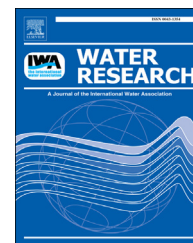




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Emerging contaminants in urban groundwater sources in Africa

J.P.R. Sorensen ^{a,*}, D.J. Lapworth ^a, D.C.W. Nkhuwa ^b, M.E. Stuart ^a,
D.C. Gooddy ^a, R.A. Bell ^a, M. Chirwa ^b, J. Kabika ^b, M. Liemisa ^c,
M. Chibesa ^c, S. Pedley ^d

^a British Geological Survey, Maclean Building, Wallingford OX10 8BB, UK

^b University of Zambia, Great East Road Campus, P.O. Box 32379, Lusaka, Zambia

^c Lukanga Water and Sewerage Company Limited, P.O. Box 81745, Kabwe, Zambia

^d Robens Centre for Public and Environmental Health, University of Surrey, Guildford GU2 7XH, UK

ARTICLE INFO

Article history:

Received 30 May 2014

Received in revised form

11 July 2014

Accepted 1 August 2014

Available online 13 August 2014

Keywords:

Emerging contaminants

Groundwater

Africa

DEET

Vulnerability

Urban tracer

ABSTRACT

The occurrence of emerging organic contaminants within the aquatic environment in Africa is currently unknown. This study provides early insights by characterising a broad range of emerging organic contaminants ($n > 1000$) in groundwater sources in Kabwe, Zambia. Groundwater samples were obtained during both the dry and wet seasons from a selection of deep boreholes and shallow wells completed within the bedrock and overlying superficial aquifers, respectively. Groundwater sources were distributed across the city to encompass peri-urban, lower cost housing, higher cost housing, and industrial land uses. The insect repellent DEET was ubiquitous within groundwater at concentrations up to 1.8 $\mu\text{g/L}$. Other compounds ($n = 26$) were detected in less than 15% of the sources and included the bactericide triclosan (up to 0.03 $\mu\text{g/L}$), chlorination by-products – trihalomethanes (up to 50 $\mu\text{g/L}$), and the surfactant 2,4,7,9-tetramethyl-5-decyne-4,7-diol (up to 0.6 $\mu\text{g/L}$). Emerging contaminants were most prevalent in shallow wells sited in low cost housing areas. This is attributed to localised vulnerability associated with inadequate well protection, sanitation, and household waste disposal. The five-fold increase in median DEET concentration following the onset of the seasonal rains highlights that more mobile compounds can rapidly migrate from the surface to the aquifer suggesting the aquifer is more vulnerable than previously considered. Furthermore it suggests DEET is potentially useful as a wastewater tracer in Africa. There was a general absence of personal care products, life-style compounds, and pharmaceuticals which are commonly detected in the aquatic environment in the developed world. This perhaps reflects some degree of attenuation within the subsurface, but could also be a result of the current limited use of products containing emerging contaminants by locals due to unaffordability and unavailability. As development and population increases in Africa, it is likely a wider-range of emerging contaminants will be released into the environment.

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* Corresponding author.

E-mail address: jare1@bgs.ac.uk (J.P.R. Sorensen).

<http://dx.doi.org/10.1016/j.watres.2014.08.002>

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1. Introduction

Organic compounds previously not known to be significant in freshwater, in terms of distribution and/or concentration, are now being more widely detected as analytical techniques improve (Farré et al., 2012). These compounds, which have the potential to cause known or suspected adverse ecological or human health effects, are often collectively referred to as emerging contaminants (ECs). ECs include newly synthesised substances as well as ones that have long been present in the environment but whose presence and significance are only now being elucidated (Daughton, 2004). They include a wide array of different compounds and their transformation products: pharmaceuticals, personal care products, pesticides, veterinary products, industrial compounds/by-products, food additives, and engineered nano-materials (Murray et al., 2010; Pal et al., 2010; Schriks et al., 2010; Hughes et al., 2012; Lapworth et al., 2012; Postigo and Barceló, 2014).

ECs are also increasingly being used as environmental tracers for characterising sources and processes which may be controlling the occurrence, transport and fate of contaminants in the subsurface (e.g. Glassmeyer et al., 2005; Stuart et al., 2014). When used in combination with groundwater residence time tracers, such as chlorofluorocarbons (CFCs) or sulphur hexafluoride (SF₆), these could be powerful techniques for understanding contaminant processes and groundwater vulnerability.

In Africa, there is an increasing use of synthetic organic compounds in the domestic context, within agriculture and industry, as well as the growing concern of exported toxic wastes to Africa from richer countries (Breivik et al., 2011). Together, these pose a potential threat to surface and groundwater quality across this region. In urban settings, these risks are likely to be most significant, due to the higher density of contaminant sources, issues of contaminant legacy and a greater concentration of anthropogenic activity. Specifically, wastewaters are likely to be a major threat to freshwater resources, as they may contain pharmaceuticals, household detergents, fragrances, flavourings, and plant and animal steroids (Ellis, 2006; Watkinson et al., 2009; Verlicchi et al., 2010). Moreover, 70% of the total urban population in many large African cities is estimated to be unconnected to a reticulated sewerage system and 80% of wastewater is discharged untreated to surface waters or the soil (Nyenje et al., 2010). Therefore, potential threats from wastewaters are enhanced in comparison to areas with more advanced water and sanitation infrastructure.

There are growing demands for freshwater sources in Africa, with groundwater continuing to form a critical component across the continent (Adelana et al., 2008; MacDonald et al., 2012). Shallow groundwater sources are particularly important as local sources of drinking water, but are also potentially very vulnerable to anthropogenic contamination (Howard et al., 2003; Cronin et al., 2006; Nkhuwa et al., 2006; Kulabako et al., 2007; Hunter et al., 2010). There is a need to understand all potential risks to groundwater resources, including understanding the occurrence and sources of ECs.

A handful of studies have characterised pesticide contamination in Africa (e.g. Karlsson et al., 2000; Schulz, 2003). There

has also been a focus on the distribution of phthalates within freshwater in South Africa (Mahomed et al., 2008; Aneck-Hahn et al., 2009; Fatoki et al., 2010) and a study demonstrating elevated polybrominated diphenyl ethers and other flame retardants in rainfall samples in East Africa (Arinaitwe et al., 2014). Lin et al. (2013) recently characterised a broad range of volatile organic compounds from pit latrines in Africa. There are no studies that have investigated many other ECs in groundwater, or indeed anywhere in the aquatic environment.

