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Status of PAHs in Environmental Compartments of South Africa: A Country Report

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This article covers the status of PAH concentrations and composition patterns in surface water, air, sediment, and soil samples from South Africa. Despite South Africa being one of the largest economies in Africa, it is only recently that researchers have reported the presence and possible sources of these compounds in various environmental compartments. This article discusses the potential hotspots and possible sources of these compounds. It also compares the total PAH concentrations and percentage composition patterns of the individual PAHs. So far, total concentrations of five PAHs determined in sediment samples from the Johannesburg area, Gauteng Province, gave the highest concentrations ranging from 1233–136,276 $\mu\text{g kg}^{-1}$. The total concentration of six PAHs found in runoff water from the Venda region of the Limpopo Province, gave the highest concentration with a range of 28.7–3192.6 $\mu\text{g L}^{-1}$. The decreasing order of percentage composition of PAHs in water samples tended to follow 3-ring > 4-ring > 2-ring PAHs. In soil samples the decreasing order of percentage composition followed 4-ring > 3-ring > 5-ring > 2-ring > 6-ring PAHs. The total freely dissolved PAHs followed solubility of the compounds with 2-ring > 3-ring > 4-ring > 5-ring > 6-ring PAHs. Some of the identified sources of PAHs using molecular ratios include petrogenic emissions such as from petroleum combustion from vehicles and pyrolytic sources such as coal combustion by coal powered power stations, as well as iron and steel production industries. Oil spills were also identified as major PAH contributor in runoff water from the Venda region of the Limpopo Province.

Key Words: air, polycyclic aromatic hydrocarbons, soil and sediments, South Africa, water

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), also known as polynuclear aromatic hydrocarbons, are organic compounds that consist of two or more fused benzene rings in a linear or cluster arrangement. They are very stable organic pollutants that are made up of only carbon and hydrogen. Generally, they occur as complex mixtures, not as single compounds. PAHs can occur naturally, but they are mostly released through human activities, especially in cities and industrial areas. These activities include aluminium, iron and steel production, coal-powered plants, and petroleum refineries (1). Combustion engines that use petroleum products such as vehicles and other machinery are also a source of PAHs (1,2). Domestic heating that uses coal and other petroleum products can be a source of PAHs. Natural sources of PAHs include accidental burning of forests. Since PAHs have diverse sources which produce them unintentionally, they are one of the pollutants which are of global concern (3–5), especially as they can travel long distances associated with air particulates co-emitted from sources (4). PAHs can break down by reacting with sunlight and other chemicals in the air, over a period of days to weeks, but their persistence in the environment increases with an increase in the ring number and degree of condensation (6,7).

PAHs enter water through discharges from industrial and wastewater treatment plants. Most PAHs do not dissolve easily in water, therefore they adsorb to solid particles and settle to the bottom of lakes or rivers as part of the sediment. This is because these are hydrophobic compounds with high octanol-water partition coefficients. Microorganisms can break down PAHs in soil or water after a period of weeks to months. In soils, PAHs are most likely to adsorb tightly to particles. Low molecular mass PAHs can move through soil to contaminate underground water. How long the PAHs adsorb on the soil depends on the type of soil, as clay absorbs PAHs more compared to sandy soil.

The main concern regarding PAHs especially with respect to humans, is their mutagenic and carcinogenic properties. Most toxic effects of PAHs are derived from studies on other organisms (8–11). Nonetheless, because of the similarity of biological systems in different species, it is likely that all mammals, including humans, will be affected in a similar way. Several PAHs (including benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(ah)anthracene, indeno(1,2,3-cd)pyrene) have caused tumors in laboratory animals by inhalation, oral ingestion, or by skin contact after long-term exposure at high concentrations (12). The International Agency for Research on Cancer (IARC) has also concluded that several PAHs are possible causes of cancer (13). The classification of PAHs as carcinogenic comes from their metabolic pathway. They are metabolized to dihydrodiols by the enzyme hydrocarbon hydroxylase present in the liver (14). The dihydrodiols and their epoxide derivatives bind to DNA and proteins and start mutagenic processes in the cells (14).

PAHs have been reported in several countries as they are a global problem and with diverse sources (3,5). In South Africa, although PAHs have been reported in various environmental media (15–23), no comprehensive review is available that provides the status of such analyses, trends in concentration levels and existing gaps. This is very important because PAHs are emitted from numerous sources in South Africa. The review can also be seen as a country report on the status of PAH analysis and concentration trends in South Africa's environmental compartments. In addition, it gives an idea of the challenges faced in as far as monitoring and source apportionment are concerned.

