Contents lists available at ScienceDirect

# Heliyon



journal homepage: www.cell.com/heliyon

Research article

5<sup>2</sup>CelPress

# Spatial occurrence and variation of the active pharmaceutical compounds in rivers and groundwater systems in Arusha City, Tanzania

# Mercy Nasimiyu Kundu<sup>a,\*</sup>, Hans C. Komakech<sup>b,c</sup>, Joseph Sang<sup>a</sup>

<sup>a</sup> Jomo Kenyatta University of Agriculture and Technology (JKUAT), Department of Soil, Water, and Environmental Engineering (SWEED), Kenya
 <sup>b</sup> Nelson Mandela Africa Institution of Science and Technology (NM-AIST), School of Material Energy, Water and Environmental Sciences (MEWES), Tanzania

<sup>c</sup> Water Infrastructure and Sustainable Energy Futures (WISE-Futures)), Tanzania

#### ARTICLE INFO

Keywords: Pharmaceutical compounds Sub-saharan Africa Arusha City Rivers and groundwater systems

#### ABSTRACT

This study investigated the occurrence of 11 pharmaceutical compounds in the rivers and groundwater systems of Arusha City, Tanzania. Each suspected individual residue of active pharmaceutical compounds in water matrices, was pre-concentrated using solid-phase extraction techniques and, then quantified using a liquid chromatography-mass spectrometer mass spectrometer (LC-MS/MS). The concentrations varied across the assessed rivers and groundwater systems. High concentrations of caffeine 520 ng/L were detected in the station downwards of a wastewater stabilization pond, discharging its partially treated effluent into the river, followed by stations whose rivers flowed through informal areas. Sampled points' located near the river's water sources reported fewer compounds with values below the detection limit, such as amoxicillin, paracetamols, and doxycycline. Except for sulfamethoxazole (94 ng/L) in the borehole, most of the concentrations detected in rivers were ten times higher than in boreholes. In addition, in boreholes, more compounds were identified in the monitoring than in the domestic ones, and concentration varied with depth of deep boreholes (25 m) were less abundant than shallow wells of less than 10 m. In conclusion, pharmaceutical compounds were frequently detected in both rivers and groundwater systems within Arusha City suggesting the need for understanding of their fates and associated risks.

### 1. Introduction

The frequent detection and prevalences of pharmaceutical compounds in the environment has raised health risk concerns worldwide. Pharmaceuticals occurs in the environment originating from septic tanks, partially treated wastewater, hospital waste, and indiscriminate disposal of solid waste [1,2]. Subsequently, they have potential adverse effects on human health and threaten the sustainability of the ecosystem owing to their behavior as (pseudo-)persistent contaminants in the environment [3,4].

These compounds have been detected in the influents and effluents of wastewater treatment plants (WWTPs) [5,6], rivers [7,8], and groundwater systems [4,9,10] in developed and developing countries. In a study conducted across world rivers [8], sub-Saharan African countries had the highest level of pharmaceutical concentrations detected, especially in the sites with poor sanitation systems,

\* Corresponding author.

https://doi.org/10.1016/j.heliyon.2024.e32681

Received 4 December 2023; Received in revised form 4 June 2024; Accepted 6 June 2024

Available online 14 June 2024

E-mail addresses: Kundumercy143@gmail.com, kundu\_mercy@yahoo.com (M.N. Kundu).

<sup>2405-8440/</sup><sup>©</sup> 2024 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC license (http://creativecommons.org/licenses/by-nc/4.0/).

#### M.N. Kundu et al.

followed by South Asia and Europe. Moreover, according to reviews of pharmaceutical compounds in different regions; sub-Saharan Africa had the highest frequency of detection and concentrations [2,3,11,12]. These depict the sub-Saharan Africa countries as a more endangered zone than their counterparts in developed countries.

Pharmaceuticals were present in all water sources assessed in sub-Saharan Africa. For instance, compounds such as sulfamethoxazole, trimethoprim, and metronidazole had an overall detection frequency of greater than 90 %, and antiretrovirals such as nevirapine and zidovudine had an overall detection frequency of 100 % [4].

In sub-Saharan Africa, informal settlements around cities with high population growth are characterized by poor, and unplanned waste handling and sanitation facilities. Most inhabitants in informal settlements rely on on-site sanitation (e.g. pit latrines, and septic tanks) for waste disposal [13,14]. Moreover, conventional WWTPs do not remove pharmaceuticals efficiently. They are point sources of these emerging contaminants in the environment [15]. As most inhabitants of sub-Saharan Africa depend on surface water, shallow wells, or boreholes for all their domestic needs, mapping environmental contaminants is paramount to understanding human exposure [16,17].

Water quality within Arusha City has been previously studied; the concentration of fluorides in rivers [18], nitrate transformations [19], and physical and chemical characteristics of the groundwater systems [20]. Furthermore, the level of progesterone hormones in rivers and stabilization ponds [21], and the quantity of macro- and microplastics within the city [22] were evaluated.

More so [8] compared the levels of pharmaceutical compounds from Arusha City on the Themi River with those from rivers worldwide. However, the study only focused on one river in Arusha, and the sampling points were very few (six points) and also excluded groundwater. Consequently, sufficiently quantifying the concentrations of compounds in the city and describing their spatial occurrence proved difficult. Therefore, it is crucial to characterize the compounds in other rivers within the city and provide the current scenario regarding the state of pharmaceutical compounds in the environment.

This study quantified the occurrence of 11 selected pharmaceutical compounds in four rivers and 22 boreholes, The 11 compounds were based on the results of a questionnaire survey on the frequently prescribed drugs within a city. The study provides the first-ever comparison of pharmaceutical compounds in rivers and other groundwater systems.