This is the first study to characterise the occurrence of a broad range of ECs ($n > 1000$) in African groundwater. The objectives are to: i) quantify the occurrence of ECs in groundwater sources in urban and peri-urban settings, ii) compare contamination in shallow sources against deep bedrock sources, iii) assess temporal variations in ECs between dry and wet seasons, iv) evaluate relationships between occurrence, land use and localised contaminant risk factors, v) understand the vulnerability of groundwater using ECs in conjunction with residence time indicators and in-situ electrical conductivity data.

2. Materials and methods

2.1. Study site

Kabwe is located on a plateau in Central Province, Zambia, about 150 km north of the capital Lusaka. The city was once the centre for Zambian lead and zinc production, which flourished during the twentieth century before the mine closure in 1994. However, sadly, the historic unregulated mining and smelting has left a legacy of heavy metal contamination (Tembo et al., 2006). The large exposed tailings piles remaining in proximity to the old mine workings are a continued source of contamination through weathering and erosion. Consequently, the city is labelled as one of the 10 most polluted places on Earth (Blacksmith Institute, 2013).

Kabwe is the provincial headquarters of Zambia's Central Province with a population of over 200,000. The central business district is encircled by higher cost housing areas, with a transition towards lower cost housing towards the periphery. The outermost limits of the city are ringed by informal settlements, such as Makululu which is home to almost 25% of the population (LgWSC, 2014). Since the mine closure, the main industries have included medical consumables, brewing, textiles, and leather tanning. Small-scale farming persists within peri-urban areas. Waste collection and disposal to the city landfill is uncommon beyond larger businesses in the town centre. Household waste is typically buried within the grounds of each property, burned, or dumped illegally in open areas.

The city is mostly underlain by the Precambrian meta-sedimentary Lower and Upper Roan Groups, which unconformably overlie granitic gneiss of the Basement Complex (Fig. S1). The Lower Roan Group consists of basal units of arkose and quartzite, totalling up to 700 m thick, succeeded by predominantly phyllite. The Upper Roan Group is locally known as the Kabwe Dolomite Formation and comprises a massive, light grey dolomite up to 870 m thick, with high degrees of lithological variation (Kamona and Friedrich, 2007).

The bedrock is blanketed by thick saprolite and laterite super-
ficials which are typically 5–20 m thick (Houston, 1982).

The groundwater system is conceptualised as a shallow
aquifer developed within the superficials and a deep bedrock
aquifer. The two units are considered to be hydraulically
connected, but perched water tables can develop within the
superficials during the wet season, owing to the abundance of
clay-rich layers (WMC, 2004). The deep bedrock aquifer in-
cludes the karstified Kabwe Dolomite Formation and the
subordinate schists of the Lower Roan Group, with trans-
boundary flow between the units. The water table is generally
within 5–10 m of the ground surface, deepest towards the end
of the dry season, and locally depressed around key abstrac-
tion sites. Natural surface water features are largely absent
due to the high infiltration capacity of the superficials. The city
experiences a sub-tropical climate with strong seasonality:
95% of rainfall generally occurs between mid-November and
mid-April (Nkhuwa et al., 2006).

Centralised water supply to the city is derived from bore-
holes within the bedrock aquifer (90% in 2013); with the
remaining provided by surface water from the Mulungushi
Dam 50 km south-east of Kabwe. Groundwater abstraction is
focused on the Kalulu, Makululu, and Mukobeko wellfields
located within peri-urban agricultural areas, although
recently there has been increasing unplanned urban
encroachment into the wellfields.

Many properties rely on self-supply of groundwater to
some extent, as piped connections are metered and supply

can be unreliable and costly. Within informal settle-
ments piped connections are unavailable with centralised supply
restricted to water kiosks. However, high levels of poverty
force many to self-supply, particularly from unprotected
hand-dug wells completed within the superficial deposits.
Unfortunately, within these areas adequate sanitation
coverage is below 11% (LgWSC, 2014), and pit latrines are
frequently sited in close proximity to groundwater sources.
Elsewhere across the city, in more formal settlements, the
sewer network has better coverage, but the system is gener-
ally aging, requiring replacement/upgrading, and is conse-
quently prone to leakage and overflow (LgWSC, 2014).
Wastewater treatment, where available, is undertaken using
natural oxidation ponds.

2.2. EC sampling and analysis

Twenty groundwater sources were sampled across Kabwe for
ECs during separate campaigns towards the end of the dry
season (September 2013) and in the subsequent wet (January
2014) season (Fig. 1). However, supply K28a was not opera-
tional during the wet season and an alternative supply, K28b
within 30 m, and similarly completed, was sampled instead.
Furthermore, K40a was not re-sampled in the wet season,
with an alternative site, K40b, selected within both a similar
lower cost housing area and proximity to the historical mine
workings.

