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Impact of organic pollutants from urban slum informal settlements on sustainable development goals and river sediment quality, Nairobi, Kenya, Africa

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ABSTRACT

The UN Sustainable Development Goals highlight the myriad of socio-economic and environmental challenges occurring as a result of anthropogenic chemical pollution. Urban sediments from informal settlements (slums) on the Nairobi, Ngong and Mathare Rivers (n = 25), were evaluated for sediment quality. Microtox bioassay identified 8 sites as toxic, 9 as moderately toxic and 8 as non-toxic. Slum sediments were characterised by high total organic carbon and Rock-Eval pyrolysis revealed bound carbon from a mix of raw sewage and domestic refuse. Sediments from Kiambio, Kibera, Mathare and Kawangware slums contained high coprostanol at 55–298 μg/g and epicoprostanol at 3.2–21.7 μg/g confirming appreciable incorporation of untreated human faeces. Hormones, antianalgeiscs, antiinflamatories, antiepileptics and antibiotics most affected Mathare > Kiambio > Kibera > Mukuru > Kawangware slums. Carbamazepine, ibuprofen, diclofenac and acetaminophen concentrations are amongst the highest reported in Kenyan river sediments and were positively correlated with faecal steroids (sewage). Common persistent organic pollutants, such as organochlorine insecticides ΣDDT 1–59 μg/kg, mean 21.2 μg/kg, Σ^{16}PAH 182–2218 μg/kg, mean 822 μg/kg and Σ^{30} PCB 3.1–157.1 μg/kg, mean of 21.4 μg/kg were between probable effect likely and unlikely sediment quality guidelines (SQG). PAH source ratios and parent to alkyl-PAH distribution suggested vehicle exhaust, power stations (heavy oil), kerosene (cooking oil) and other pollution sources. Trace metal concentrations As, Cd, Cr, Hg and Ni were below SQG whereas Pb exceeded the SQG. This multi-contaminant characterisation of sediment quality in Nairobi supports the development and implementation of policies to improve urban infrastructure to protect ecological and human health. It demonstrates the need for environmental geochemists to engage in the science-policy interface associated with both global and national development frameworks, with particular reference to the Sustainable Development Goals, New Urban Agenda, and Kenya's Vision 2030.

1. Introduction

Globally more than 1 billion people live at a disadvantage because they reside in urban informal settlements (slums) that lack amenities to supply clean water, dispose and treat human sewage and remove domestic rubbish (UN-SDG, 2021). These attributes alongside substandard housing, insecure tenure of land and poor drainage as well as unfavourable locations close to river floodplains, facilitate uncontrolled waste disposal and chemical pollution of adjacent urban rivers (waterways) (APHRC, 2014; Correa and Grace, 2014; UN-Habitat, 2003). Consequently, slum residents are more likely to suffer from a variety of life threatening water borne and soil/sediment hosted diseases including diarrhoea, typhoid, cholera, viral pneumonia, noro-virus, tuberculosis and malaria (Bauza et al., 2017; Blanton et al., 2015; Katukiza et al., 2014; Kyobutungi et al., 2008; Würthwein et al., 2001; Yé et al., 2007). The health impact of these water borne/soil/sediment hosted diseases is

Abbreviations: PAH, polycyclic aromatic hydrocarbon; PCB, polychlorinated biphenyl; DDT, dichlorodiphenyltricholorethane.

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exacerbated in many slums of Sub-Saharan Africa such as Mathare settlement in Nairobi, Kenya where approximately 12% of the population have HIV/AIDS as compared to 5% of (non-slum) Nairobi inhabitants (Corburn et al., 2019). Furthermore, children's prolonged and early exposure to excreta-related pathogens such as worms decreases cognitive development and can stunt growth (Corburn and Hildebrand, 2015). This urban-environmental health challenge is repeated to lesser or greater extent throughout the slums of sub-Saharan Africa (238 million slum dwellers), as well as Central and Southern Asia (226 million slum dwellers), Eastern and South Eastern Asia (370 million), Latin America and Caribbean (112 million), and North America and Europe (0.8 million) where it disproportionately effects the health of women and children (Corburn and Hildebrand, 2015; UN-Habitat, 2003; UN-Habitat, 2020; UN-SDG, 2021). The United Nations Sustainable Development Goals (SDGs), adopted by UN member states in 2015, collectively aim to eradicate global poverty, end unsustainable consumption patterns, and facilitate sustained and inclusive economic growth, social development, and environment protection by 2030 (UN-SDG, 2015). The SDGs include several ambitions to improve waste management, reduce pollution and contamination of all types, and protect health and wellbeing. Kenya's Vision 2030 also sets out nationally owned development priorities of improved sanitation, pollution/waste management, and urban development, and securing reductions in infant mortality and social inequalities (Kenya, 2007). The Kenya Vision 2030 also highlights the need to reduce pollution and improve waste management to achieve these ambitions (Kenya, 2007).

The cities of eastern Africa are some of the most rapidly urbanizing areas of the world, with slum inhabitants comprising the majority (>50%) of the overall urban population and about 30% of the metropolitan population (APHRC, 2014; Oyvat and wa Gīthīnji, 2020). For example, Nairobi, the capital city of Kenya, has a disconnected mosaic of between 100 and 150 slums distributed across nine administrative divisions each of which has a different developmental history, proximity to polluting industries and connection to urban rivers of the Nairobi basin which flow from west-east (Alder, 1995; Mutisya and Yarime, 2011). Nairobi's slum populations vary according to census methodology but broadly proceeds in the order Kibera (first developed in 1912), 200,000, Mathare (1963), 200,000> Kawangware 130,000>Mukuru Kwa Njenga (1970s) 100,000> Kiambio 40,000>Mukuru Kayaba 20,000 (APHRC, 2014; Desgroppes and Taupin, 2011). However, although pollution within slums is visually apparent and frequently cited as an issue there are surprisingly few soil or sediment quality evaluations that quantify organic contaminants, trace metals and biological toxicity tests in order to ascertain likely impact on ecology and protect human health.

The aim of this study is to provide a measurement-based assessment of environmental pollution in river sediments at five slums (Kibera, Mathare, Kiambio, Kawangware, Mukuru) and compare this assessment to a variety of river sites with different land-use characteristics. Given that sanitation (disposal of human faecal waste) is widely reported anecdotally as a key issue, we chose to measure faecal sterols/stanols alongside more traditional suites of persistent organic pollutants such as total extractable hydrocarbons, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and pharmaceuticals. Specific, research hypotheses being tested within this study are: 1) Is Nairobi's informal settlements (slums) pollutant geochemistry distinct from sites traversing other urban land-uses; 2) Does sedimentary pollution remain consistent irrespective of settlement or waterway-river; 3) Sediment toxicity is not driven by an individual compound class but is an aggregated effect (cocktail).

This research provides an evidence base to inform action toward sustainable urban development and improved health and wellbeing, as set out in relevant international and national development strategies (Table 1). These data can support the understanding of the complexity of development challenges, inform interventions in both policy and practice, and monitor progress towards the SDGs and Kenya Vision 2030. The comprehensive baseline established in this research can be used to support these steps.

Table 1
Goals and targets in the UN Sustainable Development Goals (SDGs) and Kenya's Vision 2030 (see United Nations, 2015; Government of Kenya, 2007).

Strategy	Goal (SDGs)/Sector of the Social Pillar (Vision, 2030)	Target (SDGs)/Detail (Vision, 2030)
United Nations Sustainable Development Goals (SDGs)	SDG 3: Good Health and Wellbeing	3.9: By 2030, substantially reduce the number of deaths and illnesses from hazardous chemicals and air, water and soil pollution and contamination
	SDG 6: Clean Water and Sanitation	6.2: By 2030, achieve access to adequate and equitable sanitation and hygiene for all and end open defecation, paying special attention to the needs of women and girls and those in vulnerable situations
		6.3: By 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally
	SDG 11: Sustainable Cities and Communities	11.1: By 2030, ensure access for all to adequate, safe and affordable housing and basic services and upgrade slums
		11.6: By 2030, reduce the adverse per capita environmental impact of cities, including by paying special attention to air quality and municipal and other waste management
	SDG 12: Responsible Consumption and Production	12.4: By 2020, achieve the environmentally sound management of chemicals and all wastes throughout their life cycle, in accordance with agreed international frameworks, and significantly reduce their release to air, water and soil in order to minimize their adverse impacts on human health and the environment
Kenya Vision 2030	The Health Sector	Shift the bias of the national health bill from curative to preventative care, and lower infant mortality ratios (p. 18)
	Water and Sanitation	Ensure improved sanitation is available and accessible to all (p. 18)
	The Environment	Ensure a clean, secure, and sustainable environment (p. 19)
	Housing and Urbanisation	Ensure effective capacity for regional and urban development planning starting with adequate housing for those now living in slums (p. 19)
	Equity and Poverty Elimination	Equitable distribution of water, sewerage, and sanitation services (p. 21)

2. Methods

2.1. Sediment collection and preparation

Sediments ($n = 25$) were collected from the three main rivers that traverse five of Nairobi's informal settlement (slum) neighbourhoods: Mathare River (Mathare settlement), Nairobi River Kiambio (Kiambiu)

and Kawangware settlement, Ngong Rivers (Kibera and Mukuru settlements) along with other domains namely, Karen (residential suburb), Karura River, (Karura Forest park), Chiromo (university) and Kikuyu (Quarry), Nairobi on January 16, 2020 (Fig. 1). Sites were pre-selected to cover a range of current urban riverside land-uses such as informal settlements, high income residential domains, commuter domains and more industrialised domains. The positions of all sampling locations were recorded using a handheld GPS (accuracy ±5 m). At each site sediment samples were recovered from four corners and the centre of a 2 m by 2 m square grid at a depth of 0–20 cm using a hand-held stainless-steel trowel (Supplementary file 2.1). The five samples were combined, sealed in a seal-tight polyethylene bag and transported in a cool box/bag at ~4 °C until frozen at −18 °C. Upon return to the laboratory all samples were freeze-dried, disaggregated, sieved to pass a brass mesh of aperture 2 mm and the <2 mm fractions ground in a ball mill to <250 μm (Vane et al., 2020c, 2021).

2.2. Sediment toxicity screening and total coliforms

Microtox® Solid Phase Test (SPT) bioassay operating conditions were identical to those applied to River Thames sediments (Vane et al., 2020c). Briefly, 7 g sediment was transferred to a beaker and 35 mL SPT diluent (3.5% NaCl) added and 1.5 mL of the suspension transferred to SPT tubes. Serial dilutions of 1:2 were performed to give 13 dilutions in duplicate and 2 control samples containing no sediment were also evaluated. Freeze dried bacteria (*Vibrio Fischeri,* strain NRRL B-1117) were reconstituted and left in the reagent well of a Microtox® M500 Toxicity Analyser prior to the addition of 20 μL test reagent to each SPT tube. After 20 min samples were filtered and 0.5 mL of filtrate analysed. The measurements were used to create a dose response curve and an EC_{50} value in mg/L. The utility of the SPT was evaluated by concurrent assessment of reference material NIST 1941b with certified moderate concentrations of organic and trace metals. For total coliforms, sediment (1.8 g) was transferred to a sterile universal container using aseptic technique. To each sub-sample 20 ml of sterile demineralised water was added and the contents centrifuged at 750 g for 10 min. The supernatant was removed and used for microbial inoculations. The supernatant was filtered through a 0.45 μm cellulose nitrate filter (Gelman). Each filter was then placed onto a Petri dish containing a pad saturated with Membrane Lauryl Tryptose Broth (Oxoid). The dishes were incubated for 24 h at 35 °C. Yellow colonies of between 1 and 3 mm were counted as presumptive coliform bacteria (total coliforms).

2.3. Organic carbon, pyrolysis and total extractable hydrocarbons

Total organic carbon (TOC % wt/wt) was determined using an Elementar VarioMax C, N analyser after acidification of 0.5 g sediment with HCl. The limits of quantification for TOC were 0.18% (Vane et al., 2020a). Sediments (~50 mg) were analysed using a Rock-Eval(6) pyrolyser (Vinci Technologies) to evaluate free hydrocarbons (S1), bound hydrocarbons (S2) and the amount of CO_2 generated during pyrolysis phase (S3) by IR detector. The maximum temperature at which bound hydrocarbons cracked was also determined (Tmax). Hydrogen index (HI) and Oxygen Index (OI) of Nairobi sediments were calculated from measured S2, S3 and TOC %. Details of the analytical operating conditions and integration parameters have been previously reported for a variety of unconsolidated matrices including agricultural soils, coastal peats and river sediments (Kemp et al., 2019; Newell et al., 2016; Thomas et al., 2019; Upton et al., 2018). For total extractable hydrocarbon (TEH), sediments were extracted with dichloromethane/acetone (1:1 v/v) by accelerated solvent extraction (ASE, Dionex-300). Extracts were reduced to dryness and reconstituted in 1 mL of toluene and TEH determined by thin-layer chromatography-flame ionization detection (Chromarods-S III - Iatroscan Mk6) calibrated for saturate hydrocarbons using pristane and aromatic hydrocarbons using triphenylene (Vane et al., 2011, 2019a). TEH concentration was calculated by summation of the saturate and aromatic hydrocarbons (Shantha and Napolitano, 1998; Volkman and Nichols, 1991). The limit of quantification (LoQ) for TEH was 3 mg/kg.

