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Distribution of 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofurans in the Jukskei and Klip/Vaal catchment areas in South Africa

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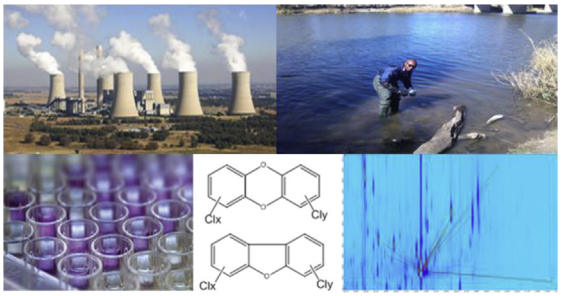
HIGHLIGHTS

- DR-Luc bioassay screening showed the presence of dioxin-like compounds.
- GCxGC-μECD analysis confirmed the presence of PCDD/Fs in sediment samples.
- TOC could not sufficiently describe the trends and distribution of PCDD/Fs.
- Particle size distribution could not account for of PCDD/F distribution and trends.

GRAPHICAL ABSTRACT



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ABSTRACT

Comprehensive two dimensional gas chromatography (GCxGC)-μECD analysis was used to determine 2,3,7,8-substituted dibenzo-*p*-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) distribution in the Jukskei and Klip/Vaal catchment areas from ten sites previously identified as persistent organic pollutant hotspots in major rivers in the Gauteng province of South Africa. Five sediment samples from the Jukskei River catchment area and five sediment samples from the Kilp/Vaal River catchment area were collected for analysis. The extracts were screened for dioxin-like activity using the DR-Luc bioassay prior to GCxGC-μECD analysis. All sediment samples tested positive for dioxin-like activity with total activity ranging from 16 to 37 pg toxic equivalents (TEQ) g^{-1} dry weight (dw) for the Jukskei River catchment and 1.5–22 pg TEQ g^{-1} dw for the Klip/Vaal River catchment, indicating that the Jukskei River catchment area had higher concentrations of total dioxin-like compounds. Confirmatory tests for the presence of the most potent seven PCDDs and ten PCDFs conducted using GCxGC-μECD revealed presence of 11 PCDD/Fs and 6 PCDD/Fs in the Jukskei and Klip/Vaal River catchments respectively. Total organic carbon (TOC) and particle size distribution analysis were conducted to understand the distribution of PCDD/Fs within the Jukskei and Klip/Vaal catchments.

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1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are a group of ubiquitous persistent organic

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pollutants (POPs) primarily of anthropogenic origin. PCDD/Fs are produced unintentionally through processes that include municipal solid waste incineration, metallurgical processing, coal fired power generation, chlorine based bleaching, pulp and paper manufacturing, manufacture of some pesticides such as trichlorophenols and pentachlorophenol, as well as natural events such as volcanic activity (de Mul et al., 2008; Hurst et al., 2004; Kim et al., 2005; Schecter et al., 2006). Together with a group of 12 non-*ortho* and mono-*ortho* polychlorinated biphenyls (PCBs), they are termed dioxin-like (dl) compounds (Hurst et al., 2004). These compounds tend to accumulate in organic rich sediment and soil and are widely spread in the environment as a result of long range transport from their point of production/release (Croes et al., 2011; Du et al., 2011). Many of the dl-compounds remain in sediment, but via the equilibrium between sediment, water and fish lipids, some will ultimately enter the food chain from where they may biomagnify (Hoh et al., 2007; Hurst et al., 2004), causing species- and tissue-specific toxic effects on the immune, nervous, reproductive, and endocrine systems in fish, humans, birds and mammals (Addeck et al., 2014; Denison et al., 2004).

Environmental spatial studies on the presence of PCDD/Fs in South African rivers are extremely rare, with once-off studies having been conducted by the Department of Water and Sanitation from sites in rivers in Gauteng, North West and Mpumalanga Provinces (Jooste et al., 2008) and three others by Vosloo and Bouwman (2005), Nieuwoudt et al. (2009) and Roos et al. (2011), concluding that detectable levels of PCDD/Fs are present in South Africa. The present study contributes with novel data on PCDD/Fs in the Jukskei River as well as in a previously studied catchment of the Klip and Vaal Rivers in the Gauteng province, two areas previously indicated as hotspots for POP contamination (Jooste et al., 2008).