Fig. 1. Map of the study area showing sampling points from rivers (R1-R9), domestic boreholes (D1-D11), and monitoring boreholes(M1-M24).

The main objective of this study was to assess the concentration levels of selected pharmaceutical compounds in rivers and boreholes, compare the upstream and downstream in the rivers, and correlate the vertical variation of pharmaceutical compounds in boreholes. This could later be used in projecting the flow pattern of the compounds in groundwater systems and iteratively adopting management options to control disposing of pharmaceutical compounds in the environment.

#### 2. Materials and method

## 2.1. Description of the study area

The study was conducted in four rivers, originating from Mount Meru's foothills: Burka, Naura, Themi, and Kijenge Rivers, and domestic and groundwater monitoring boreholes. The rivers pass through Arusha City from the mountain's slope Fig. 1. Arusha City is characterized by two distinct seasons, dry and wet, and a bimodal rainfall pattern in the Tropical climate [23]. Volcanic ashes of varying ages dominate geological materials. Recently, these ashes deposited alluvial sediments in Arusha [24]. According to the 2022 census, the area has a population of 535,000 with an annual growth rate of 3 % Tanzania National Bureau of Statistics (TNBS) [25], thus with its area size translates to 2004 people per km<sup>2</sup>.

#### 2.2. Sample collection

Water samples were collected in mid-January and early February 2022 in the study area. Samples were taken from the upstream and downstream sections of the same rivers at easily accessible locations Fig. 1. Duplicate water samples were then filled to the brim in 500 mL amber glass bottles, and water samples were taken from different boreholes dug in different locations. This was done for both domestic and monitoring boreholes. The samples were collected using a normal drawing can for domestic boreholes, whereas monitoring wells were drawn using a water pump. In total, 18 samples were collected from rivers, 22 from domestic boreholes, and 40 from monitored boreholes. The collected samples were immediately stored in a cool box and, maintained at 4 °C before being transported to the laboratory for analysis.

#### 2.3. Selection of compounds for analysis

Based on a literature review, a list of compounds repeatedly reported in sub-Saharan Africa was selected, as shown in Table 2. Using this list, a field questionnaire survey was then conducted in five hospitals and ten pharmacies within Arusha City to determine their consumption rates, where, the pharmacists had to rank the listed compounds on a scale of one to five, and if there were other active pharmaceutical compounds frequently purchased and not included in the list, they were requested to include the compound on the list.

Afterwards, all the listed compounds with high frequency of consumption, including ibuprofen, carbamazepine, ciprofloxacin, cetirizine, diclofenac, metronidazole, trimethoprim, caffeine, sulfamethoxazole, amoxicillin, doxycycline, and paracetamol (purity >99) their standards were purchased from Merck (India). Whilst the chromatography reagents were purchased from Merck Kobil, Kenya. Glass fiber filters GF/F made from Whatman (VWR, Belgium), SPE cartridges (Oasis HLB, 200 mg, 6 cc) were purchased from USA, and a column specification of luna type 34 C8 [2] Size: 50 mm by 2.00 mm 3 µm brand: phenomenex USA (310) 212–0555 was used in analysis.

#### 2.4. Analytical methodology

Pharmaceutical residues were pre-concentrated using the Solid-Phase Extraction (SPE) method and analyzed by Trippel-quad mass spectrometry, according to a previously reported method [6]. Briefly, the collected duplicate water samples (500 mL) were vacuum-filtered using a 0.4 mm glass microfiber filter within three days of collection; to prevent biodegradation of the samples. The SPE process was performed using Oasis hydrophilic–lipophilic balance (HLB) cartridges (3  $\text{cm}^3/60 \text{ mg}$ , 6  $\text{cm}^3/200 \text{ mg}$ ) to pre-concentrate the target residue from the samples. The SPE procedure consists of four steps: conditioning, washing, loading, and elution. To optimize the SPE process, pH of the samples was adjusted to 9 using a sterile solution of ammonium hydroxide (NH<sub>4</sub>OH). The cartridges were preconditioned with 6 mL of methanol followed by 6 mL of ultrapure water for washing and then loaded at a flow rate of approximately 10 mL/min. A 12-port SPE vacuum manifold available in the Material, Energy, Water, and Environmental Science (MEWES) laboratory at the Nelson Mandela African Institution of Science and Technology (NM-AIST) in Tanzania was used. After loading, the cartridges were dried under vacuum for 5 min before being stored at a cool temperature. Methanol 4 mL was used to elute SPE cartridges. Subsequently, it evaporated in a steam of nitrogen at 40 °C to dryness before being reconstituted with 1 mL of H<sub>2</sub>O/ACN 80/20 (v/v) solvent followed by filtration through a 0.2 µm cellulose acetate syringe filter, and transferred into HPLC vials of 2 mL for injection into the LC-MS/MS system.

Liquid chromatography-electrospray ionization tandem mass spectrometry (LC-ESI-MS/MS) was used to analyze the target pharmaceuticals in multiple reaction monitoring (MRM) models with unit mass resolution [26]. To separate the extracted pharmaceuticals, high-performance liquid chromatography (HPLC) was performed using a Waters Quattro Micro tandem mass spectrometer (Milford, Massachusetts) with a C8 column (50 mm by 2.00 mm 3  $\mu$ m brand). The mobile phase consisted of eluent A (0.1 % formic acid in ultrapure water) and eluent B (acetonitrile with 0.1 % formic acid), operated in gradient elution mode at a flow rate of 0.45 mL/min. LC-MS/MS analysis was performed at the Pharmaceutical and Pharmacology Laboratory of Jomo Kenyatta University of Agriculture and Technology (JKUAT) in Kenya.