2.4. Polycyclic aromatic hydrocarbons (PAH)

Sediments (1.2 g) were spiked with standards and extracted with dichloromethane (DCM)/acetone (Ace) (1:1v/v) using an ASE (Supplementary 2.4). The extract was passed through a Na_2SO_4 (1 g), and transferred to a conditioned Bond Elute cartridge. Parent and alkylated

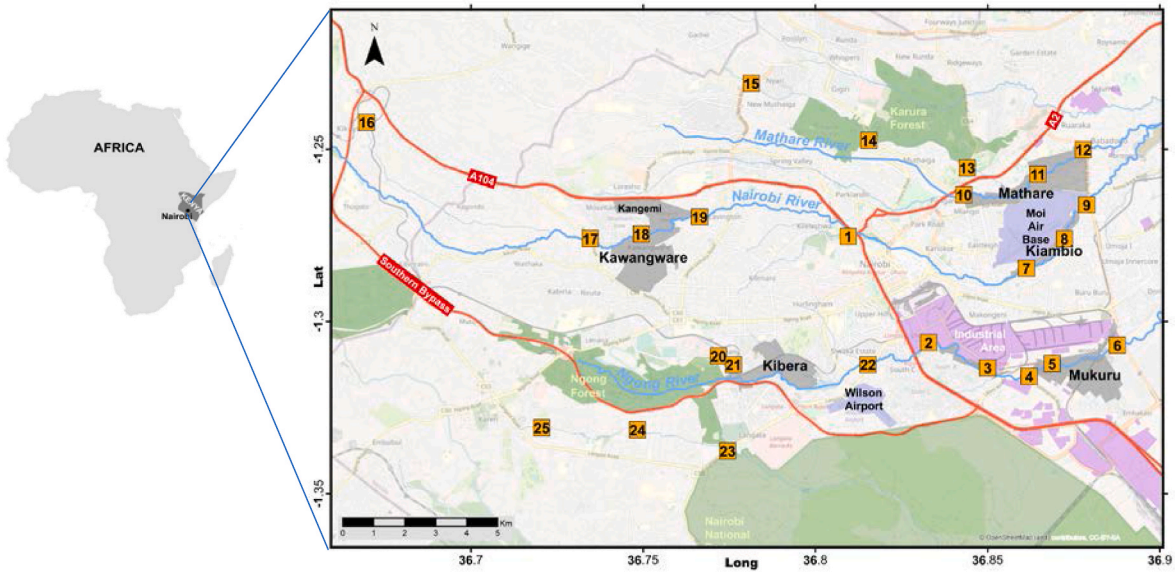

Fig. 1. Map of study area showing primary rivers and Mukuru, Kibera, Mathare and Kwangaware informal settlements (urban slums), Nairobi, Kenya. Site nomenclature: 1) Chiromo (Nairobi University) (2); Pre Mukuru Kayaba; 3) Mukuru Kayaba; 4) Post Mukuru Kayaba/Pre Mukuru Kwa Njenga; 5) Mukuru Kwa Njenga; 6) Post Mukuru Kwa Njenga; 7) Pre Kiambio; 8) Kiambio; 9) Post Kiambio; 10) Pre Mathare; 11) Mathare; 12) Post Mathare; 13) Post Karura; 14) Karura; 15) Pre Karura, 16) Kikuyu Quarry; 17) Pre Kawangware, 18) Kawangware; 19) Post Kawangware; 20) Pre Kibera (next to Jamhuri); 21) Kibera (Soweto); 22) Post Kibera (T-Mall area); 23) Post Karen; 24) Karen; 25) Pre Karen.

PAH were eluted with 6 mL hexane/iso-propanol (97:3) v/v) and the eluate reduced and spiked with internal standards. PAH were determined by gas chromatography-mass spectrometry (GC-MS) using a Thermo Scientific Trace 1300-TSQ9000 triple quadropole MS operated in single ion monitoring (SIM) mode (ionization energy 70 eV). Quality control was achieved by analysis of 1.2 g of a certified reference material (CRM; NIST-1941: Organics in Marine Sediment). One procedural blank and four CRMs (analysed in duplicate) were included in each ASE batch of 24 extractions. A comparison of the CRM PAH values revealed a good correlation to the values obtained in this study with the exception of the semi-volatile PAH naphthalene; measured mean 694 ng/g (±273) as compared to certificate mean 848 ng/g (±95) (Supplementary 2.4).

2.5. Polychlorinated biphenyl (PCB) and dichlorodiphenyltrichloroethane (DDT)

Sediments (2 g) were spiked with standards and extracted with DCM/Ace (1:1v/v) using an ASE. Organochlorine compounds were separated from other compound classes using a Bond Elute TPH SPE cartridge eluted with 6 mL hexane/iso-propanol (97:3) v/v. PCB, ∑[DDT, DDE, DDD] were determined by gas chromatography-mass spectrometry (GC-MS-MS) using a Thermo Scientific Trace 1300-TSQ9000 triple quadropole MS in selective reaction monitoring (SRM) mode (ionization energy 70 eV). Quality control was achieved with duplicate analyses of CRM (NIST-1944, New York/New Jersey waterway sediment) every 10 samples. A comparison of the CRM certified reference values revealed a reasonable/good correlation to the values obtained in this study (Supplementary 2.5).

2.6. Faecal sterols

Sediments (2 g) were spiked with deuterated standards and extracted with DCM/MeOH (1:1 v/v) using an ASE (Supplementary 2.10). Extracts were reduced to 1.5 mL and transferred to a conditioned Bond Elute, HF Mega BE cartridge. Faecal compounds were eluted with 50 mL DCM and 50 mL Ace:DCM (3:7 v/v). The two fractions were combined, reduced to dryness, reconstituted in pyridine (1 mL) and derivatized with *N,O*-bis (trimethylsilyl)trifluoroacetamide (BSTFA) and 20 μL of internal standard (5a-androstanol and 5a-cholestane-d6, 20–22 ng/μL) was added. Faecal markers (see list in supplementary) were determined by gas chromatography-mass spectrometry (GC-MS-MS) using a Thermo Scientific Trace 1300-TSQ9000 triple quadropole MS in single ion monitoring (SIM) mode (ionization energy 70 eV). (Harrault et al., 2019; Kemp et al., 2021; Rowland et al., 2020; Vane et al., 2010). Tentative identification of cholest-3-ene, lupeol and glutinol was achieved using full-scan mode. Quality control was achieved by performing repeated intra-batch analyses of human faecal material and an exemplar sample taken from the study (Supplementary 2.6).

2.7. Pharmaceuticals and hormones

Sediments (2 g) were spiked with standards, extracted with (30 mL) water:methanol (H_2O:MeOH) 2:1 using ASE (Supplementary 2.7). Extracts were diluted to 500 mL with H_2O and passed through a 6 mL/200 mg Oasis HLB cartridge, conditioned with 5 mL MeOH and 5 mL H_2O. Target compounds were eluted with 6 mL MeOH and reduced in volume prior to analysis. Pharmaceuticals and hormones were determined using a uHPLC Acella coupled to a triple-stage quadrupole (TSQ) Quantiva mass spectrometer (LC/MS) (Supplementary 2.7). Limits of detection (LoD) and quantification (LoQ) of samples were calculated using signal to noise ratio. LoD were defined as the lowest concentration having a S/N ≥ 3 and for LoQ a S/N ≥ 10.

2.8. Trace metals

In preparation for determining concentrations of stable Pb isotopes, 0.25 g of sediment was dissolved by a mixture of concentrated HF/$HClO_4$/HNO_3 in Savillex™ PFA vials. Samples were reconstituted in dilute nitric acid and diluted to: (i) within the calibration range of Pb and Sb chemical standards for concentration measurements; and (ii) within the pulse counting range (<1 Mcps) of the ICP-MS for isotope ratio measurements. Concentration and isotope ratio determinations were made using a quadrupole ICP-MS instrument (Agilent 7500c) with a conventional glass concentric nebuliser. Details of accuracy and post data collection processing methodology have been reported previously (Vane et al., 2020c). The limits of detection (mg/kg) for metals used herein for sediment quality assessments were Cr < 0.05, Cr < 0.3, Ni < 0.9, Cu, Zn < 0.4, As<0.03 and Cd < 0.4. Quality assurance was achieved by comparison with three reference materials, namely BCR-2 basalt, NIST 2711a Montana soil II and MESS-4 marine sediment (Supplementary). Total Hg was measured using a Milestone Mercury Analyser (DMA-80) instrument, operating conditions were identical to those previously reported (Vane et al., 2015, 2019b). Quality assurance was accomplished by analysing high (PACS-2, 3.04 mg/kg), mid- (TH2-1, 0.620 mg/kg) and low-level (MESS3-1, 0.091 mg/kg) sediment Hg reference materials. Measured values were 3.24 mg/kg (RSD 2.41%, *n*=4), and 0.66 mg/kg (RSD 2.1%, *n*=2), 0.10 mg/kg (11.25%, *n*=4) respectively and a limit of quantification of 0.005 mg/kg.

2.9. Sediment particle size

In preparation for particle size analysis, organic matter was first removed from 1 g of each sediment by repeat addition of 10 mL H_2O_2 and heating at 70 °C in a water bath. Particle size was measured using a Beckman Coulter LS™ 13,320 MW operated under identical conditions to that of Vane et al. (2015). The proportions of particles at each size class (117 groups, from 0.1 μm to 2000 μm) were calculated using the Fraunhofer model, based on refractive indices of 1.33 for H_2O and 1.55 for quartz. The 117 groups were then summed according to the following categorisation scheme: clay (<4 μm); silt (4–64 μm); and sand (>64–2000 μm).

3. Results and discussion

3.1. Toxicity screening and total coliforms

Microtox SPT EC_{50} of Nairobi's urban rivers ranged from 1340 to 20,670 mg/L, mean 7969 and median of 7309 mg/L (Fig. 2). Low EC_{50} values indicate higher toxicity whereas higher values confirm lower toxicity, such that three categories are defined as: very toxic <5000 mg. L (0.5%); moderately toxic >5000 to <10000 mg/L (0.5–1%) and; non-toxic >10,000 mg/L (>1%) (Kwan and Dutka, 1995; Niemirycz et al., 2007; Vane et al., 2020b). Based on these criteria and bearing in mind that they are not exact cut-offs, 8 sites are very toxic, 9 sites are moderately toxic and 8 sites are non-toxic (Fig. 2).

The majority of sediments from Kiambio, Mathare, Kawangware and Kibera were within the toxic category whereas those from Mukuru were either moderately toxic (mid and post settlement) or non-toxic (pre-settlement) (Fig. 2). Sediments from other land-use domains, namely, Karura, Karen and Chiromo as well as Kikuyu were moderately toxic or non-toxic (Fig. 2). Inspection of the data revealed non-systematic variation along each urban river, for example on the Ngong River sediments from Kibera settlement ranged from 1340 to 6364 mg/L (mean 4456 mg/L) whereas sediment collected ~5 km downstream in Mukuru were of lower toxicity and ranged from 12,230 to 20,670 mg/L (mean 16,367 mg/L). This variation in microtox SPT EC_{50} down a single reach of urban river suggests that pollution and associated toxicant(s) are deposited close to the source of input (effluent discharge points) and do not appear to increase as the urban rivers traverse informal settlements, residential and other domains within Nairobi city.