STATUS OF PAH ANALYSIS IN SOUTH AFRICA

PAH Concentrations in Water, Soil, and Sediments

Total PAHs

Most of the total minimum and maximum reported PAH concentrations in South African surface water are summarized in Table 1. Concentrations of total PAHs determined in runoff water from the Venda region, Limpopo Province are the highest with ranges of 28.7–3192.6 $\mu\text{g l}^{-1}$. Those reported from the Klip and Vaal rivers of the Johannesburg area (not included in the table) in Gauteng

Table 1: Concentration of PAHs in runoff water and river water (15,17,18)

PAH	Runoff water ¹ Range ($\mu\text{g l}^{-1}$)	River water ¹ Range ($\mu\text{g l}^{-1}$)
Indene	1.3–10.1	0.8–3.3
Azulene	9.5–134	Nd
Dibenzo thiophene	0.6–67.5	0.3–9.4
Anthracene	6.7–230	6.7–53.5
Fluoranthene	3.4–251	3.6–24.2
Pyrene	7.2–2500	0.1–52.4
Sum of minimum and maximum	28.7–3192.6	11.5–142.8
Mean values of minimum and maximum values	4.78–532.1	2.3–28.56
	Jukskei River water ²	River and Dam water ²
Naphthalene	0.025–0.145	0.022–0.239
Acenaphthene	0.036–0.239	0.053–0.407
Phenathrene	0.119–0.197	0.053–0.616
Fluoranthene	0.046–0.201	0.021–0.890
Pyrene	0.030–0.104	0.024–0.089
Sum of minimum and maximum	0.571–0.886	0.173–2.400
Mean values of minimum and maximum values	0.051–0.177	0.035–0.480

1 = samples taken from the Thohoyandou area, Limpopo Province (15), 2 = samples taken from Eastern, Central and Western areas of Johannesburg, Gauteng province (17, 18)

Province were second highest with ranges of 92–1307 $\mu\text{g } \ell^{-1}$ (20). Total concentrations of PAHs determined from river water from the Venda region rank third (11.5–142.8 $\mu\text{g } \ell^{-1}$). Total concentrations reported by Sibiyi et al. (17,18) from surface waters in the Johannesburg area with ranges of 0.173–2.400 $\mu\text{g } \ell^{-1}$ and 0.257–0.886 $\mu\text{g } \ell^{-1}$ are the lowest. Das et al. (24) also looked at PAHs in a shallow lake (Zeekoevlei lake) in the Western Cape Province and found total concentrations of 19.16 $\text{ng } \ell^{-1}$ in winter and 0.09 $\text{ng } \ell^{-1}$ in summer. These reported concentrations are much lower than those of Sibiyi et al. (17,18). The different total concentrations reported highlight the different sources and fate of these compounds in the environment. PAHs are generally very hydrophobic compounds with low solubility in water. They therefore adsorb and bioaccumulate in sediments. The high concentration of total PAHs in the Venda region of Limpopo Province which has low or no heavy industrial activities could be attributed to mostly vehicle emissions and oil spills especially in runoff water (15) and perhaps an additional contribution from biomass burning although this was expected to be one of the least polluted regions. This shows how PAH pollution is wide spread in the country as PAHs are a global pollutant (4). An et al. (25) studied the distribution, sources, and potential toxicological significance of PAHs in drinking water sources within the Pearl River Delta in China. The sum of 15 PAHs studied ranged from 58.8–3159.9 $\text{ng } \ell^{-1}$ (25). These results compare to those from the Johannesburg area by Sibiyi et al. (17,18) but are less than those reported from the Vaal River and Venda regions. The study by An et al. (25) also found that the total concentration of dissolved PAHs in the wet season (32–754.8 $\text{ng } \ell^{-1}$) was higher than in the dry season (48.1–113.6 $\text{ng } \ell^{-1}$). This indicates that seasonal variation can also influence the results. Farooq et al. (26) studied the occurrence, finger printing and ecological risk assessment of 17 PAHs in the Chenab River, Pakistan. The total concentrations ranged from 289–994 and 437–1290 $\text{ng } \ell^{-1}$ in summer and winter, respectively. These values are slightly less than some studies reported in Table 1 and much less compared to those reported by Das et al. (24) but are in the same range as those found in the Johannesburg area by Sibiyi et al. (17,18).

River water sample extraction techniques used in Table 1 determine the total concentration of PAHs in water except HF-LPME which tends to extract the dissolved concentrations only. But a comparison of the concentration found within the same study with solid phase extraction and HF-LPME did not show significant differences in concentrations (18). This may be due to minimal dissolved and suspended solids in the samples from this study. Solid phase extraction and liquid-liquid extraction both determine the total concentration of PAHs in water samples.