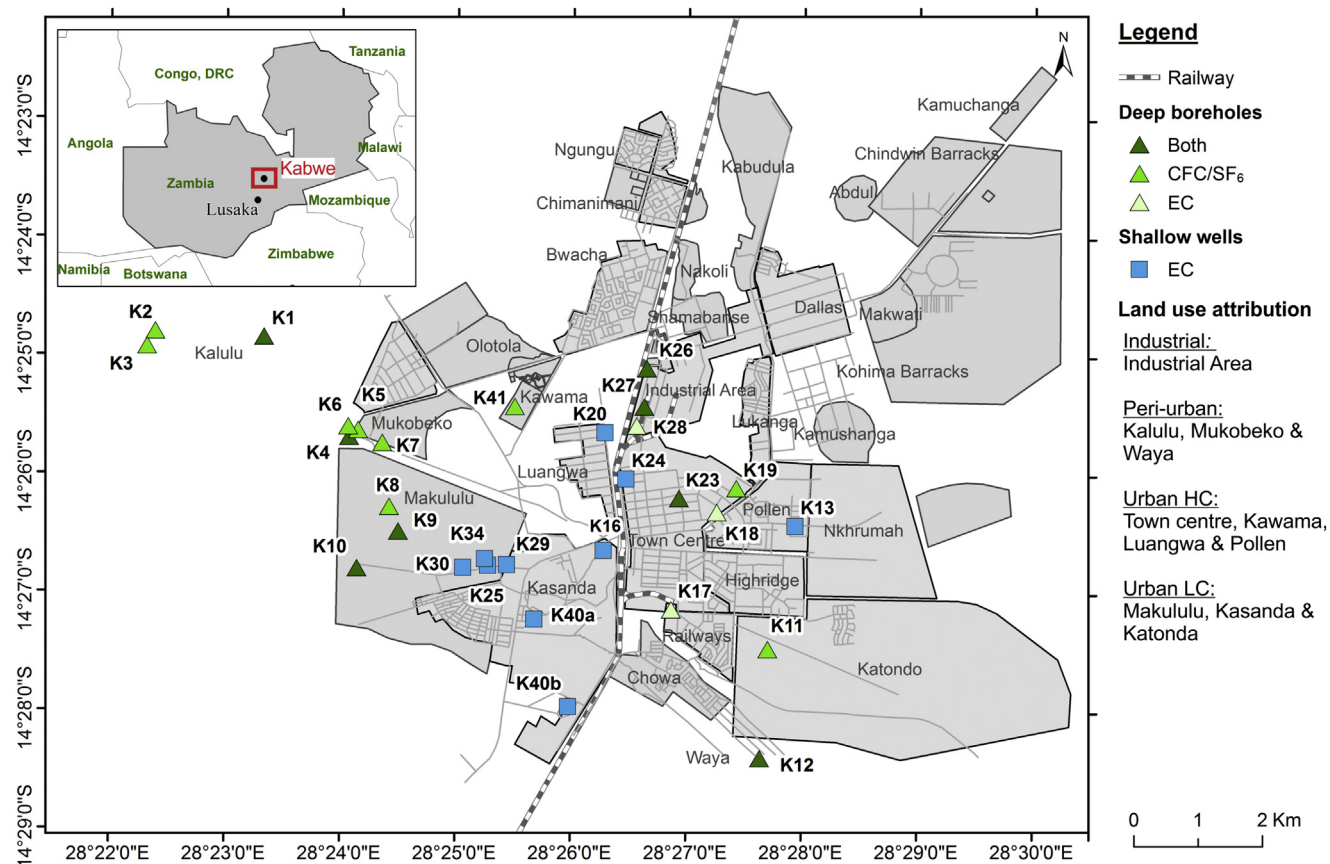


Fig. 1 – Groundwater sources sampled and distribution with land use.

The sources were distributed across a range of land uses: three peri-urban, six higher cost housing areas (Urban HC), eight lower cost housing areas (Urban LC), including Maku-lulu, and three within the industrial zone. They comprised eleven boreholes and nine shallow wells (Fig. 1). It is assumed that the shallow wells do not penetrate the underlying bedrock aquifer to any extent. There is an inherent bias in the sampling, with no shallow wells being available in the peri-urban or industrial areas.

Groundwater samples from all shallow wells and borehole K17, were taken using a submersible Proactive™ WSP-12V-5 pump attached to flexible polyester fibre reinforced PVC tubing. The remaining boreholes were sampled using existing in-situ pumps. In both instances, an assortment of PVC tubing was also used at the surface. Unfiltered samples were collected in one litre glass bottles with PTFE cap liners following purging of the relevant tubing. Insect repellents were not worn by any of the samplers, but sunscreen was regularly applied.

Samples were immediately stored in the dark in iced cool boxes, before transfer to a refrigerator at the end of each day. Samples were freighted to the UK over 24 h and analysed within 25 days of collection. Analysis was conducted by the UK Environment Agency National Laboratory Service (NLS) using a multi-residue GC–MS method which screens for over 1000 organic compounds (Table S1). Phenanthrene-d10 was added to each sample to correct for any loss of compound during the sample preparation or inlet stage. Due to the wide range of compounds contained within the target database and their variety of chemical characteristics, a double liquid–liquid extraction method was used, (neutral-acid) with dichloromethane. The combined extracts were then concentrated to 1 mL using a Zymark Turbo-Vap®, dried, and transferred to an auto-sampler vial for analysis.

The detection limits are within 0.01–0.1 µg/L for 90% of compounds, with a reporting limit of 0.01 µg/L for 75% of determinands. To improve the accuracy of concentration reported a response is obtained from running a reference standard for each individual target compound at a known concentration, typically 1 µg/l, this provides a fixed single point calibration. NLS participate in the United Kingdom Accreditation Service (UKAS) accredited proficiency scheme Aquacheck, including Group 22 ‘Qualitative Organics by GC–MS’.

2.3. EC quality control

Blank samples were collected to identify any potential contamination introduced through sampling and submitted to the laboratory ‘blind’. Assorted blanks were collected by passing ultrapure grade water through either the pump or a particular piece of tubing. The water itself was also tested and there was a confirmed absence of ECs. The WSP pump and tubing blanks included two anti-oxidants that can be incorporated into plastics to prevent degradation and an array of plasticisers (Table S2). Given the extent of plasticiser contamination in the blanks, it was considered necessary to exclude all plasticisers, and the two anti-oxidants, from any further discussion, although the data are included in the

Table 1 – Number of detections in the main sample and refrigerated (R) and unrefrigerated (UF) replicates and range in concentration of ten selected compounds across a variety of concentrations.

Source	Total number of detections			Range in concentration between sample and replicates (µg/L)									
	Sample	R Replicate	UR replicate	DEET ^a	Dieldrin	Caffeine	1,3-Dichlorobenzene	Atrazine	4,4'-DDT	Beta-BHC (beta-HCH)	Triacetin	Triclosan	o,p'-DDT
K9	1	1	2	0.50–0.50	–	–	–	–	–	–	–	–	–
K16	3	3	No sample	0.20–0.20	–	–	–	–	–	–	–	–	–
K30	3	3	3	0.19–0.22	–	–	0.10–0.13	–	–	–	–	–	–
K34	10	6	8	0.30–0.33	0.31–0.36	0.17–0.20	–	0.07–0.11	0.07–0.09	0.05–0.06	ND–0.04	ND–0.03	0.02–0.02
K40b	1	1	1	0.10–0.12	–	–	–	–	–	–	–	–	–

Notes:
 – denotes not present.
 ND denotes non-detected.
^a N,N'-Diethyl-m-toluamide.