Comparison of Nairobi's urban river EC_{50} to those from other international rivers is not straightforward because many studies report

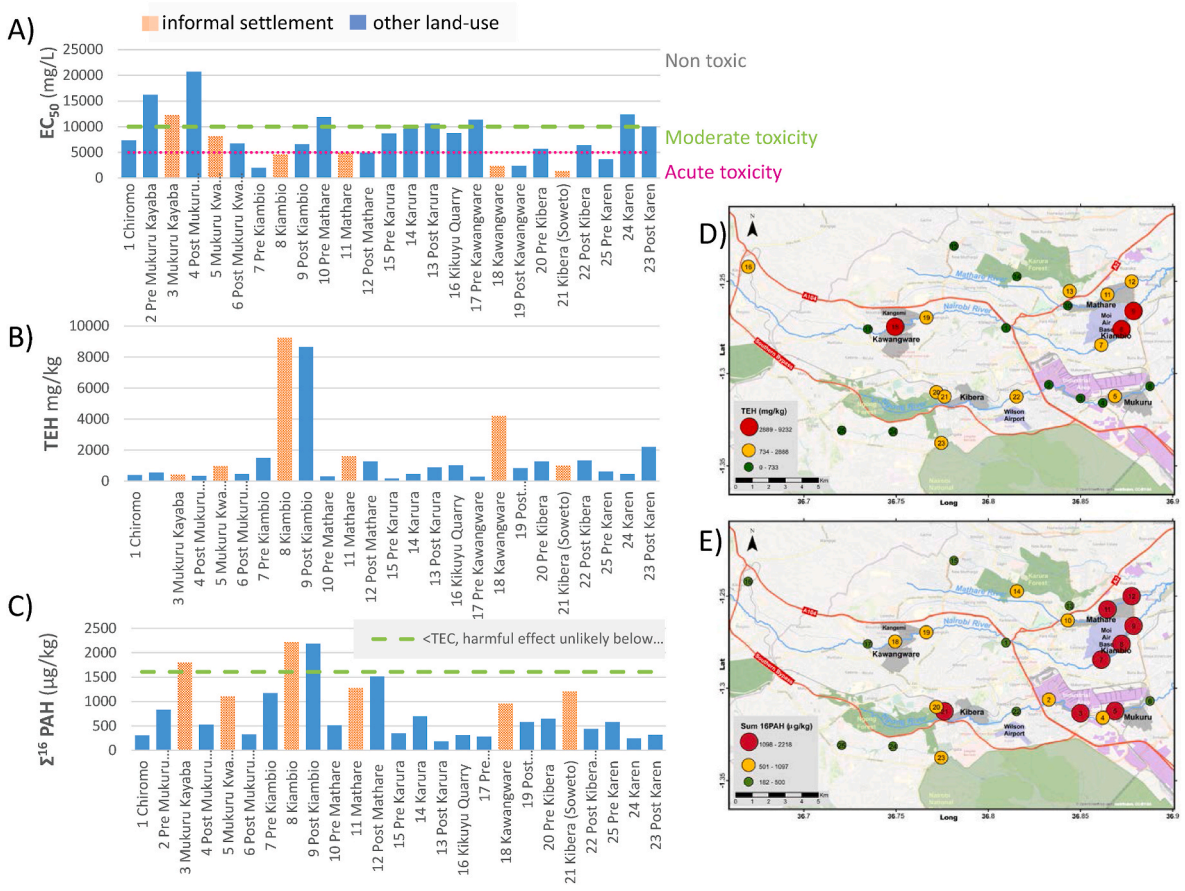

Fig. 2. Comparison of toxicity and hydrocarbon pollution in sediments of Nairobi, Kenya: A) Microtox bioassay solid phase test EC_{50}; B) Total extractable hydrocarbons (TEH); C) Parent polyaromatic hydrocarbons (Σ^{16} PAH); D) Concentration map of TEH; E) Concentration map of PAH.

sites receiving a particular effluent source (e.g. tannery, sewage works, oil spill) or only report a few locations or employed a modified microtox SPT method (e.g. longer exposure times). Consequently, the EC_{50} reported here for Nairobi urban rivers fall between those reported for as Ganga, Kanpur city, India (2104–68860 mg/L, mean 27787 mg/L), Uberabinha, Brazil (1952–17279 mg/L), Po, Italy (470–36,800 mg/L), Lake Ontario, Canada/USA (300–756,000 mg/L), Odra River, Poland (200–300000 mg/L), River Thames, UK (6330–24,346 mg/L, mean 13,426 mg/L), Conwy, UK (5587 to >500000 mg/L), Arthur Kill waterway, New York, USA (1617–28,974 mg/L, mean 5498 mg/L) (Caixeta et al., 2022; Niemirycz et al., 2007; Vane et al., 2020a, 2020b, 2020c; Viganò et al., 2003). Nevertheless, the high frequency of sites with low EC_{50} suggests that Nairobi's urban river sediments rank amongst some of the world's most toxic based on the Microtox SPT bioassay. Given the lack of sewage treatment, limited waste disposal infrastructure (within informal settlements) and generally moderate flow volume this river-toxicity ranking is understandable.

Total coliform counts are widely used in concert with other measurements to assess water quality, however, its utility as an indicator of sediment quality is less certain as it relies upon the survival of viable bacteria, which extend over a few weeks but not years or decades (Perkins et al., 2014; Stentström and Carlander, 2001; Vane et al., 2010). In this current study, the highest CFU were from Kiambio settlement (33 CFU g), Mathare settlement (17–56 g), Kibera settlement (17 g) as well as Chiromo (18 CFUg) with all other sites having very low CFU of 0–9 g. When taken together the higher number of presumptive total coliform counts appear to broadly agree with microtox EC_{50} assessment in that sediments from Mathare, Kiambio and Kibera settlements are suggested to be of greater toxicity together with elevated total coliform counts. In contrast, sediment from Chiromo were of moderate toxicity but gave slightly elevated total CFU, whereas those from Kawangware had low EC_{50} (acute toxic) but low CFU.

3.2. Total carbon, pyrolysis and total petroleum hydrocarbons

Total organic carbon content varied greatly between sites, ranging from 0.49 to 14.8%, mean 3.70% and median 2.11%. Sediments from within Kiambio (14.8%), Mathare (6.9%), Kawangware (7.9%) and Kibera (9.3%) informal settlements were higher (*t*-test $P < 0.05$) than their non-settlement counterparts which ranged from 0.5 to 2% (Supplementary 3.1). The most plausible explanation for this difference between informal settlement and non-informal settlement site TOC being elevated is the incorporation of organic waste (domestic refuse and or sewage) in the slums' river network.

Rock-Eval pyrolysis is an established technique for the assessment of free and structurally bound organic matter (OM) in source rocks during oil and gas exploration (Espitalié and Joubert, 1987; Tyson, 1995; Waters et al., 2019). Estimates of the amount of hydrogen (HI) and oxygen (OI) are compared to established reference samples and or published criteria to infer OM (kerogen)-type (Emmings et al., 2017; Hennissen et al., 2017; Slowakiewicz et al., 2015). Similarly, recent environmental studies have utilised variations in the profile of the bound hydrocarbons (S2), that broadly corresponds to strength and extent of intra and inter polymer bonding, to identify changes in OM that were used to understand hydrological-climate effects on peatland carbon, variable OM preservation in soils and historical oil spills in urban waterway sediments (Cooper et al., 2021; Girkin et al., 2018; Newell et al., 2016; Sebag et al., 2016; Thomas et al., 2019).

Pyrograms from Nairobi's informal settlement river sediments (Kibera, Mathare, Kiambio) presented bimodal profiles with greater S2a

(TpkS2 333–338 °C) relative to S2b peaks, which confirmed two distinct pools (types) of organic matter, including one of low thermal stability (Fig. 3). In contrast, river sediments adjacent to other land uses residential/parkland/quarry/university gave a single pronounced S2b peak (TpkS2 400–454 °C) confirming organic matter of higher thermal stability; most likely a mix of natural biopolymers such as cellulose, lignin and tannins (Fig. 3). Sediment from Kawangware gave an intermediate profile with a pronounced S2a shoulder but of lower intensity S2b peak whereas Mukuru Kwa Njenga was unimodal (Fig. 3). The most plausible explanation for the different pyrograms is that sediments from Kibera, Mathare, Kiambio and to a lesser extent Kawangware contain both lipid rich organic matter such as sewage and decomposed domestic refuse as compared to the more thermally stable natural carbon geo-biopolymers present in sediments under other land-uses (Fig. 2).

Extractable hydrocarbon (TEH) pollutants were detected in every surface sediment (100%) of Nairobi's urban rivers at concentrations that ranged from 171 to 9232 mg/kg, a mean of 1613 mg/kg and a median of 874 mg/kg (Fig. 2). The highest TEH pollution was at Kiambio settlement 8643–9322 mg/kg followed by that from the middle of Kawangware settlement 4196 mg/kg and surprisingly, a site just downstream of the residential area, Karen 2206 mg/kg. Sediment quality assessments using (TLC-FID, Iatroscan) TEH determinations report concentrations of <260–500 mg/kg as background carbon input (e.g. contribution from natural organic matter), whereas concentrations >500 mg/kg infer hydrocarbon input from diffuse anthropogenic sources (Kim et al., 2018; Vane et al., 2019a; Volkman et al., 1992). In contrast, sediments receiving direct point-source petroleum industry inputs from crude oil spills or end of pipe industrial/municipal discharges, typically report TEH >1000 mg/kg (Napolitano et al., 1998; Vane et al., 2020b). We therefore used literature based TEH criteria <500 mg/kg, 500–1000 mg/kg and >1000 mg/kg to define hydrocarbon pollution such that 9 Nairobi river sediments were below the <500 mg/kg criterion suggesting little to no TEH pollution, 6 sediments were within the >500 mg/kg to <1000 mg range indicating moderate TEH pollution and 10 sediments exceeded 1000 mg/kg threshold suggesting appreciable TEH pollution (Fig. 2).

Saturated and aromatic hydrocarbons showed a strong correlation to TOC content (R^2 0.75 and 0.73) as did the resin + biogenic lipid fraction (R^2 0.84) (Supplementary 3.2). This clear positive association of TEH (saturate + aromatic, saturate, aromatic and resins) to TOC is probably due to sorption of anthropogenic petroleum hydrocarbons to natural organic matter coatings of fine inorganic particles and/or active surfaces on anthropogenic soot particles (Hedges and Keil, 1999; Lohmann et al., 2005; Pignatello and Xing, 1996). Similarly strong positive TEH to TOC correlations are reported in urbanised river-estuary bed sediments accumulating mixtures of both natural particulate carbon and hydrocarbon pollution (Vane et al., 2011, 2019a). Conversely, this relationship maybe masked in river bank sediments supporting high amounts of vegetation biomass-decomposing plant roots which increase TOC content or in sediments with low TEH (Vane et al., 2009, 2020b).

Previous reports of hydrocarbons in African river sediments reveal a range of values due to factors such as catchment size, land-use, mineral-sediment dilution, seasonal flooding effects, degree of urban-industrialisation and extent of waste treatment as well as other factors such as proximity to oil processing refineries waste pipes. For example, sediments from the relatively unpolluted Buffalo River (South Africa) varied from 12.59 to 1100 mg/kg mean 209.81 ± 63.82 mg/kg whereas very high values of 25,300 to 45,800 mg/kg, mean 41,900 mg/kg were reported in Benin River (Nigeria) due to direct receipt of effluent from a local lubricating oil factory (Adeniji et al., 2017; Akporido and Ipeaiyeda, 2014; Ashiru and Ogundare, 2019). On an international basis, the TEH concentrations encountered here in Nairobi's waterways are comparable with urban tributaries of the River Clyde, Scotland (UK) 72 to 37,879 mg/kg, mean 2779 mg/kg and contaminated sediments from creeks of Staten Island, New York (USA) 2500–9586 mg/kg (Vane et al., 2019a, 2020b). Therefore, Nairobi's urban river sediment TEH concentrations presented herein are high but rank lower than those that receive contaminated waters/fluids/oils from hydrocarbon refining.