#### 2.5. Quality assurance

The analytical compounds evaluated using the SPE-LC-ESI-MS/MS process and method respectively, included blank samples, calibration curves, recovery rates, and repeatability. Working solutions with surrogate standard concentrations of 20, 40, 100, 200, 300, and 400 ng/L of all compounds were prepared in methanol. Moreso, the correlation coefficients of the calibration curves for all compounds for each standard were higher than 0.99. The recovery rate of ultra-pure water spiked with active pharmaceutical compounds, and was then extracted using a similar procedure to extract residues from the samples; ranged between 75 % and 112 % for all three samples prepared under the same conditions. The repeatability values of each sample's range were below 0.01 ng/L, and no compounds were detected in the blank samples of ultra-pure water. Table 1 shows the coefficient  $r^2$ , calibration curves for the standards, limit of detection (LOD), limit of quantification (LOQ), and recovery rates, .

## 3. Results and discussion

#### 3.1. Selected compounds for analysis

Twenty-three compounds with a very high or high frequency of prescriptions were listed from the city, belonging to the classes of Antibiotic (amoxicillin Trihydrate, ciprofloxacin, metronidazole, sulfamethazine, doxycycline hydrochl, erythromycin, ampicillin trihydrate, cefpodoxime, azithromycin, and trimethoprim), Anti-inflammatory (naproxen, diclofenac sodium salt, ibuprofen, paracetamol Sulfate Pot), Anti-Hypertensive. (hydrochlorothiazide, bendroflumethiazide), Anti-histamine (cetirizine dihydrochlor, prednisolone), Anti-viral (Levofloxacin), Proton pump inhibitors (omeprazole), Psychiatric (carbamazepine), Anti-depressant (amitriptyline Hydrochlor), and Stimulant (caffeine) (Table 2). Among the list, cetirizine, doxycycline, amoxicillin caps, and metronidazole were among the compounds that had not been previously repeatedly reported yet and were frequently prescribed in Arusha City. However, due to time required to develop analytical methods and the associated cost, only those compounds ranked with high rate of consumption were determined in this study.

# 3.2. Quantification of pharmaceutical compounds

The selected pharmaceutical compounds in the rivers and groundwater system were at least twice quantified in relation to sample matrices. Their MS/MS transitions and operating conditions (m/z, cone voltage, collision energy (eV)) used for quantification for each selected active pharmaceutical compound are presented in Table 3.

## 3.3. Concentration, frequency, and variation of pharmaceutical compounds in rivers, domestic and monitoring boreholes

#### 3.3.1. Concentration values and detection frequency in rivers

Among the assessed compounds, caffeine showed the highest concentration in the stimulant group. The values ranged from 19 to 520 ng/L. This was followed by the ciprofloxacin of the anti-biotic group and cetirizine of the Anti-histamine group with values of 486 ng/L and 411 ng/L, respectively, as shown in Table 3. In contrast, amoxicillin had the least negligible concentration, with most of sampled stations depicting values below the detection level (BDL). However, the caffeine values reported in this study were lower than the mean values reported for 24 African countries [8]. [8] reported a mean caffeine concentration of 4090 ng/L for 24 African countries. [27] recorded concentrations ranging from 400 to 9250 ng/L in South Africa, which are inconsistent with those reported in this study, even though some locations were slightly higher. Nevertheless [10], reported very low concentrations of caffeine in Kabwe, Zambia, ranging from 0.17 to 0.20 ng/L. These comparisons show a significant variation in the levels of caffeine within the continent; owing to the site, inhabitants' behavior, and probably the population density at the sampled locations [26,27]. The occurrence of slightly higher caffeine values in this study area is mainly attributed to their presence in soft drinks and their inclusion in some painkillers and flu drugs.

The detected values of sulfamethoxazole and carbamazepine in rivers ranged from BDL to 15 ng/L and BDL to 8.8 ng/L,

| Table 1 |  |
|---------|--|
|---------|--|

| Compound       | Compound Coeffiencient r <sup>2</sup> |                    | LOQ (µg/L) | LOD (µg/L) | Recovery rate (%) mean $\pm$ SD |
|----------------|---------------------------------------|--------------------|------------|------------|---------------------------------|
| Paracetamol    | 0.997353                              | 209.46x + 2949.86  | 0.141      | 0.047      | $92.42\pm3.24$                  |
| Metronizadole  | 0.993598                              | 449.64x + 11011.31 | 0.241      | 0.080      | $87.96 \pm 1.38$                |
| Caffeine       | 0.997745                              | 452.08x + 4969.22  | 0.110      | 0.036      | $98.27 \pm 2.87$                |
| Trimethoprim   | 0.977679                              | 128.07x + 798.40   | 0.062      | 0.021      | $102.91\pm5.12$                 |
| Amoxicillin    | 0.996208                              | 18.52x + 254.91    | 0.138      | 0.045      | $74.92 \pm 4.04$                |
| Carbamazepine  | 0.995956                              | 775.28x + 8253.89  | 0.106      | 0.035      | $82.60 \pm 2.87$                |
| Cetrizine      | 0.994854                              | 38.70x + 506.44    | 0.130      | 0.043      | $91.52 \pm 1.92$                |
| Doxycycline    | 0.995673                              | 5.64x + 34.79      | 0.062      | 0.020      | $88.51 \pm 2.61$                |
| Ciprofloxacin  | 0.991285                              | 29.30x + 599.51    | 0.205      | 0.068      | $107.98 \pm 4.19$               |
| Sulfamethazine | 0.996041                              | 1495.12x + 2806.16 | 0.019      | 0.006      | $112.44\pm3.06$                 |
| Ibuprofen      | 0.998783                              | 129.42x + 851.31   | 0.066      | 0.022      | $90.81 \pm 2.93$                |

Summary of method performance characteristics.