Table 2 gives a summary of the total concentration and minimum and maximum concentrations of PAHs reported in sediment and soil samples from different regions of South Africa. Concentrations reported from the Johannesburg area sediment samples are the highest and range from 1233–136,

Table 2: A: Concentration of PAHs in soil and sediment samples, South Africa (16)

PAH	Soil samples ¹ Range (ng g ⁻¹)	Sediment samples ¹ Range (ng g ⁻¹)
Naphthalene	14–59	2.2–22
Acenaphthylene	3.4–760	0.16–82
Acenaphthene	0.72–120	0.1–26
Fluorene	2.6–240	1–50
Phenanthrene	18–3700	5.9–210
Anthracene	3.2–1200	0.77–110
Fluoranthene	35–6700	7–420
Pyrene	28–5500	5–340
Benzo(a) anthracene	15–3000	2–210
Chrysene	21–3500	3.3–220
Benzo(b,j,k) fluorathene	30–6100	6.7–460
Benzo(a)pyrene	2.6–2900	3.4–230
Indenol (1,2,3-ed) pyrene	12–2900	3.4–230
Dibenz (a/c/a,h) anthracene	3.2–610	0.82–58
Benzo(ghi) perylene	7–1500	2.8–130
Sum of minimum and maximum	219.12–38789	44.5–2798
Mean values of minimum and maximum values	14.61–2585.93	2.97–186.53

B: Concentration of PAHs in runoff sediments and river sediment (15,19)

PAH	Runoff sediment ² Range ($\mu\text{g kg}^{-1}$)	Sediment samples ² Range ($\mu\text{g kg}^{-1}$)
Indene	67.5–179	27.4–161.3
Azulene	469 and 558*	Nd
Dibenzo thiophene	270–31,500	17.9–1980
Anthracene	112–23,400	1170–9870
Fluoranthene	414–15,100	505–7560
Pyrene	530–34,000	22.8–1490
Sum of minimum and maximum	1862.5–104,737	1743.1–21,061.3
Mean values of minimum and maximum values	310.42–17,456.2	348.62–4212.26
	Sediments ³	Sediments ³
Naphthalene	585–129.9	903–30,439
Acenaphthene	452–1690	770–35,919
Fluoranthene	135–904	340–45,281
Pyrene	61–2475	84–24,637
Sum of minimum and maximum	1233–6368	2097–13,6276
Mean values of minimum and maximum values	308.25–1592	524.25–8,487.25

1 = samples were taken from the Vaal triangle (Southern part of Johannesburg), Gauteng Province (16).

2 = Sample taken from the Thohoyandou area, Limpopo province (15); 3 = samples taken from Eastern, Central and Western areas of Johannesburg, Gauteng province (17,18). *Only detected in one sample.

276 $\mu\text{g kg}^{-1}$. This is followed by those reported from Venda run off sediments (18,625–104,737 $\mu\text{g kg}^{-1}$). Concentrations of total minimum and maximum PAHs from soil determined from the Vaal triangle in the Johannesburg area was the third highest with a range of 219–38,789 ng g⁻¹. The fourth and fifth

highest were those reported from the Venda and Vaal triangle sediment samples at 1743.1–21,061.3 $\mu\text{g kg}^{-1}$ and 44.55–2,798 ng g^{-1} , respectively (Table 2). The results in sediment samples from the Johannesburg area are interesting because PAH concentrations in the water samples were found to be the lowest (Table 1). The Johannesburg area along the Jukskei River where most of the sediment samples were taken is known to be one of the pollution hot spots in the country because the river passes through major industrial activity and informal settlements with poor waste management services. This could explain high concentrations in sediments and shows that these compounds accumulate. The Vaal triangle in Johannesburg has also a lot of heavy industries such as steel manufacturing and chemical industries. This may explain the high PAH concentrations observed in soil samples. High concentrations of total PAHs from Venda runoff sediments could again be attributed to vehicle and oil spills (15). A study by Okedeyi et al. (21) on the distribution and potential sources of PAHs in soils around coal-fired power plants in South Africa found the total concentration of 15 PAHs ranged from 9.73–61.24 $\mu\text{g g}^{-1}$. These values are much lower than those from the Jukskei River sediments (Table 2).

It is interesting to compare how the results in Table 2 compare with other countries. Tang et al. (27) carried out a detailed assessment of the level of PAHs in urban soil of Beijing, China. The sum of PAHs ranged from 366–27,825 ng g^{-1} . Samples were collected from campuses of universities, schools and kindergartens, public squares, fallow land, and roadsides. The highest concentrations were found in soils collected from roadside and industrial sites (27). The service station recorded the highest total concentration of PAHs at 27,825 ng g^{-1} (27). This may explain why concentrations from roadside soil from Venda and from the Vaal triangle are also high. The results from Beijing road sides are much less compared to those from the Venda region but compare well with those from the Vaal triangle soil samples. A study by Bakker et al. (28) on PAHs in Belgium from oil refinery industrial soil found total concentrations of 300,000 ng g^{-1} . This is much higher than those reported in Table 2. A study of PAHs in sediment and soil samples from oil exploration areas of the Niger Delta, Nigeria found total concentrations ranging from 65–331 ng g^{-1} and 24–120 ng g^{-1} , respectively (5). These results are much less than those in Table 2. This suggests that the results in Table 2 generally compare well with some pollution hot spots in other countries.