3.3. Polycyclic aromatic hydrocarbons (PAH)

Polycyclic aromatic hydrocarbons are amongst the most commonly

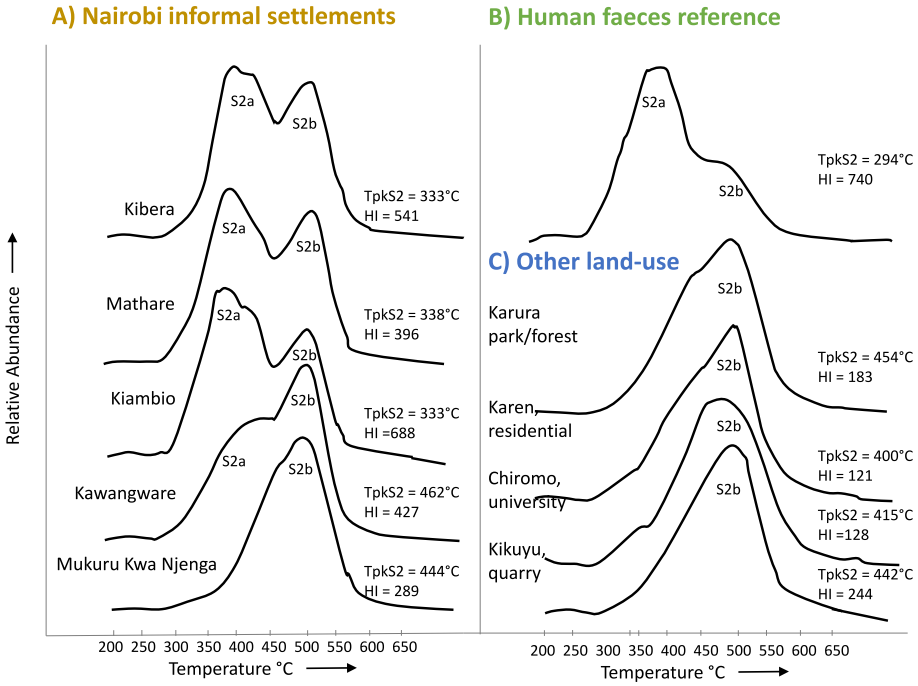

Fig. 3. Rock-Eval pyrograms of Nairobi river sediments. Contrasting bound organic matter types: A) bimodal distribution interpreted to indicate a mixture of organic matter from sewage and/or domestic refuse (high hydrogen index and low TpkS2); B) Fresh human faeces; C) Unimodal distribution interpreted to suggest contribution from natural carbon inputs (low hydrogen index and high TpkS2).

occurring organic pollutants in urban soils and river sediments (Azzolina et al., 2016; Vane et al., 2019a, 2021; Wilcke, 2007). Their presence within the urban domain is primarily associated with road-run-off, oil, diesel particulates, wood, coal and charcoal burning, waste incineration and many other industrial/manufacturing combustion sources (Kim et al., 2019). Concern over their occurrence in soils and sediments stems from a variety of human health effects including diminished respiratory health, cancer, birth defects and DNA mutations in humans as well as similar negative impacts on ecology (Cave et al., 2015; Gale et al., 2012; Hu et al., 2007; Łukawska-Matuszewska et al., 2009). Understanding the existing levels of PAH in sediments in Nairobi supports monitoring of the efforts to strengthen management of chemicals throughout their life cycle (SDG 12.4) and associated improvements to health through reduced soil pollution (SDG 3.9).

In this current study, PAH were detected at all collection sites, Σ^{16} PAH ranged from 182 to 2218 μg/kg, mean 822 and median of 581 μg/kg and the Σ^{56} PAH ranged from 359 to 7928 μg/kg, mean 2290 and median of 1673 μg/kg (Figs. 2 and 3). Sediments from the Nairobi river within the Kiambio settlement had the highest PAH concentrations (Σ^{16} PAH 2188, 2188, 1176 μg/kg; Σ^{56} PAH 7928, 6887, 3283 μg/kg), the other informal settlements had similarly elevated concentrations compared to their upstream and downstream equivalents. Based on Σ^{16} PAH the settlements ranked Kiambio > Mathare > Kibera > Mukuru > Kawangware whereas based on the broader suit of parent and alkylated PAH (Σ^{56}) ranked in the order of Kiambio > Mathare > Kibera > Kawangware > Mukuru. In contrast the sites with the lowest PAH concentrations (Σ^{16} PAH 182 to 310 and Σ^{56} PAH 359–896 μg/kg) were Karura, Karen, Chiromo and Kikuyu Quarry which is commensurate with low-PAH generating park-forest, university-riverside and quarry land-uses. It should also be borne in mind that the variations in PAH and other contaminant groups presented herein may also be explained in part by local variations in sedimentation and deposition.

Comparison with PAH concentrations from other international rivers traversing urban centres (e.g. Seine, France (n = 37, range 450–5650, mean 2510 μg/kg) Elbe, Germany (n = 9, range 200–906,000, mean 605 μg/kg), River Clyde, Scotland, (n = 68, range 600 to 4,225,614, mean 97,600 μg/kg) Delaware, USA (n = 20, range 3749 to 22,324, mean 6967 μg/kg, Shanghai, China (n = 47, 248 to 36,198, mean 3327 μg/kg)) suggested that Nairobi's urban waterway sediments have comparatively moderate $\Sigma^{14\text{-}16}$ PAH contamination levels (Kim et al., 2018; Liu et al., 2016; Otte et al., 2013; Vane et al., 2019a; Zhao et al., 2017). However, even the lower PAH concentrations (180–310 μg/kg) at Karura, Karen, Pre-Kawangware, Chiromo and Kikuyu Quarry were not pristine when compared to sediments from natural/rural catchments (e.g. River Congo, Democratic Republic of Congo (35–64 μg/kg) (Mwanamoki et al., 2014).

Inspection of the PAH to TOC bi-plot suggested two relationships; firstly, a fairly strong association for all Σ^{16} PAH (R^2 0.63) and Σ^{56} PAH at low concentrations of 600–2000 μg/kg and at the very highest concentrations at 6887 and 7928 μg/kg^{-1} (n = 2) (R^2 0.75), secondly no clear correlation for Σ^{56} PAH at middle ranking concentrations of about 3000–4000 μg kg (n = 7) (Supplementary 3.2). The loss of association for Σ^{56} PAH between 3000 and 4000 μg/kg is probably linked to a change in PAH source or possibly change in OM that coats mineral grains and sorbs PAH or both. Conversely, both Σ^{16} and Σ^{56} PAH were weakly correlated to the fine sediment fraction (clay and silt) (R^2 0.064, 0.001) (Supplementary 3.2). The decoupling between physico-chemical co-factors suggests that the usual organic-mineral sorption concept (e.g. contaminant to humic coatings on clay/silt mineral) surfaces isn't dominant as this yields strong correlations for both TOC and clay/silt (Hedges and Keil, 1999; Vane et al., 2020a). One possible explanation is that the PAH are sorbing to the faecal matter/sewage in the sediments, however, this idea is only partly supported by the PAH to coprostanol R^2 of 0.3.

The source(s) of PAH in Nairobi's urban river sediments were inferred using isomeric and non-isomeric PAH ratio plots and distribution of parent and alkylated PAH. The first approach arises from the principal that one isomer has greater thermal stability and can therefore indicate high temperature combustion (pyrolytic synthesis) as compared to low-temperature petrogenic (unburnt fossil fuels) input (Boehm et al., 2018; Tobiszewski and Namiesnik, 2012). The second approach is based upon the premise that PAH formed slowly at low temperatures yield higher amounts of alkylated relative to parent PAH (e.g. crude oil, coal) whereas rapid high temperature formation yields higher amounts of parent relative to alkyl-substituted PAH (e.g. traffic exhaust/charcoal-wood burning soot/thermal power stations)(Hindersmann et al., 2020; Vane et al., 2021). Application of fluoranthene/pyrene to phenanthrene/anthracene bi-plot to Nairobi's urban rivers sediments provided inconclusive evidence of PAH source as few of the samples clearly plotted within the assigned regions/criteria (Fig. 4). Conversely, inspection of the more nuanced, benz[*a*]anthracene to chrysene, benz[*a*]anthracene to benzo[*a*]pyrene and chrysene to benz[*a*]anthracene bi-plots indicated mainly petroleum combustion and some petroleum PAH sources as well as a few sites with ratios indicative of grass wood/wood coal combustion (Fig. 4). Evaluation of sediments from along the Ngong river (Mukuru slum reaches) suggested that pre and mid-Mukuru Kayaba settlement PAH were mainly from wood, coal combustion inputs whereas those closer to the more industrialised mid-post Mukuru Kwa Njenga settlement were from (non-combusted) petroleum sources (refined oil/petrol) (Fig. 4). The multiple inputs of PAH in Mukuru sediments may also be attributed to its close proximity to major roads (e.g. Lunga Lunga Rd) and Makadara Railway station which would deliver soot-diesel particulates as well as some petroleum PAH (e.g. leaking engine oil). Overall, the majority of mid-slum PAH (Kibera, Mathare, Kawangware, Kiambio) all indicate to a lesser or greater extent incorporation of multiple petroleum combustion sources (Fig. 4).

The concentration profile of parent to alkyl-substituted PAH in combination ratios provide a complementary approach to PAH bi-plot assignment of anthropogenic PAH inputs in urban soils and associated river-estuarine sediments (Supplementary 3.3) (Boehm et al., 2018; Hindersmann et al., 2020; Vane et al., 2021). Previous studies report that non-weathered petroleum PAH sources (crude oil) give a dome shaped profile (C0 minima to C2 maxima to C4 minima) whereas un-weathered combustion PAH sources present a sloped profile (C0 maxima to C4 minima) (Boehm et al., 2018). Measurement of PAH in German urban soils mixed in the laboratory with bituminous coal (petrogenic source) and a tar inputs (pyrogenic source) showed that a third V-shaped distribution pattern is observed in fluoranthene + pyrene (C0–C4) between 40:60 to 94:5% and that this distribution pattern is also found for summed ΣC0 and ΣC2 alkylated PAH with maximal decrease occurring for C1 PAH. In this current study, inspection of the PAH assemblages for Karura forest, the urban control and Kibera settlement gave sloped distribution for naphthalenes suggesting combustion sources, whereas phenanthrene, fluoranthene + pyrene and chrysene reveal a "V" shaped distribution indicating mixed combustion and petroleum sources (Supplementary 3.3). However, sediment from Mukuru Kwa Njenga, Kawangware and Kiambio informal settlements exhibited a variety of PAH profiles including, inverse slopes (e.g. Ph0+An0 to Ph3+An0) or non-systematic changes (e.g. F0+P0 to F3+P3) which are probably best interpreted as indicating multiple combustion inputs augmented by petroleum or variable weathering processes. Overall, we consider it imprudent to attempt more detailed source apportionment without appropriate end-member samples that have been subject to local alteration weathering effects.

The ecological significance of sedimentary PAH concentrations are usually interpreted within the frame-work of established sediment quality guidelines (SQG) (Apitz et al., 2007; Simpson et al., 2013; Vane et al., 2020b). Numerous sets of SQG informed by compilation of empirical-statistical relationships between contaminant and toxic response on benthic organisms for individual or total PAH have been developed to predict possible causal effects on sediment ecology

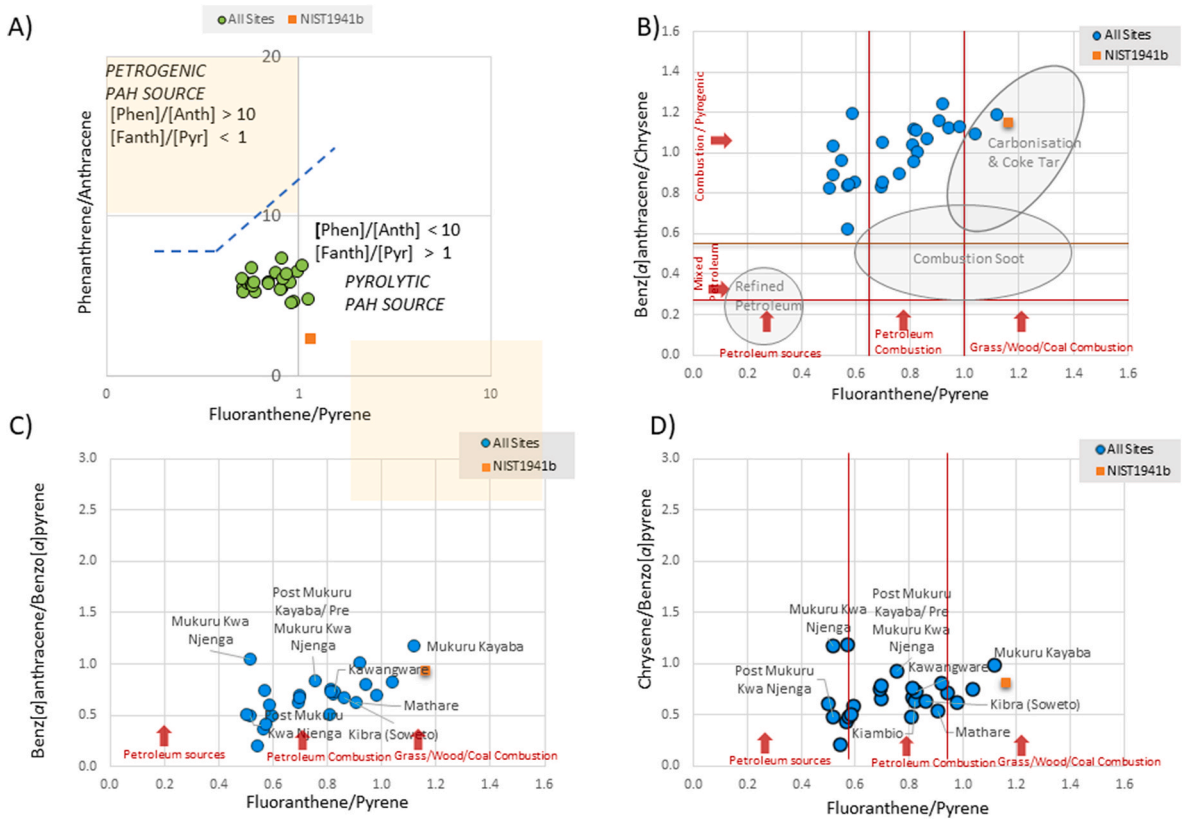

Fig. 4. Polycyclic aromatic hydrocarbon (PAH) source apportionment ratio bi-plots (A–D).