#### Table 2

Pharmaceuticals ranked by frequency of sale according to a questionnaire (see supplemental materials).

| Compounds        | The number of pharmacist-ranked compounds was as follows: |      |     |          |     |  |  |  |
|------------------|---|------|-----|----------|-----|--|--|--|
|                  | Very high   | High | Low | Very low | N/A |  |  |  |
| Acetaminophen    | 4   | 3    | 5   | 2        | 1   |  |  |  |
| Amitriptyline    | 0   | 8    | 3   | 3        | 1   |  |  |  |
| Carbamazepine    | 5   | 6    | 4   | 0        | 0   |  |  |  |
| Ciprofloxacin    | 8   | 7    | 0   | 0        | 0   |  |  |  |
| Diazepam         | 0   | 0    | 6   | 6        | 3   |  |  |  |
| Diclofenac       | 8   | 1    | 5   | 1        | 0   |  |  |  |
| Ibuprofen        | 13  | 2    | 0   | 0        | 0   |  |  |  |
| Indomethacin     | 0   | 0    | 6   | 3        | 6   |  |  |  |
| Levofloxacin     | 4   | 5    | 5   | 1        | 0   |  |  |  |
| Naproxen         | 0   | 0    | 6   | 3        | 6   |  |  |  |
| Paracetamol      | 15  | 0    | 0   | 0        | 0   |  |  |  |
| Salicylic acids  | 0   | 3    | 0   | 9        | 3   |  |  |  |
| Sulfadoxine      | 0   | 1    | 6   | 6        | 2   |  |  |  |
| Sulfamethoxazole | 11  | 3    | 1   | 1        | 0   |  |  |  |
| Sulfamethazine   | 0   | 4    | 6   | 2        | 3   |  |  |  |
| Triclosan        | 0   | 0    | 0   | 9        | 6   |  |  |  |
| Trimethoprim     | 9   | 0    | 4   | 0        | 2   |  |  |  |

# Table 3

Pharmaceuticals retention time and MS/MS operating conditions.

| Sno | Compound         | Retention time (minutes) | Parents | Daughter cells | Cone voltage | eV |
|-----|------------------|--------------------------|---------|----------------|--------------|----|
| 1.  | Paracetamol      | 1.76                     | 152     | 110            | 30           | 16 |
|     |                  |                          |         | 65             | 30           | 20 |
| 2.  | Ciprofloxacin    | 8.40                     | 332     | 314            | 27           | 24 |
|     |                  |                          |         | 288            | 27           | 24 |
| 3.  | Metronidazole    | 1.67                     | 172     | 128            | 25           | 25 |
|     |                  |                          |         | 82             | 25           | 15 |
| 4.  | Sulfamethoxazole | 4.37                     | 279     | 186            | 30           | 17 |
|     |                  |                          |         | 92             | 30           | 30 |
| 5.  | Carbamazepine    | 7.07                     | 332     | 192            | 27           | 24 |
|     |                  |                          |         | 194            | 27           | 24 |
| 6.  | Caffeine         | 2.60                     | 195     | 138            | 30           | 20 |
|     |                  |                          |         | 110            | 30           | 25 |
| 7.  | Trimethoprim     | 1.52                     | 291     | 230            | 30           | 25 |
|     |                  |                          |         | 123            | 30           | 30 |
| 8.  | Amoxicillin      | 1.40                     | 366     | 349            | 20           | 13 |
|     |                  |                          |         | 114            | 20           | 20 |
| 9.  | Cetrizine        | 6.69                     | 389     | 201            | 32           | 19 |
|     |                  |                          |         | 166            | 32           | 40 |
| 10. | 1buprofen        | 5.20                     | 205     | 161            | 20           | 8  |
| 11. | Doxycycline      | 3.60                     | 447     | 428            | 55           | 25 |
|     |                  |                          |         | 154            | 55           | 40 |

# Table 4

| Frequency of detection, average, minimum, and maximum values (ng/L) detected in rivers, domestic, and monitoring b | oreho | ol | es |
|--|-------|----|----|
|--|-------|----|----|