Individual PAHs

The individual percentage composition patterns of PAHs in water samples are shown in Figures 1 and 2. The results are difficult to compare with other studies because of the limited number of PAHs in each case. In runoff water from the Venda region in the Limpopo Province, 74% composition of the six PAHs contained pyrene followed by 14% and 8% compositions for anthracene and fluoranthene, respectively. In the same area, however, anthracene was

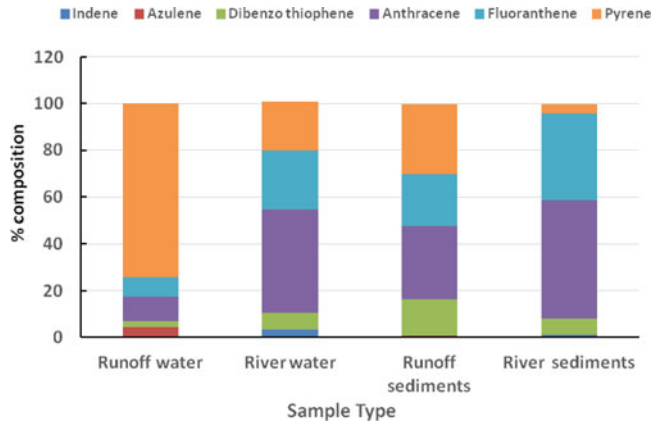


Figure 1: Mean % composition pattern of six PAHs from runoff and river water and from runoff and river sediment samples from Venda Region, Limpopo Province of South Africa (15).

most predominant in river water samples at about 44% composition followed by fluoranthene at 25% and pyrene at 21% composition. These differences in composition patterns between run off water and river water in the same area indicate the variation in behavior as these compounds move from the source to environmental compartments.

The composition pattern for the five PAHs reported in the Johannesburg area is somewhat different from that from the Venda region although target PAH compounds also differed in each study. In the two studies of river water in the Johannesburg area shown in Figure 2, a similar composition pattern was observed which is not surprising as they reflect similar sources. Phenanthrene showed the highest composition followed by either fluoranthene or acenaphthene. Naphthalene and pyrene both had very similar composition. The % composition patterns found here are not very different from those reported

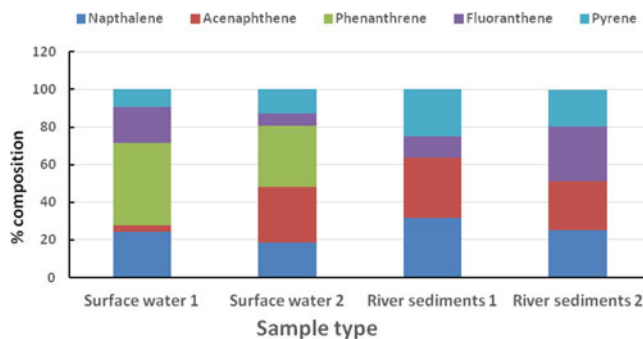


Figure 2: Mean % composition pattern of five PAHs from river water and sediment samples from Johannesburg area, Gauteng Province of South Africa (17–19).

by An et al. (25) who found out that 3-ring PAHs were most dominant in most cases followed by 4-ring PAHs and 2-ring PAHs. Acenaphthene and phenanthrene are both 3-ring PAHs while naphthalene has 2-rings. Fluoranthene has 3-rings while pyrene is a 4-ring PAH. The presence of 5- and 6-ring PAHs in surface water is low because of poor solubility.

The individual percentage composition patterns of PAHs in sediment and soil samples are shown in Figures 1, 2, and 3. In the same way as water sample results, they are difficult to compare with other studies because of the limited number of PAHs involved. From runoff sediments determined from the Venda region in Limpopo Province, anthracene had the highest composition at 51% followed by fluoranthene at 37%. The two contribute more than 80% to the total composition. In the river sediments from same area, anthracene was most predominant at 44% composition followed by fluoranthene at 31.5% composition and was followed by pyrene at 30% composition. The percentage composition pattern in the sediment samples tended to follow that of the water samples which is expected.

The composition pattern for the four PAHs in the sediments from the Johannesburg area also tended to follow that of the surface water. No individual PAH was very dominant. Acenaphthene was highest in one sample at 32% composition and fluoranthene was highest in another at 29%. Pyrene and naphthalene had similar % composition in both sediments from the Johannesburg area at round 19–25% and 24–34% composition, respectively. Das et al. (24) studied shallow lake sediment samples, and found that anthracene and 1-methyl phenanthrene were the most predominant species and accounted for 14% and 64% of the total PAHs composition. A total of nine PAHs were detected in the sediments which included naphthalene, 1-methyl phenanthrene, 2,6 dimethylnaphthalene, acenaphthene, anthracene, pyrene, benzo [b]fluoranthene, benzo [k]fluoranthene, and indenol[1,2,3-cd]pyrene.

