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Spatial monitoring of organohalogen compounds in surface water and sediments of a rural–urban river basin in Tanzania

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HIGHLIGHTS

- Levels of persistent organohalogenated pollutants in Pangani river basin are low.
- Residues of OCPs mainly originate from past applications in the sugarcane plantations.
- *p,p′*-DDE was the main metabolite recovered in the samples, indicating old inputs.
- PCB profiles dominated by low-chlorinated compounds indicating recent contamination
- Concentrations of PCBs and PBDEs linked to urbanization and transportation.

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ABSTRACT

The presence of persistent organic pollutants in Tanzanian environment is not well monitored despite the existing pollution potential from a number of sources. In this study, we investigated for the first time, the concentration profiles of different organohalogen compounds such as organochlorine pesticide residues (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in environmental samples (water and sediments) from the Pangani river basin (PRB). The PRB is one of the largest drainage basins in Tanzania, with its watershed exposed to multiple input sources of trace organic contaminants. Surface water and sediments were sampled from 12 representative stations of diverse characteristics and land-use practices, in three distinct seasons, and extracted by liquid–liquid and Soxhlet extraction methods, respectively. Water samples were analyzed by GC-ECD for OCPs only, while sediment samples were analyzed for OCPs, PCBs and PBDEs by GC/MS. Seven compounds, dominated by HCH isomers (510–4460 pg/L) and DDT analogs (160–1460 pg/L),were detected in the water samples. These concentrations are far below the WHO guidelines for drinking water quality. A total of 42 compounds (8 OCPs, 28 PCB congeners and 6 PBDE congeners) were detected in the sediment samples. Their respective total concentration ranges were 245–10,230; 357–11,000 and 38–2175 pg/g dry weight. The spatial distribution patterns and Hierarchical Cluster Analysis reflected the impact of historical agricultural usage in sugarcane plantations (OCPs), and urbanization (PCBs and PBDEs). Risk assessment using sediment quality guidelines indicated no ecotoxicological risks. The results we have found provide preliminary data on levels of the organic contaminants in Pangani river basin as a new insight on the environmental quality of the area.

1. Introduction

Organohalogenated compounds, such as organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), are of particular environmental concern due to their persistent, toxic and bioaccumulative nature (Doong et al., 2008; Sudaryanto et al., 2011). Their analysis in biological and environmental samples has remained of interest to the environmentalists, scientists, policy makers and regulatory authorities, even after cessation of their practical use (Carvalho et al., 2008; El-Shahawi et al., 2010; Navarro-Ortega et al., 2010; Yang et al., 2009). The pathways through which these contaminants enter the aquatic environment are well documented (Davis et al., 2007; Guo et al., 2008) and their ecotoxicological risks are extensively studied (Yu et al., 2010). For instance, due to their low solubility in water and high octanol–water partition coefficients, these organohalogenated compounds

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quickly become associated with particulate matter and accumulate in sediments (Connell, 1994). Sediment contamination has detrimental impacts on the ecosystems and poses potential risks to benthic organisms (Burton, 2002). Indeed, many types of sediments were polluted in areas even without urban or industrial activities (Pelley, 1999). Sediment analysis has therefore for a long time, been established as a useful way of assessing contamination levels in the environment. However, while there is a great deal of information from the developed countries, data from the developing region is rather scarce.

In Tanzania, OCPs were extensively used to control insect pests in agriculture and public health before their countrywide ban more than two decades ago (Kishimba et al., 2003). PCBs have been used in the country mainly as oil additives and in hydraulic fluids for transformers and electric equipment for decades, until it was stopped in the 1990s. However the PCB containing electric equipment still exist in the country, some are still in use and others are disposed in stores (IPEN, 2005). A 2003 PCB inventory estimated the presence of more than ten thousand tons of waste (oil) possibly contaminated by PCBs in the country, and among the suspected contaminated sites were hydropower stations close to water sources (URT, 2003). Therefore, despite the official ban of PCB containing materials in the country, the actual release of the compounds into the environment is likely not to cease for some time. Generally, studies that investigated the occurrence, concentration levels and distribution patterns of these pollutants in Tanzanian aquatic environment are just a few and mostly concentrated on a limited number of compounds. For example, most of the documented studies investigated OCP levels in environmental samples from areas with known history of large scale agricultural pesticide usage (e.g. Hellar and Kishimba, 2005; Hellar-Kihampa, 2011; Kishimba et al., 2003). The study of Mwevura et al. (2002) investigated OCP levels in sediments and biota from the coastal areas of the capital city, whereas Kruitwagen et al. (2008) assessed the levels of OCPs and PCBs in mangrove ecosystems in the country. While little information is available regarding OCP levels in Tanzanian environment, the PCB and PBDE related studies are even fewer. Overall, concentration levels of OCPs, PCBs and PBDEs in important freshwater ecosystems in the country, like the PRB, are unknown.