Table 2 – Organic compounds detected. *Italicised compounds are regarded as potential sample contamination.*

Compound	Common use	No. of detections		Site detections		Max. concentration (ng/L)	
		Dry	Wet	Dry	Wet	Dry	Wet
1,1,1,2-Tetrachloroethane	Solvent	1	–	K16	–	0.14	–
1,2,3-Trichloropropane	Solvent	1	–	K16	–	1.3	–
1,3-Dichlorobenzene	Solvent	–	1	–	K16	–	0.13
2,4,7,9-Tetramethyl-5-decyne-4,7-diol (TMDD)	Surfactant	–	3	–	K12, K13, K25	–	0.6
2,6-Dichlorobenzamide (BAM)	Herbicide metabolite	1	–	K9	–	0.01	–
2-Chloromethyl-1,3-dichloro-2-methylpropane	Solvent	1	–	K16	–	7	–
4,4'-DDT	Insecticide	–	1	–	K34	–	0.07
Atrazine	Herbicide	1	2	K30	K17, K30	0.13	0.07
Benzaldehyde	Food additive	1	–	K16	–	1.2	–
Benzophenone	Photo initiator	1	1	K34	K34	0.04	0.06
beta-BHC (beta-HCH)	Insecticide	–	1	–	K34	–	0.05
Bromacil	Herbicide	–	1	–	K17	–	0.09
Bromodichloromethane	By-product chlorination	2	–	K16, K30	–	50	–
Bromoform	By-product chlorination	2	–	K16, K30	–	0.8	–
Caffeine	Drug	–	1	–	K34	–	0.17
Chlorobenzene	Solvent	2	1	K16, K40a	K16	1.4	0.07
Chlorodibromomethane	By-product chlorination	2	–	K16, K30	–	12	–
Dicofol	Insecticide	–	1	–	K34	–	0.06
Dieldrin	Insecticide	–	1	–	K34	–	0.31
N,N-Diethyl-m-toluamide (DEET)	Insect repellent	17	20	All, but K12, K23, K28	All	0.4	1.8
o,p'-DDT	Insecticide	–	1	–	K34	–	0.02
Terbutryne	Herbicide	1	1	K30	K30	0.03	0.02
Tetrachloroethylene (PCE)	Solvent	–	1	–	K28b	–	0.4
Tri-(2-chloroethyl) phosphate (TCEP)	Flame retardant	–	1	–	K34	–	0.1
Triacetin	Food additive	–	1	–	K34	–	0.04
Trichloroethylene (TCE)	Solvent	2	1	K16, K34	K28b	0.6	0.5
Triclosan	Bactericide	3	3	K25, K34, K40a	K10, K24, K34	0.02	0.03
1,6-Dioxacyclododecane-7,12-dione (DOCDD)	Plasticiser	9	9	<i>n/a</i>	<i>n/a</i>	48	34
bis(2-ethylhexyl)phthalate (DEHP)	Plasticiser	4	4	<i>n/a</i>	<i>n/a</i>	21	5
Bis (4-chlorophenyl) sulfone (BCPS)	Plasticiser	–	1	<i>n/a</i>	<i>n/a</i>	–	0.03
Bisphenol A	Plasticiser	1	2	<i>n/a</i>	<i>n/a</i>	1.1	0.09
Butylated hydroxytoluene	Anti-oxidant	8	10	<i>n/a</i>	<i>n/a</i>	0.4	0.3
Cyclohexanone	Plasticiser	–	1	<i>n/a</i>	<i>n/a</i>	–	0.1
Diisobutyl phthalate (DIBP)	Plasticiser	1	–	<i>n/a</i>	<i>n/a</i>	1	–
Diethyl phthalate (DEP)	Plasticiser	14	–	<i>n/a</i>	<i>n/a</i>	22	–
Dimethyl phthalate	Plasticiser	5	1	<i>n/a</i>	<i>n/a</i>	1	0.1
Homosalate	UV inhibitor	–	1	<i>n/a</i>	<i>n/a</i>	–	0.05
N-butyl Benzenesulfonamide (NBBS)	Plasticiser	16	3	<i>n/a</i>	<i>n/a</i>	168	1
Octocrylene	UV inhibitor	8	2	<i>n/a</i>	<i>n/a</i>	0.12	0.04
Triphenyl phosphate	Plasticiser	3	–	<i>n/a</i>	<i>n/a</i>	1.1	–

results for completeness. Additionally, octocrylene and homosalate, common sunscreen ingredients, are also regarded as being potentially introduced artificially during sampling and are not discussed further.

To assess the repeatability of the GC–MS methodology, replicate samples were collected immediately after the main sample at five sites during the wet season and handled identically. At four of these sites an additional replicate sample was successively collected, but remained unrefrigerated to assess the importance of refrigerated storage given the challenges of using these methods overseas where freighting is necessary. These unrefrigerated replicates were exposed to a mean daily temperature of around 25 °C for 8–14 days in Zambia prior to shipping.

Identical numbers of compounds were detected across replicates at three sites, with minor differences at K9, and differences of up to 40% at a more contaminated site, K34 (Table 1). The range in concentration of compounds suggests repeatability is typically within 0.03 µg/L. However, at low concentrations of 0.03 and 0.04 µg/L, towards the typical limits of detection, the methodology cannot always consistently provide a confirmed identification. This explains the differences in the total number of detections at K34, but not in the unrefrigerated replicate at K9 where 2,4,7,9-Tetramethyl-5-decyne-4,7-diol was present at a concentration of 0.6 µg/L. The repeatability of both numbers of detections and concentrations within the unrefrigerated replicates demonstrates the lack of refrigeration during transit is not considered to have adversely influenced the results. Nevertheless, the DDT metabolite 4-4'-DDE was only detected in the unrefrigerated replicate at K34 at a concentration of 0.02 µg/L suggesting limited degradation was possible.

2.4. Residence time indicators

Residence time indicators (CFC-11, CFC-12 and SF₆) were collected from 17 boreholes (Fig. 1), according to the methods detailed in Goody et al. (2006). No samples were collected from the shallow wells because of the risks of contamination with modern air during the sampling process. Analysis was conducted in the UK by purge-and-trap gas chromatography with electron capture detection. Detection limits were 0.05 pmol/L and 0.1 fmol/L for CFCs and SF₆, respectively, with an error of roughly 5% based on repeat measurements of the calibrated air standard used. A recharge temperature of 25 °C was assumed for calculating the recharge year and relative fractions of modern water. SF₆ data were corrected for excess air at 2 cc/L.

2.5. In-situ monitoring

A continuously logging specific electrical conductance (SEC) sensor (Hydrolab MS5, Hach Hydromet, Loveland, USA) was installed within well K24 to monitor changes between the EC sampling campaigns. This well is adequately completed and surface leakage and overland flow directly into the supply were considered unlikely. Additionally daily rainfall data were available from Kabwe Meteorological Station.