A much better comparison of the PAH composition in soil and sediment samples is shown in Figure 3. This is because in a study by Niewoudt et al. (16), 15 of the US EPA priority list were included in the study. The 4-ring PAHs were found to be more dominant followed by the 3-ring PAHs. The 2- and 5-ring PAHs were similar although 5- ring PAHs seemed to have been slightly more dominant. The results in Figures 1 and 2 for sediment samples, although not containing many PAHs, seem to point towards the same trend as in Figure 3. The order of dominance in sediments among various size PAHs is somewhat different than generally observed in water bodies where five-membered ring PAHs are less significant. Tang et al. (27) is also reported the composition of PAHs from various soils from urban areas of Beijing, China. The 2- and 4-ring PAHs competed for dominance depending on the sample site and this was followed by 5-ring PAHs which often competed with 3-ring PAHs. The composition pattern shown in Figure 3 is thus not very different to those reported by Tang et al. (27).

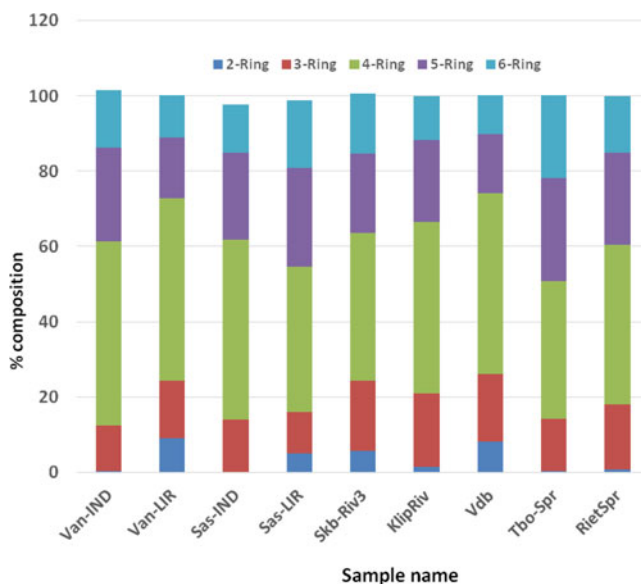


Figure 3: Composition pattern of PAHs from soil and sediments from Johannesburg area, Gauteng Province of South Africa (16).

Bioavailable PAHs in Water

Total bioavailable PAHs is always important because it gives an idea of the amount that is potentially taken up by organisms within the water body. Passive samplers such as the semi permeable device (SPMD) are now seen as an emerging technology for assessing the bioavailable fraction in environmental media (29–33). Amdany et al. (22,23) used passive samplers to assess the occurrence and seasonal trends of PAHs in water bodies around the Johannesburg area. Figure 4 shows the distribution pattern of freely dissolved PAHs in water bodies (22). The distribution pattern follows the solubility of

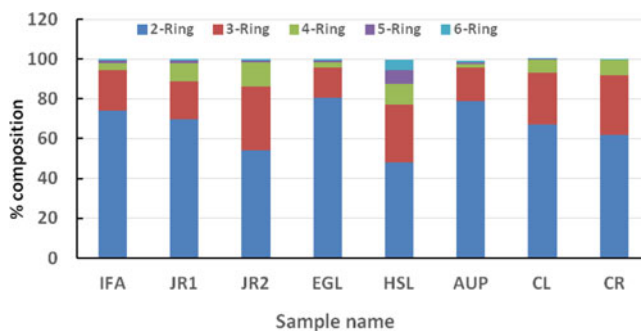


Figure 4: Composition pattern of various groups of dissolved PAHs in water bodies around Johannesburg City, South Africa (22).

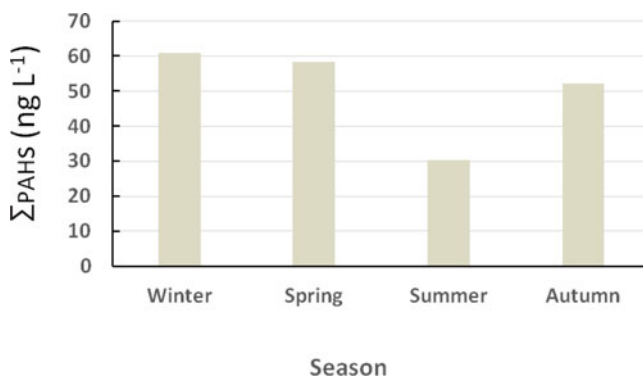


Figure 5: Temporal changes in water dissolved concentrations of some individual PAHs at the site in Johannesburg area, South Africa (23).