The Pangani river basin (43,650 km^2), located in the northern part of Tanzania, is one of the largest water resources and of vital economical importance in the country. It is spread over four administrative regions of Kilimanjaro, Arusha, Manyara and Tanga, and surrounds a population of over 2 million (PBWO/IUCN, 2007). The highland and upper parts of the basin area are characterized by urbanization, densely populated rural areas and farming activities. The lowlands have scattered croplands associated with smaller settlements, usually close to the Pangani River. Arid rangelands make up much of the remaining landscape (Beuster et al., 2006). The main Pangani River rises as a series of small streams on the southern sides of Mt. Kilimanjaro and Mt. Meru. It flows for about 500 km before draining into the Indian Ocean at Pangani town in Tanga region, with Kikuletwa and Ruvu rivers being its major tributaries. Along its course, the Pangani River and its tributaries supply a number of urban centers, rural settlements and social–economic activities.

Agriculture is the main land use sector around PRB. Due to the favorable climatic conditions and the rich volcanic soils from the slopes of Mount Kilimanjaro, the Arusha and Kilimanjaro regions are among the most agricultural intensive areas in the country, with varieties of crops being produced. Consequently, considerable quantities of pesticides are used in the regions. For example, the sugarcane plantations at Arusha Chini in the Kilimanjaro region, which have been operational since early 1940s, are one of the largest and oldest users of pesticides in the country (Mtambo and Katundu, 1996). The slopes of Mount Kilimanjaro have also been for a long time the chief producing area for the famous Arabica Coffee in Tanzania (TaCRI, 2008). At times, the plant was attacked by diseases and pests, necessitating the use of chemical pesticides to combat them (Maro et al., 2008). The regions are also among the few areas that produce cut-flowers for export in Tanzania. The rapid growing floriculture is chemically intensive, thus associated with agrochemical contamination of surface waters (Msogoya and Maerere, 2006). Moreover, small-scale farmers along the river basin grow a variety of fruits and vegetables close to the water sources (Mwamfupe, 2001), posing a threat to the quality of river waters, which are also used for drinking and other domestic purposes. Other land-use practices along the basin include livestock keeping, hydropower generation and industries. In the present study, we assessed the occurrence, levels and spatial distribution patterns of PCBs, OCPs and PBDEs in the PRB. We first characterized the water and sediment samples, and then quantified the concentrations of the contaminants. The general profiles of the contaminants are then highlighted in association with the land use practices, to elucidate the possible sources of the contaminants. Concentrations of the investigated contaminants are compared to the existing sediment quality guidelines (SQGs) as to assess the extent to which the quality of the basin environment has been affected. The study aims to provide an indication of contamination status in the basin, detect any potential threat to the river health, and identify areas of concern, as a baseline for future monitoring programs.

2. Analytical methods

2.1. Sample collection

The local climate in PRB has the rainfall season between March and May, and the dry season during the other months. More than 50% of the basin receives 500 mm–600 mm of rainfall per year, while some parts on the slopes of Mt. Meru and Mt. Kilimanjaro receive up to 2000 mm. The average temperature in the area ranges between 14 and 30 °C (PBWO/IUCN, 2007).

Three sampling campaigns were conducted in this study; the first in September–October 2009 during the dry season; the second in March–April 2010 during the rainy season and the third in January–February 2011 just before the rainy season (mid season). Water and sediment samples were simultaneously collected from twelve stations indicated in Fig. 1. Five stations are located along the main Pangani River, and seven are along its tributaries: Rivers Kikuletwa, Kikavu, Ruvu, Mkomazi and Soni. Samples were collected from exactly the same points during the three sampling campaigns. The exact geographical locations, directly obtained by a GPS receiver; and the specific characteristics of each station are listed in Table 1. The sampling stations are among those periodically monitored by the Pangani Basin Water Office (PBWO), an organization responsible for overseeing the basin environment. They are also the same stations that were previously investigated for other classes of micro-contaminants in the study of Hellar-Kihampa et al. (2012).

Water samples for analysis of organic contaminants were collected in 1 L glass Teflon-stoppered sampling bottles that were previously cleaned with de-ionized water and thoroughly rinsed with acetone. The samples were unfiltered and preserved with ~100 g of 10% NaCl. Surface sediment samples (0–6 cm depth) were collected by grabbing using a stainless steel scoop. At each location, two samples of about 50 g each were collected; one for physicochemical characterization and the other for organic contaminants analysis. Sediment samples were wrapped in clean aluminum foils and stored in polyethylene bags. Both water and sediment samples were then transported from the field in clean ice-chest boxes to the laboratory of the Department of Chemistry, University of Dar es Salaam. Upon arrival at the laboratory, the water samples were kept in a refrigerator at 4 °C and extracted within three days. The sediment samples were frozen at −18 °C to prevent degradation of the target compounds, and later on freeze-dried at −57 °C, homogenized in an agate mortar, and stored in sealed glass sample vials. Sediment samples were then