3. Results and discussion

3.1. Main compounds identified

A total of 27 organic compounds were identified in groundwater samples across Kabwe (Table 2). The most prevalent

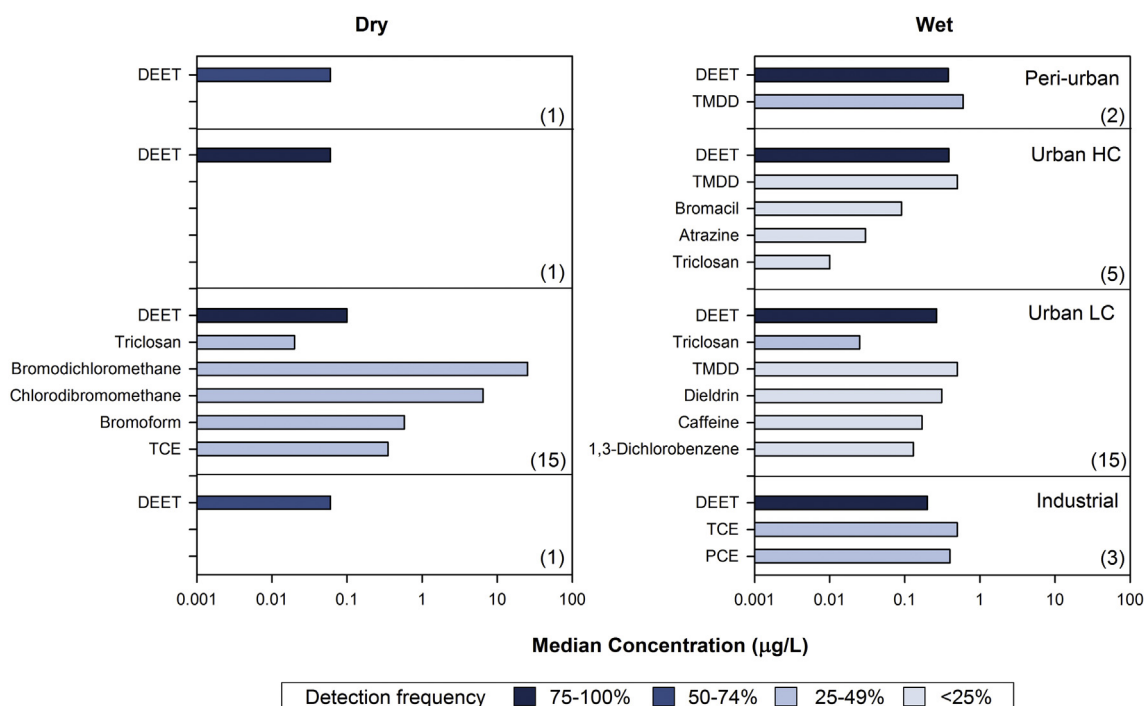


Fig. 2 – Concentration and occurrence of the six most prevalent organic compounds within each type of land use during both the dry and wet seasons. Total ECs within each land use shown in brackets.

compound was the insect repellent N,N-diethyl-m-toluamide (DEET) during both seasons. It was discovered at 85% of sites during the dry season and was ubiquitous during the wet season, with the median concentration increasing five-fold to 0.33 $\mu\text{g/L}$. Other compounds were restricted to less than 15% of sites.

Insecticides were absent during the dry season, but five were detected during the wet season at concentrations up to 0.31 $\mu\text{g/L}$ at a single site (K34) (Table 2). Three herbicides were detected, in addition to the dichlobenil metabolite 2,6-dichlorobenzamide (BAM), with atrazine found at the highest concentration. However, their occurrence was restricted to only three sites and concentrations were below 0.13 $\mu\text{g/L}$. Chlorinated solvents including TCE and PCE were identified at four sites and trihalomethanes (THMs – by-products of chlorination) were noted during the dry season at two sites.

3.2. Distribution with land use

ECs were most numerous within the residential urban areas, with their incidence greatest in the lower cost housing areas (Fig. 2). The number of ECs was greatest in the wet season for most land uses indicating contamination was associated with the seasonal rains. The bactericide triclosan, THMs, herbicides, and insecticides occurred only within the urban residential area. Specifically, contamination with THMs and insecticides was restricted to the lower cost housing areas during the dry and wet seasons, respectively.

The association of triclosan with the residential urban area is unsurprising given its frequent use in personal care products marketed as antimicrobial, such as soaps and toothpastes, which will be discharged in grey water. THMs were restricted to the lower cost housing areas where locals sometimes chlorinate the wells directly, as storage at the surface is limited and self-supply from these sources can be the main source of drinking water. Furthermore, chlorination tablets are sometimes freely distributed within these neighbourhoods by the local water company to reduce waterborne infections. Wells in such areas, where sanitation is restricted to basic pit latrines, may be particularly susceptible to the production of trihalomethanes following chlorination, as their

generation is positively correlated with dissolved organic carbon concentration (Stuart et al., 2001). Chloroform was not analysed for, but was also likely to have been present given the occurrence of the other THMs.

The absence of herbicides and insecticides in the peri-urban agricultural areas around Kabwe is considered a result of the unaffordability of these synthetic compounds to the small-scale farmers who work the land. The occurrence of an array of insecticides within a well (K34) in the urban area could be linked to the regular residual spraying of properties as part of the government's malaria control campaign, which includes the use of DDT.

Chlorinated solvents were confined to the industrial zone and the lower cost housing areas. In the industrial zone, they were absent within K28a during the dry season, but PCE and TCE were present nearby at K28b during the wet season. In the lower cost housing area, there was a decrease in both detection frequency and concentration of solvents following the onset of the wet season. Chlorinated solvents are common groundwater contaminants associated with a wide-variety of commercial and industrial uses and their occurrence beneath the industrial zone is not unexpected. Six of the ten detections were within well K16 – a local guesthouse.

The surfactant 2,4,7,9-Tetramethyl-5-decyne-4,7-diol (TMDD), an inert surfactant in herbicides, pesticides, and consumer products was present in both the urban and peri-urban environments during the wet season. As the compound occurred sporadically across all land uses, its source is unclear.