(DelValls et al., 2004; Long et al., 1995; MacDonald et al., 2000b; Swartz, 1999). One of the advantages of this approach is that it facilitates rapid comparison and categorisation; identifying sites of potential concern. However, it should be considered that the majority of SQG are underpinned by sediment-biota-toxicity data-sets from waterways in USA, Europe or Australia and New Zealand rather than those here in Kenya, East Africa (de Deckerem et al., 2011; MacDonald et al., 2000b). Nevertheless, given the commonality of many simple sediment dwelling biota and the need for a broad evaluation of sedimentary PAH concentrations such an approach seemed warranted.

Consensus based SQG provide a threshold effect concentration (TEC) below which harmful effects are unlikely and a probable effect concentrations (PEC) above which harmful effects are likely (Long et al., 1995; MacDonald et al., 2000b). Comparison of Nairobi's urban river concentration data to established USA freshwater sediment SQG are presented in Fig. 2. This confirmed that 16 sites spanning pre-settlement sites and non-settlement locations Karura, Karen, Chiromo, and Kikuyu Quarry were unlikely to cause harm to sensitive sediment dwelling biota. In contrast, all other sites namely those associated with settlements (Kibera, Mukuru, Mathare, Kiambio) gave values between TEC and PEC (Fig. 2). Interpreting sediment PAH concentrations between TEC and PEC is challenging because neither are exact ecotoxicological endpoints. However, it has been shown more generally that biota-toxicity rises with increasing chemical concentration. Therefore, the intermediate values presented here could be taken to infer that the individual PAH compounds could have a limited negative effect on sediment biota. On the other hand, it may also be argued that the values are less likely to cause harm because the majority of degree of exceedance above TEC is small.

3.4. Faecal sewage compounds

Before proceeding with a characterisation of Nairobi's urban river faecal steroid (lipid) chemistry it is worthwhile considering that the organic fraction of human faeces constitutes 84–93% by dry weight and is comprised of 25–54% bacterial biomasss, 2–25% protein, 25% carbohydrate and 2–15% lipids as well as other components as well as a range of bacteria and viral pathogens (Rose et al., 2015). Within the lipid fraction faecal sterols follow known transformation pathways enabling distinction between organic matter that has passed through the human and herbivore gut as well as microbial reworking and anthropogenic sewage treatment in waters, soils and or sediments (Bull et al., 2002; Leeming et al., 1996; Vane et al., 2010, 2022b).

In this current study, sediment concentrations of total faecal sterols and stanols (Σ^{16} sterols) ranged from 0.18 to 560 μg/g and individually ranked in the order coprostanol > ethylcoprostanol > cholesterol > epicoprostanol> β-sitosterol > stigmastanol > cholestenol > stigmasterol (Fig. 5). Minor but quantifiable concentrations of ethyl-epicoprostanol, camperstanol, fucosterol, brassicasterol, epicholestanol and cholestane were also observed. For eighteen sites coprostanol constituted 32–59.0% of the Σ^{16} sterols which confirmed faecal matter from humans or possibly humans and other omnivore/carnivores (Fig. 3). The lower concentrations of plant sterols and stanols such as β-sitosterol and stigmastanol could be from herbivore animal faeces as the latter compound is produced during intestinal microbial reduction of the plant derived marker sitosterol (Grimalt et al., 1990b). However, minor amounts of β-sitosterol and stigmastanol were observed in the human reference faeces sample (Supplementary 3.4) a finding that has also been reported in faeces from archaeological sites (Bull et al., 2003; Harrault et al., 2019). Given the high human population densities of the adjacent informal settlements and comparatively low herbivore animal populations of urban Nairobi we speculate that the minor amount of β-sitosterol and stigmastanol and other plant related sterols and stanols are from human excrement, although the possibility of minor contribution from domestic animal or even wild animal dung sources cannot be entirely ruled out (Correa and Grace, 2014; Kemp et al., 2021).

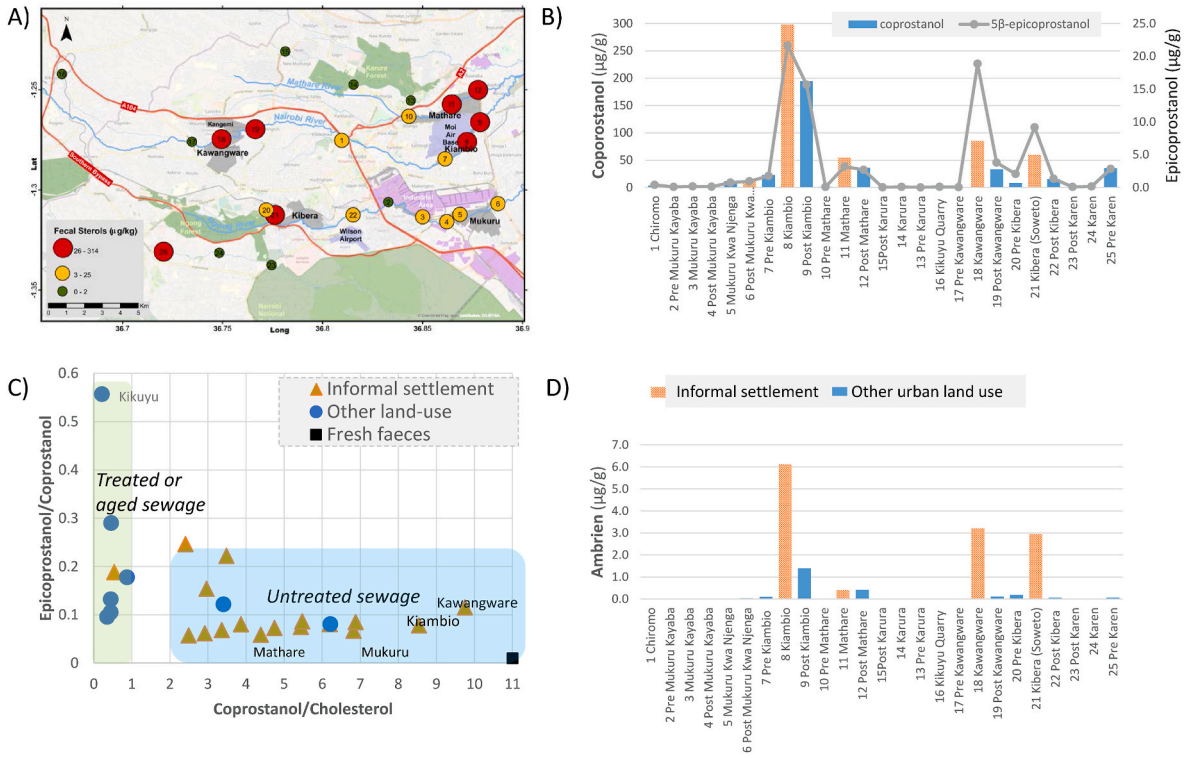

Fig. 5. Molecular faecal marker compounds and source ratios: A) Map of faecal sterol concentrations; B) Comparison of coprostanol and epicoprostanol in informal settlements and other land use domains; C) Faecal sterol sewage treatment bi-plot; D) Ambrein concentrations. Box and whisker plot of individual faecal sterols presented in supplementary 3.4.

Coprostanol, is an established marker compound found in human faeces. Nairobi's waterway sediments (Ngong, Mathare and Nairobi rivers) coprostanol concentration ranged from 0.015 to 298 µg/g, mean 35 µg/g, median 8 µg/g whereas a control sample of human faeces was 1851 µg/g (Fig. 5). Taken together and not withstanding variations caused by human age/diet/health, preferential decay of other constituents as well as inorganic mineral dilution, these concentrations suggested that Kiambio slum (Nairobi River) sediments were comprised of approximately 10 and 16% faecal matter and that from Kawangware and Kibera slum 5 and 3% whereas the others were far lower 0.1–2%. Sedimentary coprostanol values of >0.1 µg/g are considered as moderately contaminated whereas values > 0.5 µg/g are used to infer significant sewage pollution to aquatic sediments (González-Oreja and Saiz-Salinas, 1998; Hatcher and McGillivary, 1979). Using these rather conservative criteria, 22 of 25 sites were contaminated with faecal matter with only Karura (Karura River), Kikuyu Quarry and pre-Kawangware being below the faecal boundary value.

A systematic rise and partial decrease in coprostanol from pre-mid-post slum for Kiambio (22.7, 298, 195 µg/g), Mathare (1.5, 55, 36 µg/g) and Kawangware (0.27, 85, 33 µg/g) was shown confirming faecal input from mid portions of the slums and possible transfer of particulate faecal matter downstream. However, the transport and deposition must be localised as a systematic increase in coprostanol concentration that would indicate a stepwise accumulation of faecal matter along the Ngong river which first traverses Kibera slum and then Mukuru slum was not observed. Comparison of Nairobi waterways coprostanol concentrations to sediments from other rivers (Daube, Serbia (n = 11, 0.002–1.9 µg/g, mean 0.97 µg/g), Bilbao and Plentiza River estuaries, Spain (n = 10, 2.2 to 137.7, mean 54.7), Erewash River, UK (n = 54, 0.01–2.2 µg/g), Nhundiquara river, Brazil, (n = 11, 0.02 to 0.19, mean 0.06 µg/g), Barigui river, Brazil (n = 6, 0.25–196 µg/g, mean 44.2 n = 6), Malaysia and Vietnam 0.005–15.5 µg/g, mean 0.38, 0.17 µg/g, n = 10 and 25), New York coast (n = 10, 0.08 to 5.2, mean 2.0 µg/g) confirmed that Nairobi's urban rivers are amongst the most polluted in the world (Carreira et al., 2002; González-Oreja and Saiz-Salinas, 1998; Hatcher and McGillivary, 1979; Isobe et al., 2002; Matić Bujagić et al., 2016b; Vane et al., 2010). The high coprostanol concentration in Ngong, Nairobi and Mathare rivers cannot be wholly attributed to transfer of faecal matter from the informal settlements (slums) because many of the sites are situated away from the slums on stretches of the river(s) that traverse residential, park and industrial land-uses. An alternative explanation is that Nairobi's sewer network only connects about 28% of the cities buildings to the two main sewage treatment plants (STP) at Ruai and Kariobangi which have a capacity of 160,000 m^3 32,000 m^3 respectively. Therefore, the widespread presence of human sourced faecal pollution (inferred from coprostanol) at sites away from the informal settlements (slum) sediments may be attributed to transfer from local sanitation solutions (soak pits/sceptic tanks/latrines) and limited extent of the municipal sanitation network and STP. Implementation of SDG targets 6.2 and 6.3, ensuring adequate sanitation facilities for all and reducing the amount of untreated wastewater is needed to reduce faecal contamination and address cascading effects on public health.

The extent of sewage contamination as well as degree of treatment and or age can be inferred from a combination of coprostanol/cholesterol and epicoprostanol/coprostanol and comparison with associated end-member values (Grimalt and Albaiges, 1990; Grimalt et al., 1990a; Mudge et al., 1999; Vane et al., 2010). The coprostanol to cholesterol ratio tracks human to background sources (plant/herbivore/other) and epicoprostanol to coprostanol tracks the degree of anaerobic bacterial alteration of coprostanol which can occur either during anaerobic sewage treated or prolonged environmental exposure to anaerobic bacteria (Leeming et al., 1996). Inspection of the Nairobi rivers sediment bi-plot suggested that Karura, Kikuyu Quarry and Kawangware (pre--settlement) as well as Karen (post and mid) did not contain much fresh sewage or that it was old or had undergone though anaerobic treatment (Fig. 5). In contrast, sediments from Mukuru Kwa Njenga (mid and post settlement), Kiambio (mid and post settlement), Kawangware gave

coprostanol/cholesterol values of 3–10; similarly, a reference faecal samples yielded coprostanol/cholesterol of 11 and an epi-coprostanol/coprostanol of 0.01 confirming the presence of significant amounts of untreated raw sewage across multiple settlements and elsewhere within Nairobi (Fig. 5).