| Compound         | Rivers (ng/L) |        |       |        | Domestic boreholes (ng/L) |       |      | Monitoring boreholes (ng/L) |        |       |       |       |
|------------------|---------------|--------|-------|--------|---------------------------|-------|------|-----------------------------|--------|-------|-------|-------|
|                  | Freq (%)      | Avg    | Min   | Max    | Freq (%)                  | Avg   | Min  | Max                         | Freq   | Avg   | Min   | Max   |
|                  |               |        |       |        |                           |       |      |                             | (%)    |       |       |       |
| Amoxicillin      | 40            | 46.00  | 26.00 | 162.00 | 0.00                      | BDL   | BDL  | BDL                         | 25.00  | 1.40  | 0.10  | 14.00 |
| Caffeine         | 90            | 230.00 | 19.00 | 520.00 | 70.00                     | 22.00 | 2.00 | 34.00                       | 75.00  | 48.00 | 5.00  | 92.00 |
| Carbamazepine    | 90            | 3.60   | 0.20  | 8.80   | 100.00                    | 0.60  | 0.10 | 1.80                        | 100.00 | 1.40  | 0.10  | 14.00 |
| Ciprofloxacin    | 100           | 161.90 | 24.00 | 411.00 | 45.00                     | 0.80  | 0.10 | 2.00                        | 45.00  | 28.00 | 2.00  | 90.00 |
| Cetirizine       | 75            | 152.00 | 22.00 | 486.00 | 55.00                     | 12.00 | 4.00 | 19.00                       | 60.00  | 28.00 | 14.00 | 38.00 |
| Doxycycline      | 68            | 85.70  | 8.00  | 200.00 | 40.00                     | 2.00  | 9.60 | 21.00                       | 45.00  | 24.00 | 2.00  | 64.00 |
| Ibuprofen        | 75            | 72.70  | 20.00 | 184.00 | 30.00                     | 21.00 | 1.00 | 24.00                       | 30.00  | 30.00 | 6.00  | 52.00 |
| Metronidazole    | 80            | 53.00  | 1.20  | 178.00 | 35.00                     | 15.00 | 0.60 | 35.50                       | 60.00  | 15.00 | 7.00  | 44.00 |
| Paracetamols     | 70            | 47.90  | 12.20 | 160.60 | 80.00                     | 12.00 | 6.00 | 18.00                       | 92.00  | 32.00 | 10.00 | 50.00 |
| Sulfamethoxazole | 100           | 3.40   | 0.10  | 6.20   | 100.00                    | 12.00 | 0.10 | 19.00                       | 100.00 | 16.00 | 0.10  | 94.00 |
| Trimethoprim     | 85            | 9.60   | 2.00  | 16.00  | 0.00                      | BDL   | BDL  | BDL                         | 55.00  | 2.50  | 0.10  | 14.00 |

BDL: below detection Level.

respectively. These sulfamethoxazole values were 100 times lower than those reported for the Nairobi River in Kenya. Since [4] measured up to  $39 \mu g/L$  and [28]  $13.8 \mu g/L$  separately on the Nairobi River. On the other hand, the concentrations in this study were ten times lower than the mean values reported for 24 African countries [8]. However, in Cameroon [29], values below 2.0 ng/L, which is less than the one reported in this study were detected. Solid waste management plans and the population size in the locality could influence this significant variation in the measured values of sulfamethoxazole. Conversely, the concentration values reported in this study conducted on Themi River, as the reported values are the mean values for 24 countries in Africa.

In addition, sulfamethoxazole and ciprofloxacin were frequently detected in 100 % of the assessed rivers (Table 4). The frequent detection of antibiotics of sulfamethoxazole and trimethoprim has been described in almost all studies assessing the occurrences of pharmaceutical compounds in sub-Saharan Africa [3,4,7,30]. [4] reported sulfamethoxazole, trimethoprim, and metronidazole with a frequency detection of greater than 90 % in aquatic environments. The frequent detection of sulfamethoxazole attributed significantly to the highly variable removal rate caused by the transformation of its metabolites, Na-sulfamethoxazole and Glu-sulfamethoxazole, back to sulfamethoxazole in rivers, which often results in a net negative removal [31]. Amoxicillin was the least frequently detected compound in the assessed river stations. This is because the compound is easily degraded by abiotic and biotic factors, yielding various intermediate products [32].

#### 3.3.2. Variation of detected compounds among rivers

The detection of pharmaceutical compounds varied across the four rivers. The commonly detected location was station R8, downstream of the Themi River, as shown in Fig. 1. All detected concentrations had higher values than those of the other stations. The elevated concentration detected at this station resulted from the effluent of old Arusha Wastewater stabilization ponds. This is due to the stabilization ponds draining its partially treated effluent into Themi River a few kilometers from station R8. These values could result from the overloading and inability of WWTPs to effectively remove pharmaceutical compounds. WWTPs are the primary sources of pharmaceutical compounds released into the aquatic environment [33]. This is because of the system design and required removal mechanisms of the compounds [11,32].

At station R9, Burka downstream was the second station in which the most active compounds were detected. This station is located downstream of a highly populated community, including Sombetini, Morombo, and other informal settlements. Dispensable hospital materials such as syringes and medicine packaging caps were predominantly visible at the station. These materials could originate from hospitals and are poorly disposed of by inhabitants into the environment. The visible materials from hospitals at station R9 complement another study by Ref. [22], which reported an abundance of similar materials of macroplastics at the locality.

A comparison between the total accumulation of pharmaceutical compounds detected upstream and downstream of the assessed rivers was determined. The downstream stations R5, R6, R7, R8, and R9 had higher values than their respective upstream counterpart stations for all the assessed compounds. Upstream (R1-R4), the accumulative values showed a similar trend, with their values depicting a minimum deviation from the detected values. The variation in the total accumulation concentration increased along the river. This is mainly attributed to the total accumulation of compounds as the river flows downwards. Similar findings were found for Nairobi River in Kenya [7] and Cameroon [29], where the concentration increased downstream of the river and catchment, respectively.

Low-frequency detection was rendered at stations R1 and R4, where most of their detected values had a concentration BDL that was lower than that of other stations. These low values are attributed to their respective positions, since they are both far from the residential homes, and station R4, whose water source is a few meters from the sampled location. Thus minimal effect from indiscriminate disposal of waste.



Fig. 2. Box plot of pharmaceutical compounds in rivers.

The concentrations of rivers [18] were plotted in a box plot, as shown in Fig. 2, to evaluate the descriptive statistics of the compounds assessed. The values of most compounds were negatively or positively skewed, except for doxycycline compounds, which had a normal distribution. The large variation in the distribution of compounds within the locality is mainly attributed to the characteristics of the area, such as disposal mechanisms and the source of the river. Outliers were observed in cetirizine and paracetamol compounds. These concentrations were detected at station R8, which received a contribution from stabilization ponds.