3.3. Comparison of groundwater source type

The number of EC detections was greatest within shallow wells in the low cost housing areas and specific wells such as K16 and K34 were particular hotspots (Fig. 3). Wells in this setting are most vulnerable: they are poorly completed (Fig. 4), and these areas have the lowest levels of sewer coverage and household waste collection is non-existent. Therefore, there are greater potential sources of ECs and, significantly, contaminants can migrate into groundwater via rapid pathways that are absent elsewhere: for example, overland flow as any surface completion is limited, shallow lateral flow as the wells

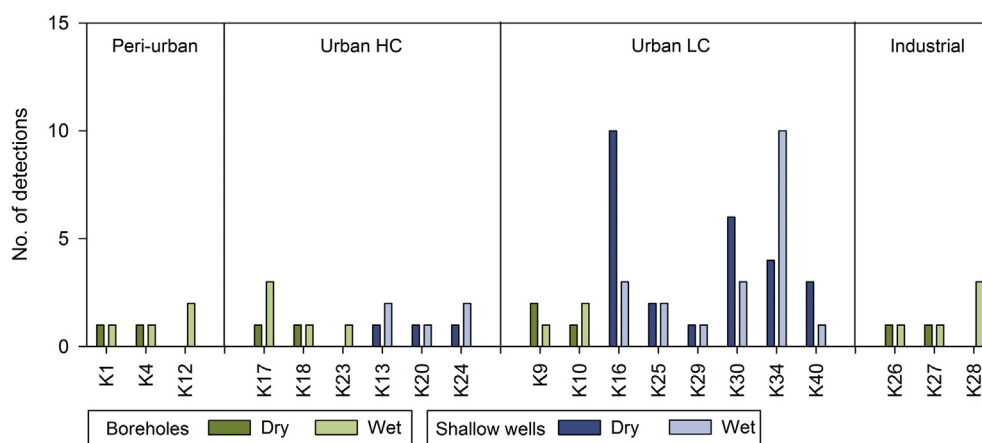


Fig. 3 – Number of ECs detected in boreholes and wells during the dry and wet seasons.



Fig. 4 – Relating groundwater source vulnerability to land use (a) vulnerable unlined shallow well (K34) adjacent to the road in lower cost housing area, (b) shallow well (K20) and borehole (K18) with protective headworks located in gated properties within higher cost housing areas (c) fully sealed public water supply borehole within secure compound in the peri-urban Mukobeko wellfield.

are unlined, and soil and waste can fall directly in. Consequently, ECs with limited leaching potential, such as triclosan (Cha and Cupples, 2010), are unsurprisingly found in a higher proportion of these wells than elsewhere in Kabwe (Fig. 2). However, not all such wells in the lower cost housing areas are highly contaminated suggesting that groundwater contamination is on a localised scale.

On the other hand, both wells and boreholes sited in higher cost housing areas often contained only DEET, with only two sites having more than two compounds (boreholes K17 and K28). These sources are less vulnerable to surface-derived contamination as they are generally completed to a much higher standard (Fig. 4). Furthermore, sewerage connections are present, even if the system is prone to leakage, and at some properties waste is collected. It should be noted that borehole K17 was a vulnerable source: being unlined and uncapped at the surface.

The highest concentrations of DEET in the dry season were noted within shallow wells in the residential urban area (Fig. 5). DEET was seasonally ever-present in shallow wells and absent from three boreholes within the dry season.

Following the onset of the rains, DEET was omnipresent across the whole of Kabwe and there was a five-fold increase in its median concentration. This indicates a contaminant pulse associated with recharge and a near-surface diffuse source.

3.4. Identifying the source of DEET

DEET is a common insect repellent in consumer products and these are widely available in Kabwe given the prevalence of malaria, although there are questions regarding the scale of its use due to the levels of poverty in parts of the city. It is generally considered that many residents prefer the use of mosquito nets impregnated with alternative repellents, which have been freely distributed as part of the nationwide anti-malarial campaign (Mwiimbu, 2013).

Nevertheless, the annual loading into the bedrock aquifer is only estimated to be in the order of 40 kg, based on an increase in median concentration of 0.26 $\mu\text{g/L}$, an effective porosity of 5% (Lusaka Dolomite from Jones and Topfer (1972)) and an aquifer thickness of 60 m (typical maximum depth of

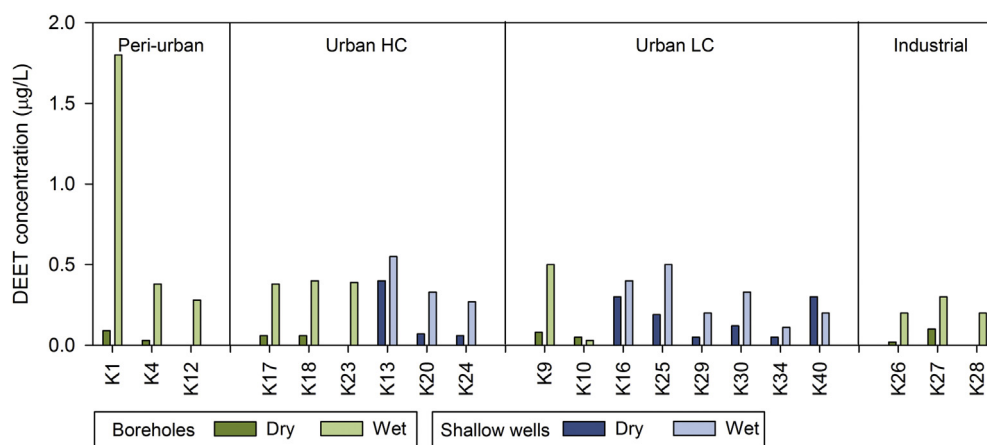


Fig. 5 – DEET concentrations in the dry and wet seasons.

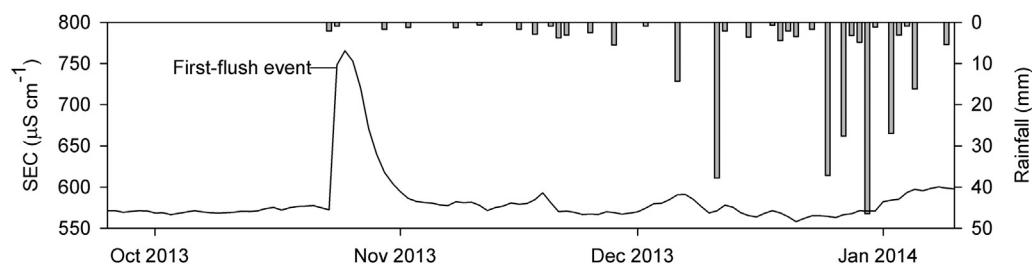


Fig. 6 – Changes in mean daily specific electrical conductance (SEC) following rainfall at well K24 between the dry and wet season EC sampling.

Kabwe boreholes sampled). Health Canada (2002) estimated a mean of 3.7 g of insect repellent product is applied during application (Antwi et al., 2008). Therefore, only 60 people applying 50% DEET repellent once per day would equate to 40 kg of DEET usage annually, neglecting potential degradation and sorption. Consequently, the source of contamination could be considered on a domestic scale, particularly given that such repellent sprays are on sale to a population of over 200,000. Alternative agricultural and industrial sources, such as an insect repellent for livestock and crops, a resin solvent, a dye carrier, a flame retardant carrier, surface plasticiser, and levelling agent (Aronson et al., 2012), seem less likely.