A variety of other coprostanol based faecal marker ratios have been used to infer sewage input and overcome physico-chemical partitioning effects that sometimes confound direct comparisons using chemical concentrations alone (Bull et al., 2002; Carreira et al., 2002; Grimalt et al., 1990b; Matić Bujagić et al., 2016a; Mudge and Duce, 2005; Readman et al., 2005; Vane et al., 2010). Evaluation using four key ratios, namely, coprostanol/coprostanol + cholesterol (Ratio 1), coprostanol + epicoprostanol/coprostanol + epicoprostanol + cholestenol (Ratio 2), coprostanol/cholesterol (Ratio 3) and coprostanol/coprostanol + cholestanol (Ratio 4) as well as associated faecal input benchmarks all suggested appreciable faecal waste input particularly at Kiambio, Mathare, Kawangware and Kibera settlements and other sites except Karura and Kikuyu Quarry (Supplementary 3.4).

Although faecal sterol/stanols are the most widely applied molecular tracer of sewage other compounds can provide useful complementary evidence. For example, ambrein, the triterpene alcohol formed from the bacterial metabolism of squalene, has recently been reported in the faeces of a variety of land mammals including humans (Rowland et al., 2020). This occurrence together with its apparent survival in marine settings in coproliths (>1000 yrs) suggested it may have use as a chemical marker for faecal matter (Rowland et al., 2020). Nairobi's urban river sediments contained ambrein at 0.001–6.1 μg/g with mean of 0.60 and median of 0.021 μg/g (Fig. 3). Sediments from Kiambio (mid-informal settlement (slum)), Kawangware (mid-informal settlement (slum)) and Kibera (mid-informal settlement (slum)) as well as Kiambio (post-slum) and Mathare (mid and post-slum) had 4 to 60 times more ambrein than the other sites. In addition, ambrein showed a good correspondence to the established faecal compound coprostanol (R^2 0.75) suggesting that ambrein may, like coprostanol, be used to track faecal input in sediments (Fig. 3). The strong but still imperfect correlation with coprostanol is probably best explained by differences in environmental microbial degradation or possibly different partitioning characteristics of the faecal marker compounds. In contrast, both coprostanol and ambrein showed a weak positive correlation to bacterial counts (R^2 0.2) (Supplementary 3.4). This weak correspondence highlights a consistent problem with the use of bacterial enumeration techniques to trace faecal matter, in that different microbes not only have variable survival rates but also have differential rates of decay (Rees, 1993; Vane et al., 2010). On balance, the good agreement between faecal stanols and ambrein support their utility as a sewage tracer in sediments and soils as compared to bacterial enumeration methods.

3.5. Pharmaceuticals

The environmental fate of pharmaceuticals and hormones has been extensively investigated over the past 20 years owing to increasing use and prevalence in urban waste waters and associated health risks such as estrogenic effects and association to increasing antimicrobial resistance (AMR) in bacteria that can harm human health (Langston et al., 2005; Richardson, 2007). However, to the best of our knowledge only a few studies of pharmaceuticals in Kenyan rivers are available and these focus on waters (Bagnis et al., 2020; K'oreje et al., 2012; Kairigo et al., 2020; Kimosop et al., 2016; Ngumba et al., 2016; Segura et al., 2015) with only two studies (Kairigo et al., 2020; Kimosop et al., 2016) reporting selected antibiotic concentrations in river sediments. Therefore, the present survey is particularly important as it provides a broader baseline inventory of pharmaceuticals from which future regulatory criteria maybe drawn in line with the ambitions of SDG target 3.9 (reduce the number of illnesses from hazardous chemicals and soil pollution and contamination).

Total pharmaceutical concentrations ranged from 0.2 ng/g in the post-Karura sediment to 239.4 ng/g in Mathare mid-slum (Fig. 6, Supplementary 3.5). The anti-epileptic carbamazepine and its metabolite epoxicarbamazepine as well as the anti-inflammatory diclofenac were the only pharmaceuticals found with a frequency of detection of 100% (Supplementary 3.5). Concentrations of carbamazepine ranged from 0.1 to 43 ng/g epoxicarbamazepine from 0.1 to 2 ng/g and diclofenac from 3 ng/g to 18 ng/g. The hormone estrone, the b-blocker atenolol and the analgesic acetaminophen all showed a high frequency of detection 92%, 68% and 64% with maxima of 17, 78 and 89 ng/g respectively. Ibuprofen, the popular anti-inflammatory drug ranged from 7 to 27 ng/g whereas antibitoics clarithromycin and azithromycin were measured at 1 ng/g.

Salbutamol a drug used to treat asthma, ifosfamide and cyclophosphamide used for cancer treatment and the hormone estradiol had a frequency of detection <10% with maximal concentrations of 1.5, 1, 0.6 and 8 ng/g respectively. Other pharmaceuticals analysed were not considered to be present in the sediments as they were below LOD. Although different watch lists of priority pharmaceutical contaminants have been issued by the European Union (Water Framework Directive) and the United States Environmental Protection Agency (USEPA) no sediment quality guidelines (SQG) have been developed to predict possible effects of pharmaceuticals on the sediment ecology. Consequently, in contrast to many of the other traditional contaminants (TEH, PAH, PCB, DDT, trace metals) a further evaluation of risk posed by pharmaceuticals was not possible.

Based on the concentration and distribution of pharmaceuticals in the slum's sediments the 5 most polluted slum areas are Mathare > Kiambio > Kibera > Mukuru kayaba > Kawangware (Fig. 6). The high pollution levels at Mathare is expected because it is one of the closest slums to the city centre with a population of over 200,000 people. Kiambio and Kibera followed with high concentrations of anti-analgesics/anti-inflammatories supporting the notion that distance from the city centre is an important factor on the distribution of pharmaceuticals in the slum sediments. Kibera is also one of the largest slums in Nairobi with an estimated population of nearly 200,000. Karura and Karen are the least polluted areas, located further away from Nairobi city centre. Distance of the slum areas to the city centre/central business district defines job accessibility and living conditions (Nakamura and Avner, 2021). Therefore, it's plausible that this affects pharmaceuticals affordability and accessibility in the different areas. Sediment from Chiromo and Kikuyu Quarry also yielded low concentrations of pharmaceuticals. In general, most of the locations with higher pharmaceutical concentrations were from mid-slum sites followed by post and pre-slum locations. This distribution supports the increased population density and poorer provision of sanitation that exist in the informal settlements (slums).

The analgesics/anti-inflammatories (acetaminophen, diclofenac, ibuprofen) are the dominant pharmaceutical group in the Nairobi urban river sediments. This result agrees with the general finding that diclofenac, ibuprofen and acetaminophen are some of the most common analgesics/anti-inflammatory in the aquatic environment both in Africa and Europe (Fekadu et al., 2019). Similarly, the anti-epileptic carbamazepine is one of the 10 most frequently detected and quantified pharmaceutical in waters of both continents supporting the 100% frequency of detection here. Previous evaluation of Nairobi River waters that passed through Mathare and Kibera slum areas as well as the city centre also showed 100% frequency in detection of carbamazepine (Bagnis et al., 2020). Acetominophen (e.g. paracetamol/tylenol) and atenolol had >50% frequency of detection and propranolol was not present in the water samples (Bagnis et al., 2020) similar to their frequency of detection in the sediments (this study). Only clarithromycin showed a slightly higher frequency of detection in sediments (28%) than in waters (~10%) whereas caffeine showed 100% frequency of detection in waters but was not present in the sediments.

It is widely reported that hydrophobic pollutants have a strong affinity for silt and clay size fraction of sediments due in part to organo-

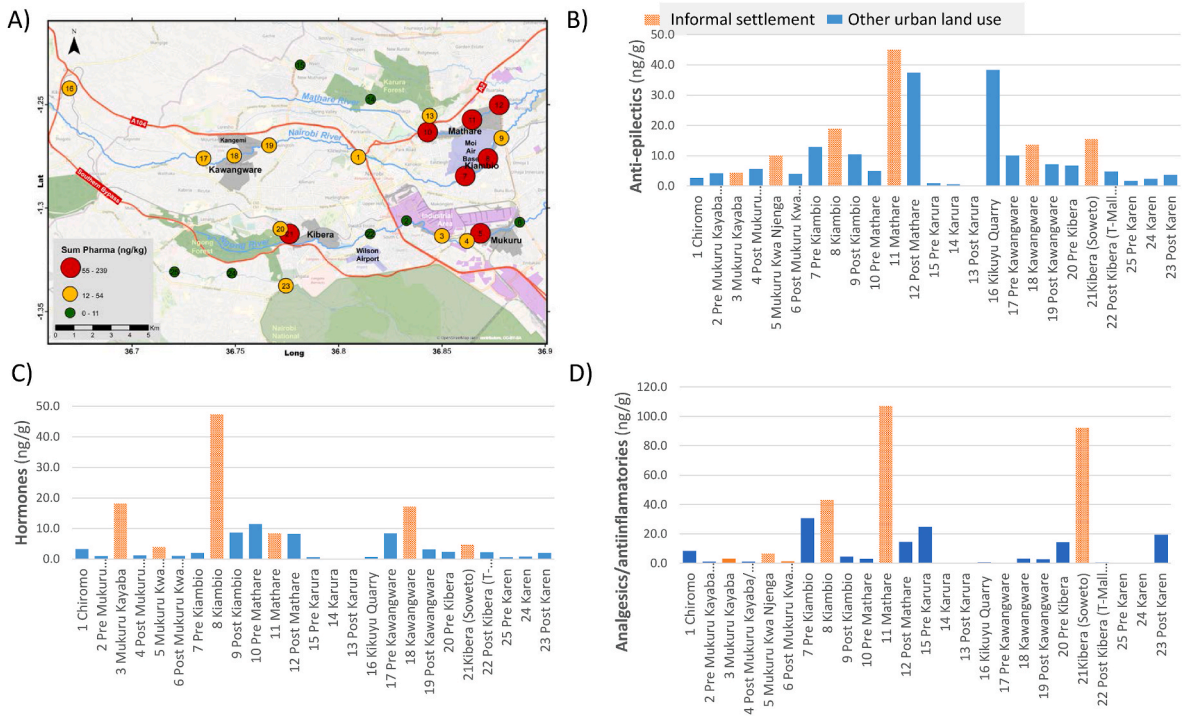

Fig. 6. Pharmaceuticals in urban river sediments of Nairobi, Kenya: A) Concentration map of pharmaceuticals; B-E) Comparison of anti-epileptics, hormones and analgesics/anti-inflammatory compounds.

functionalisation of their surfaces (Huang et al., 2003; Vane et al., 2007, 2020a). In this current study, the total pharmaceuticals to TOC association was weak (R^2 0.26) and of the various pharmaceutical groups assessed, only hormones (estriol, estrone, estradiol) showed a moderate correspondence to TOC (R^2 0.45) which together with the stronger coprostanol and ambrein to TOC (R^2 0.64 and 0.68) suggests faecal matter as possible source of hormones to the sediments whilst other pharmaceuticals may have a more direct input to the sediments. The association between pharmaceutical and Microtox EC_{50} was weak (R^2 0.13) suggesting that pharmaceuticals are not the main driver of sedimentary toxicity (Fig. 2).

Given that neither of the published studies reporting sedimentary pharmaceuticals from Kenyan sediments contained the same compounds as those reported here we compared concentrations with those from South African rivers (Agunbiade and Moodley, 2016; Matongo et al., 2015a, 2015b; Rimayi et al., 2018). Nairobi pharmaceutical concentrations are broadly comparable between Kenyan and South African rivers (Supplementary 3.5). However, the maximum concentration found in Msunduzi River sediments in South Africa were an order of magnitude higher for ibuprofen and diclofenac compared to Nairobi. This difference is probably best explained by the location of these South African sample sites as the highest ibuprofen concentration was reported to occur near the Hemley Dam (Matongo et al., 2015a) and the maximum diclofenac concentration was recorded in the biosolid separated from WWTP inlet (Agunbiade and Moodley, 2016). In contrast, the Kenyan slum sediments reported herein show slightly higher concentrations of acetaminophen and carbamazepine than South African river sediments. On an international basis, the carbamazepine maxima of 43 ng/g reported here for Nairobi urban rivers is similar to the 31 ng/g reported in River Thames and 50 ng/g in Medway, UK but higher than maxima of 11 ng/g in River Seine, France 0.12 ng/g in Llobregat River, Spain (Osorio et al., 2016; Thiebault et al., 2017; Vane et al., 2022a; Zhou and Broodbank, 2014) and the acetaminophen 90 ng/g maxima at Kibera is higher than River Seine, France, 1.22 ng/g and Llobregat River, Spain, 35 ng/g. Similarly, the anti-inflammatory ibuprofen maxima 27 ng/g, pre-Kiambio is higher than the maxima of 13 ng/g reported in sediments from River Thames, London, UK and 13 ng/g Llobregat River, Spain (Osorio et al., 2016; Vane et al., 2022a). In general, the pharmaceutical concentrations of the Nairobi slums are comparable to those in European values with mainly acetaminophen showing higher values than European sediments; which is best explained by cheaper cost and higher availability compared to other pharmaceuticals. On balance, these results however do not support previous studies that showed a much higher presence of some pharmaceuticals in waters of African countries when compared to European countries (Fekadu et al., 2019). One plausible explanation for this divergence being that controlling sedimentary processes (flocculation of particles, sorbtion to fine sediment fraction, anaerobic conditions) are more uniform in terms of chemical preservation than those encountered in the more dynamic water phase.