PAHs, unlike in sediments and that of total concentration in water bodies. PAHs that are most soluble in water are also the most dominant. Thus, 2-ring PAHs are most abundant followed by 3-ring PAHs with 6-ring PAHs the least dominant. The distribution shown in Figure 4 is similar to what has been reported by Vrana et al. (34). Vrana et al. (34) used passive sampling to monitor seasonal and spatial variability of dissolved organic contaminants and metals in the Danube River. The results revealed that the freely dissolved concentration of PAHs decreased with increasing compound hydrophobicity and reflected the adsorption of hydrophobic compounds on particles or colloids. The total concentrations of the freely dissolved portion reported by Amdany et al. (23) was also much less compared to those of the total concentrations reported in the same area by Sibiya et al. (17,18). A remarkable seasonal variability in the amounts of sequestered PAHs was shown by the deployed SPMDs (23). Estimated total analyte concentrations ranged from 30.0 ng ℓ^{-1} (in summer) to a high of 60.8 ng ℓ^{-1} (in winter). These concentrations are comparable to those reported by Wang et al. (35) (13.8–97.2 ng ℓ^{-1}) at the three Gorges River in China and by Vrana et al. (34) (5–72 ng ℓ^{-1}) in the Danube River, Slovakia/Austria. The trend of total concentrations of PAHs dissolved in water was as follows: winter > spring > autumn > summer. Individual PAH concentrations obtained in the various seasons also generally followed the same trend as the totals (Figure 5). Smaller molecular weight PAHs constituted the highest percentage of the sequestered compounds.

PAHs in the Atmosphere

The monitoring and risk assessment of PAHs in air samples has been reported by Forbes et al. (36–40). In general, more research is needed in this area as well. The problem is not unique to South Africa but to many developing countries that includes all African countries. Hindrances to air monitoring

and means by which they are being addressed has been discussed in detail by Forbes and Rohwer (36), which includes socio-political priorities, and lack of resources which results in unavailability of funding, skilled human capital and suitable equipment (36).

Research by Forbes et al. (36–40) has focused on the development and application of a novel denuder device for the simultaneous monitoring of both the gas and particle associated phases of PAHs in air. The technique involves the use of two multi-channel silicone rubber traps in series joined by a Teflon connector containing a quartz fiber filter (39). The first trap is called the primary trap that samples the gas-phase PAHs. Particle-bound PAHs are trapped with particulates by the quartz fiber filter, while the secondary multi-channel silicone rubber trap samples any desorbed PAHs from the particles on the quartz fiber filter and any gas phase PAHs which break through the primary trap under high sampling volumes.

The multi-channel silicone rubber trap based denuder has been used to investigate PAH emissions from household fires, vehicle emissions and underground mine diesel engines in South Africa (39,40). A number of organic compounds including PAHs and PAH derivatives were identified as part of the gas phase emissions from domestic heating fires and underground mine diesel engine emissions (39,40).

Sources of PAHs

Some of reported publications on PAHs in South Africa include PAH molecular ratios (19,21– 23,41). PAHs molecular ratios are often used for possible identification of the sources of these compounds whether it is petrogenic or pyrolytic (5,25–27). Table 3 below shows selected molecular ratios of PAHs in a study by Okedeyi et al. (21). The calculated values shown in Table 3 from soil samples taken at different coal power stations indicate pyrolytic sources of PAHs. This is obvious in this case as PAHs are emitted during the production of energy from coal. Further, higher molecular weight PAHs (5- to 6-ring

Table 3: Characteristic values of selected molecular ratios of PAHs from petrogenic and pyrolytic sources (21)

PAHs	Petrogenic	Pyrolytic	Matla power plant (Mpumalanga province)	Lethabo power plant (Free State Province)	Rooiwal power plant (Gauteng Province)
Phen/Anth	>15	<10	1.1 ± 0.23	1.3 ± 0.30	1.9 ± 0.38
Anth/(Anth+Phen) ^b	<0.1	>0.1	0.5 ± 0.06	0.4 ± 0.04	0.4 ± 0.08
Flan/(Flan+Pyr)	<0.4	>0.4	0.5 ± 0.03	0.5 ± 0.04	0.5 ± 0.08
LMW/HMW	High	low	0.4 ± 0.15	0.3 ± 0.10	0.4 ± 0.08

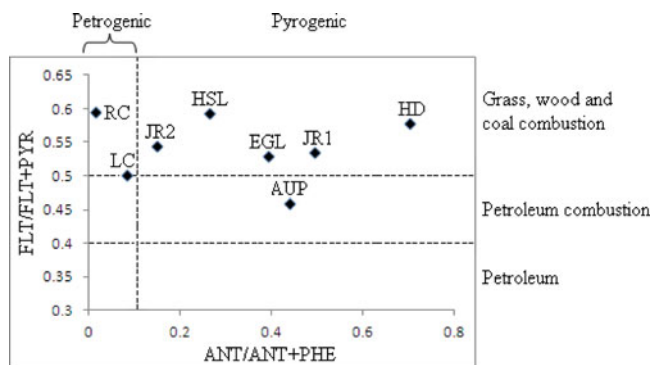


Figure 6: PAH cross plots for the ratios Ant/(Ant+Phe) vs. Flt/(Flt+Pyr) (22).

compounds) were predominant suggesting coal combustion sources and a good correlation existed between most PAHs implying similar sources (21).