Following topical application to humans, DEET absorption through the skin has been shown to be only 10%, with all product completely metabolised prior to excretion (Selim et al., 1995). Therefore, the main source to the aquatic environment

is likely to be from the washing of skin/clothes following application. Consequently, it is considered the majority of DEET enters the environment through grey water disposed at the surface and leakage from the sewerage network.

3.5. Groundwater vulnerability

Rapid increases in SEC within 24 h of rainfall events (Fig. 6) highlight the vulnerability of sources in the superficial aquifer to surface-derived contaminants. Wells are likely to be most vulnerable following the first-flush event at the start of the rainy season (Fig. 6), when the accumulation of surface and near-surface organic residuals during the dry season are first mobilised through the soil profile. Vulnerability is enhanced by poor well completion in lower cost housing areas, as partially evidenced by the higher number of ECs in such sources.

Within the bedrock aquifer, CFC bulk recharge ages generally ranged from the early to mid-1970s to present day. Ages in excess of the present day indicate some CFC contamination. Agreement between CFC-11 and CFC-12 ages was generally good, though some CFC-11 apparent ages were older indicating some removal of this compound through reduction (Horneman et al., 2008). In terms of fraction of modern water, these ranged from slightly less than 50% modern to 'over-modern', i.e. in excess of present day air saturated water. SF_6 bulk ages ranged from the mid-1980s to present day, with the modern fraction ranging from 20% to 100%.

The apparent disparity between CFC and SF_6 ages can be reconciled through considering the dominant groundwater flow mechanism (Fig. 7). The majority of data (excluding those with an 'over-modern' fraction) fall between a Piston Flow Model (PFM) and an Exponential Mixing model (EMM) which is indicative of older water being progressively mixed with more recent recharge. On this basis it is clear that the waters were generally recharged between 10 and 30 years ago. K2 and K23 are more indicative of a Binary Mixing Model (BMM) and suggest the waters mostly comprise modern recharge mixing with a small amount of older water.

A bulk residence time of 10–30 years and a large fraction of more modern water suggest the bedrock aquifer has been at risk from the ingress of a range of modern organic compounds; yet the number of observed compounds is low. This is most evident at K23 which is mostly comprised of modern recharge, yet contained no ECs in the dry season and one in the wet season. This supports a recent groundwater vulnerability assessment of the bedrock aquifer, which concluded

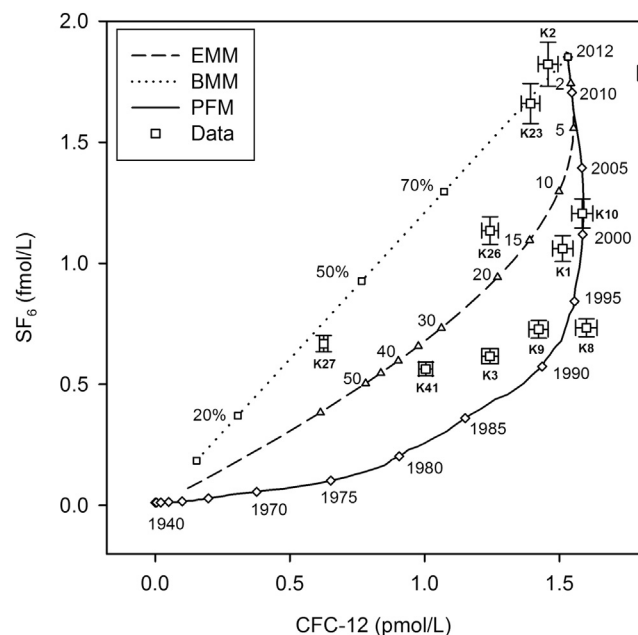


Fig. 7 – CFC-12 and SF_6 data superimposed on three different lumped parameter models (Małozewski and Zuber, 1982) representing an exponential mixing model (EMM) with numbers indicating average years since recharge, a binary mixing model (BMM) with percentage of modern tracer concentration shown, and a piston flow model with bulk water ages (PFM).

that the bedrock aquifer was not at risk currently, due to the extensive overlying clay-rich superfcials which were likely to provide a significant barrier to contamination (Museteka, 2013). However, DEET concentrations have been demonstrated to significantly increase in the bedrock aquifer during the wet season indicating limited attenuation of this compound. It is unknown whether this is because the deposits are more permeable or thinner in places than anticipated, or the wide-spread coverage of vulnerable shallow wells facilitates artificial bypass routes. Either way, the seasonality in DEET concentrations demonstrates that more mobile compounds can rapidly reach the bedrock aquifer and sources are more vulnerable than previously considered.

Once in the aquifer, the degradation of organic contaminants is likely to be much lower than the half-lives reported for the near surface, particularly within the bedrock. This is due to generally limited microbial populations and activity (Sorensen et al., 2013), combined with more limited nutrient and oxygen availability within groundwater (Tesoriero et al., 2007). For example, Weeks et al. (2012) indicates a half-life of days to weeks for DEET in soil and freshwater, yet DEET was still present in the bedrock at the end of the dry season four months after the cessation of the previous year's rains. Whilst this may reflect perennial artificial recharge of wastewater, it is possible these lower concentrations may simply be a result of dilution via throughflow of water recharged beyond the city boundaries. DEET is likely to be very persistent in groundwater.

3.6. Risks posed by ECs

Most of the compounds detected beyond a single source are not generally considered to present a risk to human health or the environment at the concentrations detected. For example, maximum groundwater concentrations of DEET are orders of magnitude below that suggested to present a risk to human health or the freshwater environment. Blanset et al. (2007) considered an acceptable daily intake of 0.1 mg/kg body weight/day in humans for DEET, whilst it is not considered bioaccumulative (Weeks et al., 2012). Acute and chronic toxicity of DEET in the freshwater environment has only been observed at concentrations exceeding 0.5 mg/L (Costanzo et al., 2007; Weeks et al., 2012).

Nonetheless, the maximum observed concentration of bromodichloromethane is close to the WHO guideline value of 60 µg/L, and may actually exceed it given the likelihood of analyte losses to evaporation. This compound is carcinogenic and can adversely affect reproduction in humans (Hrudey, 2009). However, the benefits derived from water purification to eliminate the transfer of waterborne diseases are likely to far outweigh the potential adverse health risks in Kabwe.