3.6. Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) are a class of organochlorine compounds that originate from electrical transformers, capacitor leakage, incinerators and other sources, their production and new usage were banned in 1984 under the Stockholm Convention on POPs due to their environmental persistence and ability to concentrate up trophic levels and thereby harm ecology and humans (UN-EP, 2004). In Kenya, a survey of equipment from 29 industrial and manufacturing sites across Nairobi found transformers (pre-1985) and PCB cooled capacitors suggesting some limited potential sources (Saoke, 2005).

In this current study, PCBs were observed at all 25 sites and Σ^{30} PCB ranged from 3.1 to 157.1 μg/kg, mean of 21.4 μg/kg, median of 8.6 μg/kg whereas the narrower but more commonly reported international congress of the sea suite (ICES) Σ^7 PCB ranged from 1.1 to 88.5 μg/kg, mean 11.7 μg/kg, median 11.7 μg/kg (Fig. 7, Supplementary 3.7). Three consensus-based sediment effect criteria for total PCB in sediment are: 1) Threshold effect criteria (TEC) no effect expected 40 μg/kg and; 2) Midrange effect criteria 400 μg/kg and 3) extreme effect (EEC) 1700 μg/kg are reported (MacDonald et al., 2000a, 2000b). Benchmarking against these criteria suggests that only Mukuru Kayaba, Pre-Kiambio

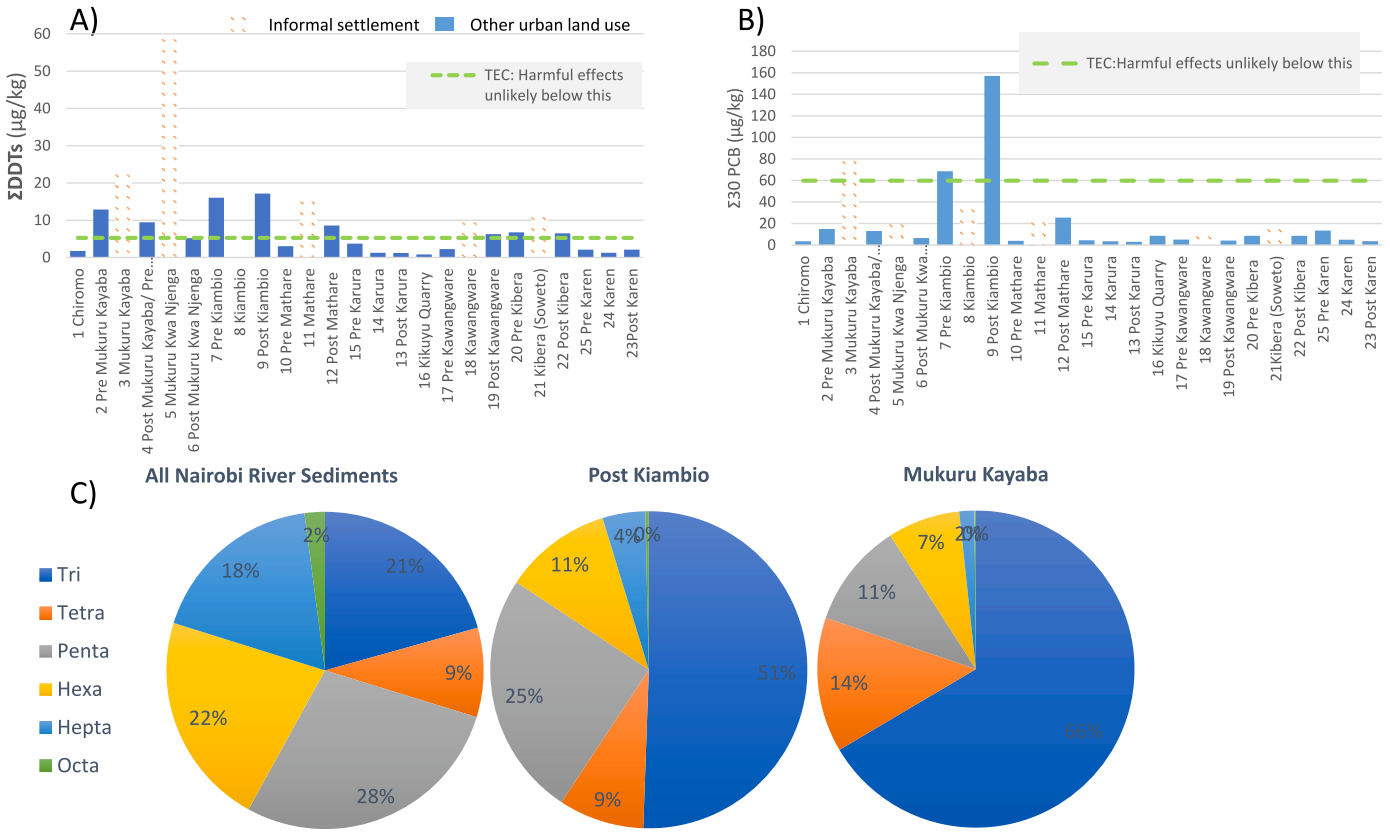

Fig. 7. Sedimentary organochlorine compounds in Nairobi urban rivers: A) PCB concentration map showing higher levels in Mathare, Kiambio and Mukuru slums; B) Bar chart of Σ30 PCB; C) Comparison of average PCB homologue groups (Tri-Octa chlorinated) to selected informal settlements; D) Dichlorodiphenyltrichloroethane and decay product (DDTs) concentration.

and post Kiambio sediments exceed TEC and no sediment contained PCBs over MEC or the higher EEC (Fig. 7). This current study therefore confirms that PCB concentrations alone are unlikely to have a strong negative effect on biota living in Nairobi's urban rivers. However, this does not necessarily mean that intermediate PCB concentrations observed in Nairobi urban river sediments can be taken to have no effect whatsoever because PCB contaminated sediments have enhanced toxicity when occurring with other common contaminants PAH (cocktail effect) (Escher et al., 2020). From a human and mammal health perspective PCBs with a planar stereochemical configuration are of the greatest interest because of their dioxin-like toxicity with toxic equivalency factors (TEF) relative to 2,3,7,8- tetracholoridobenzo-*p*-dioxin (TCDD) toxicity ranging from 0.005 to 0.1 for non-*ortho* PCBs (PCB 77, 126, 169)> 0.0005 to 0.00001 mono-ortho planar PCBs (PCB 105, 114, 118, 123, 156, 157, 167, 189)>di ortho planar PCBs (PCB 170, 180) (Safe, 1998). However, comparison of the individual concentrations from the Nairobi urban rivers revealed mainly PCB 31, 28, 118, 153 and 118 with comparatively lower amounts of the more toxic congeners (e.g. PCB 77). Evaluation of the tri-octa chlorinated groups suggests a higher degree of tri-chlorinated PCBs at post-Kiambio and Mukuru Kayaba and as compared to the other sites which could be due to local post depositional de-chlorination of the higher homologues or possibly a different source of PCB (aroclor) (Fig. 7).

At a national (Kenya) level the concentrations of PCBs presented in Fig. 7 are similar to those from recent monitoring three sites on the Nairobi River concentrations ranging from ~0.01 to 157.6 µg/kg and are slightly higher than those nine PCBs in 59 soils collected from agricultural, conservancy and suburban sites surrounding Nairobi ~0.025–55.5 µg/kg mean 8.23 µg/kg (Ndunda and Wandiga, 2020; Sun et al., 2016). On an international basis these values are at the lower end of those encountered in African, European and North American urban river sediments. For example, sediments of urban tributaries of the River Clyde (Glasgow, Scotland, UK) contain Σ^7 PCB 3–809 µg kg^{-1}, River Thames (London, England, UK) give Σ^7 PCB 10.5 to 121, mean 39.0 µg kg^{-1}, River Mersey (Liverpool, England, UK) contain Σ^7 PCB 0.13–410 µg kg^{-1} mean 30.9 µg kg^{-1} which is best explained greater industrialisation (1950s–1980s) environmental supply (air/water/particulate matrices) and enhanced incorporation due to high TOC and clay-silt particle size (Vane et al., 2007, 2019a, 2020c).

3.7. DDT insecticide

The organochlorine insecticide DDT and its metabolites were observed above the limits of detection and quantification in 25 of 24 sites. The ΣDDT (DDT, DDE, DDD) from mid-Kiambio settlement situated on the Nairobi River could not be determined due to chromatographic and mass spectral interferences from other compounds. Nevertheless, ΣDDTs ranged from 1 to 59 µg/kg (mean 21.2 µg/kg for informal settlements and 9 µg/kg for all sites) ranking in the order Mukuru Kwa Njenga (mid settlement)>Mukuru Kayaba (mid settlement)> pre and post Kiambio > Mathare (mid settlement)>pre Mukuru Kayaba > Kibera (mid settlement)>Kawangware (mid settlement) which confirmed that informal settlements had higher ΣDDT concentrations (Fig. 6). In contrast, low ΣDDT concentrations ranging from just 1–3 µg/kg were observed in river sediment sites adjacent to or within other land uses Karura (parkland), Karen (residential), Kikyu (Quarry) and Chiromo (university). The presence of DDT metabolites at low concentrations throughout Nairobi's urban river sediments is probably best explained by widespread historical usage and environmental persistence as well as some minor contemporary use in the health sector (Lalah et al., 1994; van den Berg et al., 2017).

Due to DDTs known harmful effect, environmental persistence

coupled with its widespread use as an insecticide for the protection of agriculture (1947–1985) and occasional use in malarial control a number of surveys report values generally varying from 1 to 100 μg/kg (Table 2)(Biscoe et al., 2005; Lalah et al., 1994; Olaka, 2020; van den Berg et al., 2017). Concentrations of sedimentary ΣDDT in this current study were broadly similar to those reported at three sites on the Nairobi River monitored over the dry and rainy seasons and sediments from remote alkaline Lakes of Natron and Bogoria but higher than those from sediments from Winam Gulf-Lake Victoria and Tana, Sabaki or Kuja Rivers (Table 2). Fresh, industrial technical mixtures of DDT are usually dominated by *p,p*-DDT (77% w/w) and *o,p*-DDT (15% w/w) with only minor amounts of p,p-DDD (4%), *p,p*-DDE (0.3%) whereas environmental degradation (chemical and biological decomposition) causes DDT to breakdown to more stable DDE and DDD. Therefore, recent DDT input can sometimes be inferred from ratio of *p,p*-DDT to total DDT metabolite such that a value > 0.5 indicates recent exposure and a value of <0.5 suggests incorporation of past DDT (Wasswa et al., 2011). In this current study of Nairobi's urban rivers, the *p,p*-DDT to total DDT metabolite ranged 0 to 0.64 with the majority of sediments yielding a low ratio of ~0.1 (e.g. dominated by *p,p*-DDD and *p,p*-DDE) confirming past-legacy use. In contrast sediment from Mukuru Kwa Njenga (mid settlement only) gave a value of 0.64 which possibly suggests more recent application. Although agricultural usage was banned in 1985 (Kenya) and isn't currently used directly by government ministries, a reality is that DDT is on occasion used during fumigation by private firms undertaking vector control related indoor residual spraying (IRS). Therefore, its entirely plausible that *pp*-DDT/total DDT metabolite value of 0.64 represents release, transport and accumulation of IRS DDT.

Comparison to established freshwater SQG for ΣDDT (TEC 5.28 μg/kg and PEC 572 μg/kg) revealed that none of the sites exceeded the upper criterion (PEC-harmful effect on ecology likely), 13 sites had concentrations between PEC and TEC and 11 sites were beneath the lower criterion (TEC-harmful effect unlikely) (MacDonald et al., 2000b). Interpretation of sedimentary ΣDDTs concentrations that sit between lower TEC and upper PEC consensus-based effect benchmark concentrations is challenging as qualitive descriptors are not provided. However, in the light that incidence of toxicity increases with chemical concentration and that the 13 sites with ΣDDTs at the lower end of the >TEC to < PEC banding it seems reasonable to assume the concentrations are less likely to cause less environmental harm, although an effect cannot be entirely discounted.