Amdany et al. (22) also attempted to use ratios of Anthracene/(Anthracene + Phenanthrene) $[(Ant/(Ant + Phe))]$ against Fluoranthene/(Fluoranthene+Pyrene) $[(Flt/(Flt+Pyr))]$ to determine the source of PAHs in samples. As shown in Figure 6, the majority of the sites sampled gave Flt/(Flt+Pyr) ratios that were greater than 0.5, indicating pyrogenic origins. PAHs at sampling sites AUP and CL were clearly inclined towards petroleum combustion sources. In general, the use of Ant/Ant+Phe ratio in differentiating petrogenic from pyrogenic sources is at times limited by photolytic degradation of anthracene which can result in lowered ratios (42,43).

Das et al. (24) looked at the dominance of either low molecular weight (LMW) or high molecular weight (HMW) PAHs so as to have an idea of possible sources. PAHs from petrogenic origin are mostly dominated by LMW whereas pyrogenic processes mainly produce HMW compounds (24). The dominance of LMW compounds in surface waters could indicate automobile exhaust as the main source of PAHs in Zeekoeflei. High concentrations of both LMW and HMW PAHs during the rainy winter season suggested influence of storm water input and atmospheric deposition of PAHs in the lake (24). In the sediments, the LMW/HMW ratio ranged from 4–21 between 16 and 30 cm in sampling depth, with the highest value at 24 cm deep. The sediment depth and its highest value obtained indicate the time when recreational activities such as yachting occurred on the lake and with associated oil spills thus introducing LMW PAHs.

Comparison of the Levels with Regulatory Bodies

South Africa has no maximum allowed limits of PAHs in various environmental compartments. Therefore the results presented in this review can only

be compared with other regulatory bodies or agencies from other countries (Table S2). Details of some available maximum allowed limits from other regulatory bodies are given in the appendix. A comparison of the concentration levels of PAHs in surface waters (Table 1) to Table S2, indicate that most of them are below the maximum allowed limit set by the Agency of Toxic Substances and Disease Registry (ATSDR). It should be noted that for pyrene, the maximum reported concentration of $2.5 \text{ mg } \ell^{-1}$ was very close to the maximum allowed of $3.0 \text{ mg } \ell^{-1}$.

Table 2 shows that a number of PAHs were over the maximum allowed limits in soil samples. Fluoranthene, phenanthrene and pyrene both have maximum limits allowed in soil of 3.0 mg kg^{-1} by ATSDR but the maximum reported concentrations of 6.7, 3.7, and 5.5 mg kg^{-1} , respectively exceeded this. Benzo (a) anthracene and benzo(a)pyrene reported maximum concentrations of 3.0 and 2.9 mg kg^{-1} which also exceeded the maximum allowed concentrations of 0.3 and 1.5 mg kg^{-1} (Table S2), respectively. This shows that the concentrations of PAHs in soil samples are of concern. It is these PAHs in soils that end up in water systems during heavy rainfall as they are washed away with other soil constituents. In the end they may deposit and accumulate in sediments. It is difficult to compare the concentration levels of PAHs in sediments as there are few standards. In Table 2, the concentration of PAHs in sediments is much higher than reported in soil samples and this indicates that these sediments are highly polluted.

CONCLUSION AND FUTURE DIRECTION IN PAH ANALYSIS IN THE SOUTH AFRICAN ENVIRONMENT

This country report on the status of PAHs in surface water, soil, sediments, and air has highlighted major potential hotspots, sources and gaps. It is evident that more studies are needed to obtain a complete picture of the country wide distribution of these pollutants. Studies have been reported mainly in the Johannesburg area of the Gauteng Province (about six studies), two in Limpopo Province and one in Mpumalanga and the Western Cape Provinces, respectively. Nothing has been published in Kwazulu-Natal and only one in the Western Cape Province which are also major industrial provinces. KwaZulu-Natal is more particularly of concern because of major oil refineries based there in addition to the presence of shipping industry. The Eastern Cape Province is also another area that is of interest because of the presence of shipping industry. Further, most of the reported studies never looked at all 16 PAHs listed by the US EPA as priority pollutants, which makes it difficult to compare and draw conclusions with other studies elsewhere. This suggests that while expertise capable of carrying out such studies is present, there is limited access to suitable analytical instrumentation. This is supported by the fact that most

of those that analyzed 15 or more PAHs had collaborations with other institutions outside the country. More studies including PAH derivatives, such as alkylated PAHs, is still needed. This is important because of South Africa's reliance on coal for its energy generation. In addition, besides determining the presence of these compounds in potential hotspots, there is also a need to determine levels in places far from industrial activities in the country so as to have an idea of the country's background levels, which are really an indicator of global pollution.