#### 3.3.3. Occurrence and frequency in the groundwater system

In groundwater system, sulfamethoxazole had the highest concentration detected at 94 ng/L, followed by caffeine and ciprofloxacin at 91 ng/L and 90 ng/L, respectively. Paracetamol, metronidazole, ibuprofen, and doxycycline had values ranging from BDL to 64 ng/L (Table 3). The values reported in this study are comparable with those from Jianghan Plain in China [34], where mean values of 20.3 and 33.7 ng/L were observed in the summer and winter, respectively, of the analyzed compounds in the groundwater samples. In addition [29], reported slightly higher values of sulfamethoxazole (max 1285 ng/L) at one of the stations; otherwise, most of other stations had values within the range in this study. According to Ref. [4], the values in groundwater ranged between 5 and 50 ng/L, which are as per the values reported in this study. The characteristics of the study area mainly influenced the variation of pharmaceutical compounds in the groundwater system. In this study, we collected samples from an informal settlement characterized with high population growth (3 % per annum), which could have prompted a slightly higher value than some studies suggested. Also, geological materials within the locality would control the transport of compounds into the groundwater system.

Sulfamethoxazole and carbamazepine were frequently detected at 100 %, whereas amoxicillin and ibuprofen were detected in 25 % and 30 % of groundwater system, respectively (Table 4). Frequent detection of sulfamethoxazole and carbamazepine are associated with their physicochemical properties. They both have low biodegradability and neutrality for carbamazepine and are anionic for sulfamethoxazole, making them persistent and mobile in soil [35]. Carbamazepine with a frequency of occurrence of 100 % has also been reported in other studies, Ceyhan in Turkey and Méfou watershed in Cameroon [28,36],.

### 3.3.4. Variation of pharmaceuticals in the groundwater systems

The concentrations detected in the shallow wells, medium depth boreholes, and deep boreholes varied across locations. Likewise, the values varied across the types of groundwater systems obtained from either monitoring or domestic sources, as shown in Fig. 3. The monitoring boreholes had higher values than those of the domestic boreholes. This discrepancy might be attributed to the frequent withdrawal of water from the domestic boreholes. Furthermore, domestic boreholes had a low detection frequency (Table 4). In addition, negative and positive skewness was observed in the compounds shown in Fig. 3, with most of the compounds associated with outliers.

For monitoring boreholes, higher concentrations were detected in shallow wells (5–10 m) than in deep wells (20–26 m). This probably results from the slow transportation of compounds into the groundwater systems or biodegradation of the compounds as they travel downwards. To our knowledge, no study in sub-Saharan Africa has shown a relationship between depth. However, for other regions, similar studies on the relationship between depth and level of pharmaceutical compounds have been reported in the USA; where concentrations showed a decreasing order with an increase in groundwater depths [37] and no correlation between the deep and medium boreholes [1] reported. Whereas irregular fluctuation of pharmaceuticals in the vertical distribution in boreholes were reported in China [38].

Shallow wells located near pit latrines and septic tanks in densely populated cities with informal settlements tend to be more susceptible to contamination due to a lack of protection. Hence they have high contamination values [39]. The vulnerability of shallow wells exposes inhabitants to unknown health hazards and ecotoxicology. Therefore, continuous assessment of the compounds and determination of their health risks are vital for implementing regulation laws, especially in areas where inhabitants rely on shallow boreholes for domestic purposes.

#### 3.3.5. Comparison between rivers and groundwater systems

The frequency of occurrence of pharmaceuticals in the rivers was higher than that in the groundwater systems, except for carbamazepine and sulfamethoxazole, whose detection rate was 100 % in both matrices. Furthermore, the concentrations detected in rivers were higher than those detected in groundwater systems except for sulfamethoxazole, where the highest values were detected in the groundwater systems at 94 ng/L. High levels of sulfamethoxazole in groundwater correspond with the study conducted in the Méfou watershed [30] in Cameroon, except that their values (335 ng/L) were higher than those reported in this study. The disparity in the values could result from the difference in the anthropic activities, contributing to contamination in aquatic environments.

## 4. Conclusion

The occurrence of 11 active pharmaceutical compounds was investigated in the river and groundwater systems of Arusha city in Tanzania. These compounds were selected as the most frequently prescribed drugs by the inhabitants of the study area. Sulfameth-oxazole and carbamazepine were detected at a frequency of 100 % in both matrices. However, the values detected in surface water (rivers) were higher than those assessed in boreholes, except for sulfamethoxazole, where high values (94 ng/L) were detected in boreholes. Among the four rivers, the concentration varied with the distance from the source water, distribution of housing, effluent discharge, and visible materials at the locality. More compounds were detected in domestic boreholes than in boreholes constructed for groundwater monitoring, although the shallow wells had high values in both cases. Therefore, the frequent detection of pharmaceutical compounds in both surface and groundwater system, implies there is a need for removal from drinking water to limits their



Fig. 3. Box plot of the pharmaceutical compounds in borehole.

ecotoxicological effects on humans and the environment.

#### Data availability statement

Data will be available on request.

#### CRediT authorship contribution statement

**Mercy Nasimiyu Kundu:** Writing – original draft, Visualization, Validation, Software, Methodology, Formal analysis, Conceptualization. **Hans C. Komakech:** Writing – review & editing, Validation, Supervision, Software, Funding acquisition, Conceptualization. **Joseph Sang:** Writing – review & editing, Supervision, Investigation.