It is unclear how representative the range of compounds and concentrations are of the seasonal worst-case scenario. It is possible that both of these may be higher following the first-flush event before the likely subsequent dilution of these compounds via throughflow. Additionally, the harmful effects of ECs have only been examined on a single compound basis and it is possible that combinations of ECs may have additive or synergistic effects.

3.7. Comparison with developed world studies

DEET is commonly detected in groundwater in the developed world with 35% of sources in the USA (Barnes et al., 2008) and 83% in the EU testing positive (Loos et al., 2010). Whilst average concentrations are not reported in the USA, Loos et al. (2010) identified a median concentration of only 1 ng/L in the EU. In the tropics, DEET has been shown to be omnipresent in Singaporean groundwater at a higher median concentration of 49.5 ng/L (Tran et al., 2013). Therefore, the median concentrations in Kabwe of 70 and 330 ng/L in the dry and wet seasons, respectively, are in excess of that reported elsewhere for groundwater. DEET is likely to be more prevalent and at higher concentrations throughout the tropics because of the incidence of mosquito borne disease. The risks from endemic malaria may explain the higher concentrations in Kabwe than that found in Singapore where the incidence of the disease is much lower.

Within the developed world, emerging contaminants related to personal care products, life-style compounds, and pharmaceuticals are commonly detected in the aquatic environment (Barnes et al., 2008; Nakada et al., 2008; Loos et al., 2010; Lapworth et al., 2012). These types of compounds are frequently linked to wastewater ingress into groundwater (Kuroda et al., 2012). Commonly detected examples which were screened for in this study (Table S1) include caffeine, carbamazepine, sulfamethoxazole, and the nicotine metabolite cotinine. With the exception of a single caffeine detection, these compounds were absent in this study. This is despite the fact that pit latrines are frequently sited in close proximity (<30 m) to groundwater sources in the lower cost housing areas. Therefore, although latrines are an important source of groundwater contamination in Africa (Graham and Polizzotto, 2013), there is no evidence to suggest that they contribute significant quantities of ECs to groundwater in Kabwe. Furthermore, the absence of these ECs in such a setting, highlights that the level of consumption of these products must be low, due to both low levels of income and poorer accessibility.

Insecticides and herbicides are common groundwater contaminants in the developed world (Hallberg, 1989; Stuart et al., 2012) as farmers strive to optimise crop yields and profits. For example Atrazine has been detected in 56% of groundwater sources in the EU (Loos et al., 2010). However, the use of these compounds by the small-scale farmers in peri-urban Kabwe is limited because of the associated costs. Their use is generally restricted to occasional large-scale outbreaks of pests, such as African armyworms, when they are freely distributed by central government to minimise wide-spread crop destruction. Consequently, these compounds were absent beneath agricultural peri-urban areas.

Chlorinated solvents are ubiquitous in industrial and commercial areas in developed counties from both current and historical uses (Rivett et al., 1990). In Kabwe, chlorinated solvents were identified in a borehole in the industrial zone, but also in the lower cost housing areas. However there were relatively few detections, presumably since Kabwe is not industrialised on any scale.

4. Conclusions

This is the first study to provide an insight into the occurrence of a broad range of ECs in the aquatic environment in Africa, with a focus on groundwater beneath Kabwe, Zambia. A total of 27 compounds were identified including the omnipresent DEET, at a median concentration greater than that observed in other groundwater studies across the globe. Triclosan, THMs, herbicides, insecticides and chlorinated solvents were observed at a limited number of sources. Contamination was most extensive within shallow wells sited in areas of low cost housing, due to inadequate sanitation, household waste disposal, and, significantly, poor well protection and construction. The compounds detected are not directly linked to human waste and consequently there appears to be no association with sewage disposal in pit latrines in Kabwe.

The bedrock aquifer has previously been considered non-vulnerable to contamination, due to the assumed extensive overlying clay-rich superfcials. Although residence time indicators presented here showed groundwater (<60 m bgl) to be reasonably young, and therefore at risk from the ingress of a range of modern organic compounds, ECs are largely absent. Therefore, the superfcials do appear to be providing some groundwater protection by attenuation of a range of contaminants, in agreement with existing understanding. However, the average five-fold increase in median DEET concentration following the onset of the wet season highlights that more mobile contaminants can transit rapidly from the surface to the bedrock aquifer. Thus the deep groundwater resources that provide the majority of the water supply to the city may be more vulnerable than previously considered.

The large-scale absence of many ECs in contrast to studies within the developed world could be related to generally low levels of income and consequently limited consumption of products which contain them presently. This could be reflected across many parts of Africa, and potentially the developing world. As levels of personal income rise with development, an increasing number of ECs are likely to be released into the environment. Regulation limits the use of some compounds, such as triclosan which has been partially banned in Europe and some parts of North America, where there are concerns over adverse impacts on human health and the aquatic environment. However, this type of regulation may be more difficult to implement and enforce in Africa.

Currently, the majority of African wastewater is discharged without treatment. Therefore, the continent's water resources near urban areas could be particularly vulnerable to higher levels of ECs discharged within wastewater, unless advanced treatment systems capable of removing these compounds develop in line with rising incomes. However, this presently appears unlikely as resources for infrastructure improvements remain limited and continued rapid urbanisation means local authorities are more hampered in efforts to provide even the most basic services.

Nevertheless, it should also be considered that the levels of ECs in Kabwe groundwater may not be representative of the current situation across other parts of Africa. It is possible that other urban areas in Africa may be more contaminated: particularly those that have higher degrees of

industrialisation (e.g. Cairo), are more affluent (e.g. Cape Town), have greater population densities (e.g. slum areas of Ndola, Lagos or Kisumu) and import more of the West's waste (e.g. Accra). There is a knowledge gap on the occurrence of emerging anthropogenic pollutants in the aquatic environment and further work is required across the continent to assess the currently unknown risks that ECs are posing to human health and the environment.

Acknowledgements

We are grateful to Makondo Wencyslouw, Managing Director of Lukanga Water and Sewerage Company, for his cooperation throughout the study. Additionally, Wayne Civil (NLS-UK) provided the chemical database for the GC–MS screen and further details concerning the laboratory methodology. This paper is published with permission of the Executive Director of the British Geological Survey, NERC. The work was funded by the Department for International Development (DFID), the Economic and Social Research Council (ESRC), and the National Environmental Research Council (NERC) under the UPGro Programme, NERC grant number NE/L002078/1.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2014.08.002>.

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