SUPPLEMENTAL MATERIAL

Supplemental data for this article can be accessed on the publisher's website.

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APPENDIX

Standard Exposure Limits and Analytical Challenges of PAHs

PAHs are regulated (Tables S1 and S2, see Supplemental Data) and many environmental bodies have set limits for various environmental compartments due to their toxicity, especially with respect to mutagenic and carcinogenic effects. In 1995, PAHs were added to the hazardous substance list produced by the Agency for Toxic Substances and Disease Registry (44) and the Environmental Protection Agency (EPA) in the US (45). In 2001, PAHs were ranked by ATSDR as the ninth most threatening compounds to human health (46). Although over 100 PAHs have been identified in the environment, the US EPA has only 16 of them on the priority list (Table S1), which requires monitoring in various environmental compartments, such as water and soil. The maximum allowed limits given by the Agency for Toxic Substances and Disease Registry in water and soil vary but are much higher in soil (Table S2). No standards exist for the amount of PAHs allowed in the air, but it is recommended that the levels be no higher than 0.004 ppm (47).

Generally, the lower the allowed limit of the PAH in the environmental compartment, the higher is the risk associated with it (Table S2). Benzo[α]pyrene and indeno[1,2,3-ghi]pyrene are two of the most toxic PAHs. The partitioning of PAHs into the soil-water environment is governed by their solubility in water. Assuming similar emissions of PAHs, the concentrations in both soil and water environments can therefore easily be correlated to their solubility in water. However, since benzo[α]pyrene is regarded as the most carcinogenic PAH, its presence in various environmental compartments is considered as an indicator of others. The EPA has also set up the maximum uptake ranges of different PAHs, with maximum acceptable concentrations of 0.3 mg of anthracene, 0.04 mg of fluoranthene, acenaphthene and fluorene, and 0.03 mg of pyrene per kg of a human's body weight (47).

Further, the EPA has provided estimates of levels of total PAHs in lakes and streams that are associated with risk of human cancer development, and that if the following amounts of individual PAHs are released within a 24 h period, the EPA must be notified: 1 lb of benzo[b]fluoranthene, benzo[α]pyrene, or dibenzo[α]anthracene; 10 lb of benzo[α]anthracene; 100 lb of acenaphthene, chrycene, fluoranthene, or indeno[1,2,3-c,d]pyrene; 5,000 lb of acenaphthylene, anthracene, benzo[k]fluoranthene, fluorene, phenanthrene, or pyrene (47).

The European Union (EU) and World Health Organisation (WHO) also follow the maximum acceptable concentrations of several PAHs in water for human consumption from the Agency for Toxic Substances and Disease Registry. However, the EU list is not exactly the same as that of US EPA (Table S1). The EU has further proposed that the total maximum concentration of PAHs in sewage sludge for agriculture use should be 6.0 mg kg⁻¹, where

the source of these organic pollutants is mainly from human excretion products and household disposal (49). In order to minimize the harmful effects on health, the EU recently established a maximum level of 2 ng g⁻¹ wet weight for benzo[α]pyrene in the muscle meat of fish. This is the marker for carcinogenic risk of PAHs (50). Further, the EU recommends that its priority PAHs be monitored in various foods commodities (51).

In South Africa, there are no official allowed limits of PAHs from such bodies as the South African Bureau of Standards (SABS), Department of Environmental Affairs (DEA) and Department of Water and Sanitation (DWS).

PAH analyses at trace levels usually consist of several steps that proceed to the final analyses. These steps include sampling, transport, storage, preservation, sample preparation, analyte separation and detection (52). All these steps influence the reliability of the analytical results to a large degree. Typically, two thirds (61%) of analysis time is spent on sample processing and this step has been reported to account for approximately 30% of the error generated during the entire analytical method (53). Thus, the analyst has to perform each step knowing the potential sources of errors, how to reduce them and how to check for them. For PAHs, the major problem is adsorption on the surface of containers especially five to six ring PAHs as they are the most hydrophobic. Suitable containers should thus be used such as glass with PTFE lined caps. All transfers of the samples must be quantitative to make sure no amount remains adsorbed on the surface. Thus, to ascertain quality assurance, replicates, spiking of samples, internal standards, surrogate standards and certified reference material analyses are often performed (17,19).