## Determination and distribution of polycyclic aromatic hydrocarbons in rivers, surface runoff, and sediments in and around Thohoyandou, Limpopo Province, South Africa

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## ABSTRACT

Water quality in rural areas is affected adversely by build-up of traffic-generated organic compounds on road surfaces, leading to their presence in water runoff and sediments. Characterising these compounds is a first step in developing measures for the removal of such pollutants from water courses. In this study, liquid-liquid extraction of water samples from several rivers and surface run-off enabled quantification of major PAHs. Soxhlet extraction of sediment samples was followed by clean-up of samples using column chromatography. The PAHs were quantified by gas chromatography. In water and sediment samples, 6 PAHs were identified and quantified. In river water samples, individual PAH levels ranged between  $0.1 \ \mu g/\ell$  and  $137 \ \mu g/\ell$ , while in sediment samples levels ranged between  $17.9 \ \mu g/kg$  and  $9870 \ \mu g/kg$ . For surface run-off, levels ranged between 0.6 µg/l and 2 500 µg/l for water samples and between 112 µg/kg and 34 400 µg/kg for sediment samples. Total levels of PAHs in sediment samples were relatively high (111.6 to 61 764 µg/kg) compared to those in water from both river and surface run-off (29.2 to 3 064.8  $\mu$ g/ $\ell$ ), and PAH levels in surface runoff were much higher than in river waters, implicating tarred roads and parking lots as main point sources of PAHs. PAH ratios also indicate that the PAH content of runoff and sediment is more likely due to pyrogenic sources, i.e. vehicle emissions, although petrogenic sources (mainly oil spills) also play an important role. Toxic Equivalence Quotient (TEQ) values in river and runoff waters ranged from 0.10 to  $4.03 \ \mu g/\ell$  and for sediments the TEQ ranged from 0.50 to 272.23  $\ \mu g/kg$ . These results are of concern, as the calculated TEQ is likely to be an underestimate of the actual TEQ, since only 6 PAHs with relatively low toxicities were analysed. Long droughts and low rainfall, and washing of automobiles in and near the rivers are important factors which may have contributed to the observed levels of PAHs in both river water and sediments.

Keywords: Polycyclic aromatic hydrocarbon, river water, runoff, sediment

## INTRODUCTION

The toxicity of polycyclic aromatic hydrocarbons (PAHs) and their widespread distribution has led to more interest in the presence of these compounds in the aquatic and terrestrial environment. Many studies have been done in developed countries (e.g., Crystal and Foster, 1991; Maldonado et al., 1999), but in South Africa few studies have been conducted to determine the presence and levels of PAHs in the environment (Butler and Sibbald, 1986). Das et al. (2008) followed the sources of, and historic changes in, PAH inputs to Zeekoevlei since the early 1990s, and found very low levels of low molecular weight (MW) PAHs, attributable to low traffic volumes in the catchment, with higher concentrations of high-MW PAHs during the rainy winter season, suggesting stormwater input and atmospheric deposition from non-point sources. Nieuwoudt et al. (2011) extensively investigated soils and sediments collected from central South Africa, specifically targeting industrial, residential, and agricultural areas. The total concentration of PAHs was found to range between 44 and 39 000 ng/g with pyrogenic processes the most likely sources. PAH levels were in the same range as levels reported from other countries.

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Received 9 May 2013; accepted in revised form 6 May 2014.

http://dx.doi.org/10.4314/wsa.v40i3.4 Available on website http://www.wrc.org.za ISSN 0378-4738 (Print) = Water SA Vol. 40 No. 3 July 2014 ISSN 1816-7950 (On-line) = Water SA Vol. 40 No. 3 July 2014

The Limpopo Province of South Africa has a number of rivers receiving PAHs from rainfall runoff from parking lots, tarred roads, brickyards, formal and backyard incineration areas and scrap yards. For example, in the Thohoyandou area, at least 20 scrap yards can be found (looking4spares, 2014). This study was aimed mainly at investigating the state of sediments, water quality and surface runoff of selected rivers in Limpopo Province with respect to the levels of PAHs, focusing on 6 PAHs, viz. pyrene, azulene (used in dyes, cosmetics and lightemitting diodes), indene (produced by pyrolysis of higher boiling petroleum fractions), anthracene, dibenzothiophene, and fluoranthene. These PAHs were considered representative of PAHs occurring generally in water, sediments and surface runoff in rivers of the Thohoyandou area. Although not generally considered with other PAHs, dibenzothiophene was included as a water-soluble marker for heavier oil fractions (Wang and Fingas, 1995; Zeng et al., 2004) and persistent in older petroleum residues (Sauer and Boehm, 1991; Passivirta, 1991).

The scarcity of water resources in South Africa, combined with limited health budgets, pollution by different industries and lack of proper waste management, call for improved measures to manage the release of PAHs into the environment. The fact that few studies have been conducted in South Africa makes this study unique and important. Exposure of humans and wildlife to PAHs occurs via different pathways, such as inhalation, consumption and skin contact (Deutsch-Wenzel et al., 1983; Crystal and Foster, 1991). The present study was conducted in water because water forms an important component