3.8. Trace metals and Pb isotopes

Key trace metal concentrations for ecological and human health are presented in supplementary 3.8. In summary, antimony (Sb) ranged from 0.81 to 14.1 mg/kg, mean 3.54 mg/kg, median 1.7 mg/kg, arsenic (As) 3.8–19.3 mg/kg, mean 6.2 mg/kg, median 5.2 mg/kg, cadmium (Cd) 0.3–2.9 mg/kg, mean 0.9 mg/kg, median 0.7, chromium (Cr) 18.6 to 406.6, mean 56.7 mg/kg, median 37.9 mg/kg, copper (Cu) 10.0–239 mg/kg, mean 60.5 mg/kg, median 23.0 mg/kg, lead (Pb) 40.4–201 mg/kg, 80.3 mean mg/kg, median 55.1 mg/kg, manganese (Mn) 1973–13750 mg/kg, mean 4848 mg/kg, median 3622 mg/kg, mercury (Hg) 0.1–0.3 mg/kg, nickel (Ni) 7.9–31.3 mg/kg, mean 18.0 mg/kg, median 18.5, silver (Ag) 0.13–3.06 mg/kg, mean 0.6 mg/kg, median 0.3 mg/kg, zinc 178–802 mg/kg, mean 378 mg/kg, median 314 mg/kg.

Table 2
Inventory of ΣDDTs (DDT, DDE, DDD) in East African river and lake sediments.

Country	Location	Range (μg/kg)	Mean (μg/kg)	Reference
Kenya	Ngong, Mathare, Nairobi Rivers (*n*=5)	9–58	21.2	This study
Kenya	Ngong, Mathare, Nairobi, Mokoyeti, Masongo Wai Rivers (*n*=25)	1–58	9	This study
Kenya	Nairobi River (*n*=54)	6.8–112	20.4	Ndunda et al. (2018)
Kenya	Lake Natron and Lake Bogoria (*n*=9)	5.9–30.9	14.4	Bettinetti et al. (2011)
Kenya	Lake Victoria – Winam Gulf (*n*=19)	<1.0	<1.0	Werimo et al. (2009)
Kenya	Tana and Sabaki Rivers (wet weight)	<0.036	<0.036	Lalah et al. (2003)
Kenya	Kuja River drainage basin	–	1.5	
Tanzania	Tabata, Jangwani, Salender, Kursini, Mtoni, Kizinga Rivers (*n*=24)	12–48.4	28.6	Mwevura et al. (2002)

The ecological risk significance of Sb, As, Cd, Cr, Cu, Pb, Hg, Ni and Zn concentrations were assessed using consensus-based sediment quality threshold effect concentrations (TEC) and probable effect concentrations (PEC) for trace metals which provide a benchmark, above and below which adverse effects on sensitive sediment dwelling organisms occur respectively (Ingersoll et al., 2000; MacDonald et al., 2000b). It should be noted that the SQG used herein were developed for valuation of biota-contaminant effects in Florida, USA. Nevertheless, despite the obvious geographic mismatch these SQG utilise a database that spans many hundreds of tests thereby covering many different approaches to match biological effect and chemical concentration in laboratory and sediment studies. Comparison of the Nairobi sediment data to the consensus-based quality guidelines showed that for Sb 13 sites were below TEC unlikely effect and 12 between TEC and PEC. For As, Cd, Cr, Hg and Ni concentrations fall below the TEC and PEC suggesting they are unlikely to have a harmful effect on sediment dwelling biota. In contrast, at all 25 sites Pb concentrations (range 40.4–201 mg/kg, mean 80.3 mg/kg, median 55.1 mg/kg) exceeded TEC and 3 sites Pb values exceeded PEC. Equally 25 sites Zn concentrations exceeded TEC and 7 sites exceed the Zn PEC sediment quality benchmark. This initial evaluation therefore indicates that Pb and Zn concentrations are likely to have harmful effect on biota at some sites. Overall, the majority of Nairobi River sediment Zn and Pb concentrations fall between TEC (unlikely harm) and PEC (likely harm) criteria which presumably reflect an intermediate effect on sediment dwelling organisms.

Lead (Pb) concentrations from Nairobi's river sediments are significantly lower than those previously reported for street soils (Onyari et al., 1991); where a range between 137 and 2196 mg/kg was reported for the city environment and a range of 148–4088 mg/kg for an industrial area. They also observed that the concentration in the soils decreased rapidly away from major roads and suggested that much of the lead was from leaded petrol, but also noted that high concentrations were found close to garages specialising in the repair of car radiators that contained lead alloys. In this current study there are correlations between Pb and other heavy metals (Sn > Cu > Sb > Cd > Zn). The relationship with Sn (Supplementary) potentially being explained by solder, whilst Cu and Sb have been associated elsewhere with vehicle activities.

Leaded petrol is known to have well defined Pb isotope ratios due to a large portion of the world's supply being previously provided from a single source (Kemp et al., 2012; Vane et al., 2011). A plot of 1/Pb concentration versus $^{206/207}$Pb isotope ratio can demonstrate mixing lines between Pb background and contaminant sources (Supplementary 3.8). Where the mixing line impinges on the y-axis is indicative of the isotope ratio of that contaminant source. In this case, one potential end-member is that defined as "A" and associated with Broken Hill, Australian Pb used in petrol additives (Bollhöfer and Rosman, 2000). This figure also suggests a contaminant end-member with a higher $^{206/207}$Pb ratio (c. 1.11) from a different source. The lowest Pb concentrations agree with the geogenic signature for local basaltic rocks from the Kenyan Rift Valley (Rogers et al., 2000).

3.9. Principal component analysis

Multivariate assessment of the chemical data, toxicity and grain size by principal component analysis (PCA) was undertaken to aid interpretation of the relationships and thereby assist pollutant source

attribution (Fig. 8). The loading plot confirmed that PC1 main variables are % TOC followed by coprostanol (presumed to be from human sewage) and TEH (Fig. 8A). The component score plot shows that Kiambio are the samples with higher values for PC1 suggesting that the amount and/or type of organic carbon is the principal driver of this component because Kiambio has particularly high values of TOC (Fig. 8B). Conversely Pb and DDT had higher coefficients in PC2. Analysing the component scores we can see some clustering of the sites depending on informal settlement (slum) area. One plausible explanation for the distinct PC2 driven Mukuru cluster maybe related to its close proximity Nairobi's main industrial area in which hosts a wide variety of manufacturing, auto repair, metal fabrication and oil storage depots as well as pesticide, pharmaceuticals and agrochemical factories. The component loadings also confirm that PAH, PCB, pharmaceuticals, TEH and sewage have a stronger affinity for the fine sediment fraction (silt and clay) as compared to sand.

3.10. Results in the context of global and national development frameworks

The results set out in Sections 3.1 to 3.9 reinforce the importance of including targets on reducing sediment pollution in global and national development frameworks. The links between sediment quality and facets of sustainable development (e.g., health and wellbeing, clean water and sanitation, sustainable cities, responsible consumption and production) are clearly made in the SDGs and associated targets (Table 1). The detailed assessment of sediment quality in informal settlements (slums) on the Nairobi, Ngong and Mathare Rivers, in Nairobi, directly supports understanding of the current challenges, regulatory requirements to reduce pollution and contamination, and informs monitoring efforts by establishing a baseline by which progress towards the SDGs can be assessed.

While soil and sediment quality is clearly embedded into the SDG targets, this has not translated through to other UN development frameworks. The New Urban Agenda, adopted at the Habitat III summit in 2016, outlines standards and principles for the planning, construction, development, management and improvement of urban areas (Rudd et al., 2018; UN-Habitat, 2017). While this emphasises the need for environmentally sustainable and resilient urban development, it makes no reference to soil, sediment or land pollution or contamination. There is one generic reference to 'pollution' in the context of ensuring environmentally sustainable urban development, one reference to reducing 'marine pollution' and five direct or indirect references to 'air pollution'.

Our characterisation of sediment pollution in Nairobi demonstrates the need to think beyond air pollution when planning, delivering, and monitoring progress towards sustainable urban development. Kenya's Vision 2030 states *"Kenya's cities and towns are now poorly planned and that must change (Kenya, 2007). There is an acute need, therefore, for an effective capacity for regional and urban development planning starting with adequate housing for those now living in slums"*. As urban spaces expand and slums are upgraded, planners will need to deal with the legacy of industrial activity, chemical use, and lack of effective waste management procedures if they are to achieve their desired objectives of improved settlements and housing, health and wellbeing, and environmental protection.

4. Conclusions

Prior to this study very little was known about the complex chemical mixtures of persistent organic pollutants in river sediments receiving wastes from urban slums of Nairobi. This study shows that sediments from the Mathare, Kawangware, Kibera, Kiambio slums are more toxic than those from rivers traversing other urban land-use domains in Nairobi. Data revealed that slum sediments have a bimodal bound-hydrocarbon composition attributed to sewage and domestic refuse whereas river sediments traversing other land-uses (higher income-residential, university, park, quarry) were from natural biopolymers. Molecular level assessment of sewage input using coprostanol and its decay product epicoprostanol as well as other faecal marker compounds confirmed elevated amounts of untreated human sewage associated with Kiambio, Mathare, Mukuru, Kawangware and Kibera slums. The presence of high concentrations of untreated sewage is of concern for two reasons, firstly, untreated faeces can provide a growth medium for bacterial and viral pathogens that if ingested by humans lead to diseases such as salmonella, cholera, diarrhoea, typhoid, gastroenteritis and hepatitis A. Secondly, the presence of high concentrations of faecal matter can lead to nutrient enrichment, eutrophication, water column anoxia and toxic algal blooms which can cause ecosystem instability.

This study demonstrates that sediments accumulating in urban slums are characterised by multiple groups organic contaminants (TEH, PAH, PCB, DDT and pharmaceuticals) that originate from a variety of local point sources (industry, small businesses, domestic refuse disposal, sanitation) as well as broader urban background (vehicle road-run-off, power stations). Benchmarking against established SQG thresholds shows that each suite measured herein typically falls between upper and lower criteria. Nevertheless, despite this ambiguity it is known that organic chemicals in mixtures can cause adverse health effects in humans and biota even when present below their respective individual effect threshold. In contrast, trace metals concentrations were generally below SQG suggesting these are not the main driver of toxicity in Nairobi slum sediments. However, it may be concluded that both local metal working activities such as soldering and residual persistent lead from petrol, plus other elements (Cu, Sb) associated with vehicle activity contribute to the current heavy metal load.

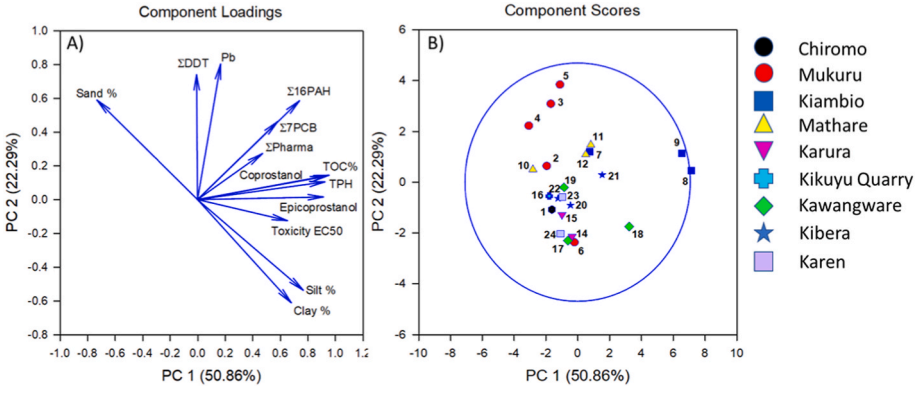

Fig. 8. Output of the principal component analysis (PCA); A) represents pollutant geochemistry with PC 1 being driven by organic carbon content (TOC %); B) Effect of PCA on a informal settlement land-use basis where Kiambio settlement site is driven by PC1 but Mukuru settlement driven by PC2. Geographic locations presented in Fig. 1.

This multi-chemical survey establishes a baseline understanding of sediment and soil quality in informal settlements (slums) that can be used to understand the health, infrastructural and urban planning challenges that must be addressed if the ambitions of the SDGs and Vision 2030 are to be realised. It informs understanding of the policies and actions that may be required to improve sediment quality and underpins effective monitoring of progress as these are implemented. Beyond Nairobi, we highlight the value of explicitly referencing sediment pollution in global development frameworks. There is a particular opportunity for researchers working on sediment and soil quality to support implementation of the New Urban Agenda and strengthen the science-policy interface work associated with this framework.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2022.105468.

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