### 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.

#### Acknowledgment

The authors appreciate financial support from **Water Infrastructure and Sustainable Energy Futures (WISE-Futures)**. Also, we acknowledge the support of the Technical team in the Pharmaceutical and Pharmacology Laboratory, Department of Chemistry in JKUAT, Kenya. We thank the many borehole owners and T-group, who allowed us to collect samples from their boreholes.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e32681.

#### References

- M.S. Fram, K. Belitz, Occurrence and concentrations of pharmaceutical compounds in groundwater used for public drinking-water supply in California, Sci. Total Environ. 409 (18) (2011) 3409–3417, https://doi.org/10.1016/j.scitotenv.2011.05.053 [Internet].
- [2] L.M. Madikizela, S. Ncube, L. Chimuka, Analysis, occurrence and removal of pharmaceuticals in African water resources: a current status, J Environ Manage [Internet] 253 (August 2019) (2020) 109741, https://doi.org/10.1016/j.jenvman.2019.109741.
- [3] S. Fekadu, E. Alemayehu, R. Dewil, B. Van der Bruggen, Pharmaceuticals in freshwater aquatic environments: a comparison of the African and European challenge, Sci Total Environ [Internet] 654 (2019) 324–337, https://doi.org/10.1016/j.scitotenv.2018.11.072.
- [4] K.O. K'oreje, L. Vergeynst, D. Ombaka, P. De Wispelaere, M. Okoth, H. Van Langenhove, et al., Occurrence patterns of pharmaceutical residues in wastewater, surface water and groundwater of Nairobi and Kisumu city, Kenya, Chemosphere 149 (2016) 238–244, https://doi.org/10.1016/j.chemosphere.2016.01.095 [Internet].
- [5] F.O. Agunbiade, B. Moodley, Occurrence and distribution pattern of acidic pharmaceuticals in surface water, wastewater, and sediment of the Msunduzi River, Kwazulu-Natal, South Africa, Environ. Toxicol. Chem. 35 (1) (2016) 36–46.

