The geological make up of the study area is predominantly that of shale. Transport of contaminants through fractured rocks has the potential for contaminants to migrate through fractured planes, a mechanism controlled predominantly by advection instead of diffusion. However, researchers have argued that diffusion can not be ignored totally as attenuation mechanism. If the direction of diffusion transport is the same as the direction of advection flow, then it will increase the amount of contaminant transported and decrease the time it takes a contaminant to move to a given point away from the sources. Thus, if there is considerable transfer of organic contaminants from fractures to the matrix due to high diffusion rates, it can be expected that the weak sorption capability of the shale may result in significant organic solute transportation. This mechanism can explain the observed difference in PBDEs levels in the groundwater and leachate samples in the present study. Furthermore, the observed difference may also be attributed to the role of natural attenuation. Natural attenuation, a remediation strategy that relies on intrinsic physical, chemical, and biological processes to decrease contaminant concentrations, is gaining widespread acceptance in aquifer restoration efforts.

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