PCDD/F concentrations in aquatic sediments are normally low but are potent at those low levels (Hurst et al., 2004). Therefore PCDDs and PCDFs need to be measured at low concentrations (pg-fg range). As they are present in complex matrices, they need very efficient sample pre-treatment and cleanup and that makes their analysis very challenging (Focant et al., 2005; Danielsson et al., 2005). Due to its high mass accuracy, congener specificity, selectivity and sensitivity the globally accepted reference method for estimation of individual dl-congeners is gas chromatography combined with high resolution mass spectrometry (GC-HRMS) (Danielsson et al., 2005; Schroijen et al., 2004). However, this technique is laborious, time consuming and instrumentation is very expensive. Hence, it is difficult to swiftly analyse large numbers of samples (Denison et al., 2004; Du et al., 2011). Most analytical laboratories in South Africa have no access to GC-HRMS (de Vos et al., 2013).

An alternative to GC-HRMS is the application of *in vitro* bioassays, which can measure the total dl-potency of a sample, including 17 PCDD/Fs, 12 dl-PCBs, their brominated and mixed chloro/bromo substituted analogues as well as polybrominated diphenyl ethers (Dabrowska et al., 2010). Dl-compounds are present in environmental samples as complex mixtures in varying concentrations. Hence, the total toxicity of a particular sample is the result of the sum of the concentrations of the individual congeners multiplied by their corresponding toxic equivalency factor (TEF) values, and is expressed as toxic equivalency quotient (TEQ) (van den Berg et al., 1998). The dioxin-receptor luciferase (DR-Luc) bioassay, is the most widely used bioassay and has been described as the best method for screening PCDD/Fs and dioxin-like compounds (Hoogenboom et al., 2006; Pieke et al., 2013) as it offers lower detection limits and much faster analysis time than other bioassays such as ethoxyresorufin-*O*-deethylase (EROD) assay (Murk et al., 1996; Zhang et al., 2002). It is based on manipulation of the AhR signal transduction pathway, and ultimately mimicking cytochrome P450 monooxygenase (CYP1A1) gene expression (Dabrowska et al., 2010; Denison et al., 2004; van Wouwe et al., 2004). Bioassays are extremely useful, particularly when dealing with incidents where rapid screening is required to eliminate non-positives prior to conducting confirmatory chemical analysis (Behnisch et al., 2001).

An alternative chemical analytical approach to measure PCDD/Fs in complex matrices is the use of comprehensive two-dimensional GC (GCxGC) with micro-electron capture detection (μECD) instrumentation. This two-dimensional analytical technique provides a formidable sensitivity, although with a narrow linear calibration range (Danielsson et al., 2005). GCxGC analysis allows separation of the dl-compounds from the co-eluting matrix components (Hoh et al., 2007). However, due to the presence of high matrix interference, an extensive cleanup and/or fractionation step is also required, which makes GCxGC-μECD also a time and labour-intensive method (Adahchour et al., 2008; Molina et al., 2000). Nevertheless, the two-dimensional separation technique provides extensive information about the composition of the analysed sample.

The aim of this study was to determine the spatial distribution of PCDDs and PCDFs in hotspots along two major rivers passing through industrial areas in Gauteng Province, the most industrialised region in sub-Saharan Africa. The DR-Luc bioassay was selected as a screening method to include all acid stable dl-compounds to evaluate the full dl-potency of the sediment extracts. GCxGC-μECD analysis confirmed the presence and distribution of PCDD/Fs in the Jukskei and Klip/Vaal catchments. In addition, total organic carbon and particle size distribution were measured to investigate if they influenced the distribution of the PCDD/Fs.

2. Materials and methods

2.1. Sampling and sample site description

In order to ensure representivity, sampling was conducted by random grab sampling either over a 5 m radius in the river bed or over a 5 m length along the river bank where the river bed had a depth >1 m, particularly in the Vaal River. The details of the sampling sites are given in Table 1 and are illustrated in Fig. 1 with the map of the Jukskei and Klip/Vaal Rivers. The Jukskei, Klip and Vaal Rivers are sometimes prone to seasonal flooding into the flood plain in the summer season from February to March.

2.1.1. Jukskei catchment

The Jukskei River catchment area in the Gauteng Province, South Africa, covers an area of 800 km^2 and is situated in the most industrialised region in southern Africa (Pitman, 1978). The Jukskei River flows in a north-western direction and passes within 7 km of

Table 1
Jukskei and Klip/Vaal River catchment sampling sites and GPS coordinates.

Sampling site name	Catchment	Latitude (south)	Longitude (east)
Marlboro	Jukskei	−26.08494	28.10881
Buccleuch	Jukskei	−26.05700	28.10400
Midrand	Jukskei	−26.03139	28.11222
Kyalami	Jukskei	−26.00560	28.07836
N14	Jukskei	−25.94933	27.95878
Alberton	Klip	−26.26393	28.12418
Henley Weir	Klip	−26.54939	28.06443
Klip/Vaal	Klip	−26.67055	27.95527
ArcelorMittal	Vaal	−26.68916	27.93638
*ds ArcelorMittal	Vaal	−26.70829	27.89960

*ds = downstream.

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