- [6] L. Vergeynst, A. Haeck, P. De Wispelaere, H. Van Langenhove, K. Demeestere, Multi-residue analysis of pharmaceuticals in wastewater by liquid chromatography-magnetic sector mass spectrometry: method quality assessment and application in a Belgian case study, Chemosphere 119 (2015) S2–S8.
- [7] S. Bagnis, A. Boxall, A. Gachanja, M. Fitzsimons, M. Murigi, J. Snape, et al., Characterization of the Nairobi River catchment impact zone and occurrence of pharmaceuticals: implications for an impact zone inclusive environmental risk assessment, Sci. Total Environ. 703 (2020) 134925, https://doi.org/10.1016/j. scitotenv.2019.134925 [Internet].
- [8] J.L. Wilkinson, A.B.A. Boxall, D.W. Kolpin, K.M.Y. Leung, R.W.S. Lai, D. Wong, et al., Pharmaceutical pollution of the world 's rivers 119 (8) (2022) 1–10.
   [9] W. Gwenzi, N. Chaukura, Organic contaminants in African aquatic systems: current knowledge, health risks, and future research directions, Sci. Total Environ.
- 619–620 (2018) 1493–1514, https://doi.org/10.1016/j.scitotenv.2017.11.121 [Internet].
  [10] J.P.R. Sorensen, D.J. Lapworth, D.C.W. Nkhuwa, M.E. Stuart, D.C. Gooddy, R.A. Bell, et al., Emerging contaminants in urban groundwater sources in Africa, Water Res [Internet] 72 (2015) 51–63, https://doi.org/10.1016/j.watres.2014.08.002.
- [11] A.J. Ebele, M. Abou-Elwafa Abdallah, S. Harrad, Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment, Emerg Contam [Internet] 3 (1) (2017) 1–16, https://doi.org/10.1016/j.emcon.2016.12.004.
- [12] N.J. Waleng, P.N. Nomngongo, Occurrence of pharmaceuticals in the environmental waters: African and Asian perspectives, Environ Chem Ecotoxicol [Internet] 4 (2022) 50–66, https://doi.org/10.1016/j.enceco.2021.11.002.
- [13] J.W. Foppen, F. Kansiime, SCUSA: integrated approaches and strategies to address the sanitation crisis in unsewered slum areas in African mega-cities, Rev Environ Sci Bio/Technology. 8 (4) (2009) 305–311.
- [14] F. Nantaba, J. Wasswa, H. Kylin, W.-U. Palm, H. Bouwman, K. Kümmerer, Occurrence, distribution, and ecotoxicological risk assessment of selected pharmaceutical compounds in water from Lake Victoria, Uganda, Chemosphere 239 (2020) 124642.
- [15] A.J. Watkinson, E.J. Murby, D.W. Kolpin, S.D. Costanzo, The occurrence of antibiotics in an urban watershed: from wastewater to drinking water, Sci. Total Environ. 407 (8) (2009) 2711–2723.
- [16] P.A. Pantaleo, H.C. Komakech, K.M. Mtei, K.N. Njau, Contamination of groundwater sources in emerging African towns: the case of Babati town, Tanzania, Water Pract. Technol. 13 (4) (2018) 980–990.
- [17] H.C. Komakech, C. de Bont, Differentiated access: challenges of equitable and sustainable groundwater exploitation in Tanzania, Water Altern. (WaA) 11 (3) (2018) 623–637.
- [18] A.J. Kitalika, R.L. Machunda, H.C. Komakech, K.N. Njau, Fluoride variations in rivers on the slopes of mount meru in Tanzania, J. Chem. 2018 (2018).
- [19] E. Elisante, A.N.N. Muzuka, Sources and seasonal variation of coliform bacteria abundance in groundwater around the slopes of Mount Meru, Arusha, Tanzania, Environ. Monit. Assess. 188 (7) (2016).
- [20] J.R. Selemani, J. Zhang, A.N.N. Muzuka, K.N. Njau, G. Zhang, A. Maggid, et al., Seasonal water chemistry variability in the Pangani River basin, Tanzania, Environ. Sci. Pollut. Res. 24 (33) (2017) 26092–26110.
- [21] H.R. Kasambala, M.J. Rwiza, R.H. Mdegela, Levels and distribution of progesterone in receiving waters and wastewaters of a growing urban area, Water Sci. Technol. 80 (6) (2019) 1107–1117.
- [22] Kundu M.N., Komakech H.C., Lugomela G., Analysis of macro and microplastics in riverine , riverbanks , and irrigated farms in Arusha , Tanzania, Arch. Environ. Contam. Toxicol. 82 (2022) 142–157.
- [23] A.L. Kijazi, C.J.C. Reason, Analysis of the 1998 to 2005 drought over the northeastern highlands of Tanzania, Clim. Res. 38 (2009) 209-223.
- [24] G. Ghiglieri, D. Pittalis, G. Cerri, G. Oggiano, Hydrogeology and hydrogeochemistry of an alkaline volcanic area: the NE Mt. Meru slope (East African Rift-Northern Tanzania), Hydrol. Earth Syst. Sci. 16 (2) (2012) 529–541.
- [25] Census, The 2012 Population and Housing Census: Population Distribution by Administrative Areas. Nation Bureau of Statistics (NBS) and Ofce of the Chief Government Statistician, United Republic of Tanzania, 2013.
- [26] Waters corperation. Micromass Quattro Ultima Pt Mass Spectrometer.
- [27] S. Matongo, G. Birungi, B. Moodey, P. Ndungu, Occurrence of selected pharmaceuticals in water and sediment of Umgeni River, KwaZulu-Natal, South Africa, Environ. Sci. Pollut. Res. 22 (13) (2015) 10298–10308.
- [28] E. Ngumba, A. Gachanja, T. Tuhkanen, Occurrence of selected antibiotics and antiretroviral drugs in Nairobi River Basin, Kenya, Sci. Total Environ. 539 (2016) 206–213, https://doi.org/10.1016/j.scitotenv.2015.08.139 [Internet].
- [29] P. Branchet, N. Ariza Castro, H. Fenet, E. Gomez, F. Courant, D. Sebag, et al., Anthropic impacts on Sub-Saharan urban water resources through their pharmaceutical contamination (Yaoundé Center Region, Cameroon), Sci. Total Environ. 660 (2019) 886–898, https://doi.org/10.1016/j.scitotenv.2018.12.256 [Internet].
- [30] P. Branchet, N.A. Castro, H. Fenet, E. Gomez, F. Courant, D. Sebag, et al., Science of the total environment anthropic impacts on sub-saharan urban water resources through their pharmaceutical contamination (Yaoundé, center region, Cameroon), Sci. Total Environ. 660 (2019) 886–898.
- [31] A. Göbel, C.S. McArdell, M.J.-F. Suter, W. Giger, Trace determination of macrolide and sulfonamide antimicrobials, a human sulfonamide metabolite, and trimethoprim in wastewater using liquid chromatography coupled to electrospray tandem mass spectrometry, Anal. Chem. 76 (16) (2004) 4756–4764.
- [32] A. Elizalde-Velázquez, L.M. Gómez-Oliván, M. Galar-Martínez, H. Islas-Flores, O. Dublán-García, N. SanJuan-Reyes, Amoxicillin in the aquatic environment, its fate and environmental risk, in: M.L. Larramendy, S. Soloneski (Eds.), Environmental Health Risk, Rijeka: IntechOpen, 2016.
- [33] F. Of, O. Compounds, T.H.E.S. Environment, Fate and Transport of Organic Compounds In(to) the Subsurface Environment, 2011, pp. 215-231.
- [34] L. Yao, Y. Wang, L. Tong, Y. Deng, Y. Li, Y. Gan, et al., crossmark, Ecotoxicol. Environ. Saf. 135 (October 2016) (2017) 236–242.
- [35] M. Bizi, F.-E. El Bachra, Transport of carbamazepine, ciprofloxacin and sulfamethoxazole in activated carbon: solubility and relationships between structure and diffusional parameters, Molecules 26 (23) (2021) 7318.
- [36] E.Y. Guzel, F. Cevik, N. Daglioglu, Determination of pharmaceutical active compounds in Ceyhan River, Turkey: seasonal, spatial variations and environmental risk assessment, Hum Ecol Risk Assess [Internet] 25 (8) (2019) 1980–1995, https://doi.org/10.1080/10807039.2018.1479631.
- [37] K.K. Barnes, D.W. Kolpin, E.T. Furlong, S.D. Zaugg, M.T. Meyer, L.B. Barber, A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States - 1) Groundwater, Sci. Total Environ. 402 (2–3) (2008) 192–200.
- [38] L. Yao, Y. Wang, L. Tong, Y. Deng, Y. Li, Y. Gan, et al., Occurrence and risk assessment of antibiotics in surface water and groundwater from different depths of aquifers: a case study at Jianghan Plain, central China, Ecotoxicol Environ Saf [Internet] 135 (October 2016) (2017) 236–242, https://doi.org/10.1016/j. ecoenv.2016.10.006.
- [39] D.J. Lapworth, N. Baran, M.E. Stuart, R.S. Ward, Emerging organic contaminants in groundwater: a review of sources, fate and occurrence, Environ Pollut [Internet] 163 (2012) 287–303, https://doi.org/10.1016/j.envpol.2011.12.034.