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Tracing contaminants of emerging concern in the Awash River basin, Ethiopia

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ABSTRACT

Study region: Awash River basin, Central Ethiopia
Study focus: The study focuses on characterization of Emerging Organic Contaminants (EOCs) in the Awash River basin. Characterization of the EOCs was supplemented by chemical analysis of samples from river, boreholes, tap water, and surface water reservoirs. Analyses of environmental isotopes (δ 2 H, δ 18 O, and 222Rn) were used to investigate the exchange of contaminants between surface and groundwater supply sources.
New hydrological insights for the region: More than 100 EOCs are identified in all water supply sources. The EOCs are linked to agricultural applications, urban, and industrial sources. Based on the analysis of chemical and environmental tracers, the deep groundwater has greater protection from contamination than the river and the shallow groundwater. The heavy metal analysis prevails the same. The shallow aquifers are affected by urban, industrial, and agricultural pollutants. Attributed to the different contaminant sources, distinct variations in terms of compound types were observed at different locations. Water supply sources located upstream are dominated by urban and industrial contaminants while compounds from agricultural applications dominate the downstream sites. Artificial infrastructures serve as attenuation points for urban and industrial sourced compounds. Characterization of EOCs showed new contaminant loads in the water supply sources, which haven't been tested before, with potential impact on human and wider environmental health, and may necessitate a revision of the customary water quality test and monitoring practices.

1. Introduction

The state of water quality (physical, chemical, and biological) has been continuously altered by natural and human activities (Chaudhry and Malik, 2017; Owa, 2013). Consequently, water quality deterioration has become one of the primary issues in the world (Adeba, 2015; Austin, 2010; Khatri and Tyagi, 2015; Li, 2016; Serre and Karuppannan, 2018; Youse et al., 2018). The most common human influence on water quality is the introduction of disease-causing chemicals and organisms due to industrialization and agricultural applications (fertilizers, manures, and pesticides) (Boyd, 2014; Khatri and Tyagi, 2015). However, in recent decades, emerging contaminants (natural and synthetic organic compounds) affecting freshwater quality have become a rising concern with adverse

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effects on human health and the environment (Ali et al., 2018; Bai et al., 2018; Bayabil et al., 2022; Mohan et al., 2019; Pereira et al., 2015; White et al., 2019).

Emerging contaminants are a group of organic compounds that are not widely regulated and have not been previously detected through conventional water quality analysis (Rodriguez-Narvaez et al., 2017; Stefanakis, 2017). These contaminants are recognized as significant water pollutants detected both in the surface and groundwater (Bayabil et al., 2022). Their occurrence is observed in different ranges and concentrations in surface water, wastewater, groundwater, and drinking water in different countries (Agunbiade and Moodley, 2016; Balakrishna et al., 2017; Damkjaer et al., 2018; Galindo-miranda et al., 2019; Gogoi et al., 2018; Houtman, 2010; Jesus et al., 2014; K'oreje et al., 2016; Kermia et al., 2016; Lapworth et al., 2012; Murray et al., 2010a; Ngumba et al., 2016; Odendaal et al., 2015; Richards et al., 2021; Rimayi et al., 2018; Sorensen et al., 2015; Subedi et al., 2015; Wanda et al., 2017; White et al., 2019).

The research conducted by (Murray et al., 2010b) showed the frequent occurrence of emerging contaminants such as industrials, pesticides, pharmaceuticals, and personal care products in surface and groundwater and recommends the need to set acceptable daily intake levels for humans. According to (Lapworth et al., 2012) understanding the spatial and temporal variation of EOCs can be used to set a drinking water standard for EOCs. (Lapworth et al., 2019) outlined the process undertaken in Europe to develop a groundwater watch list for emerging organic contaminants to monitor groundwater quality. (Xabadia et al., 2021) mentioned the urgent need for economic research that guides regulating these organic compounds. Moreover, some research showed the use of EOCs to fingerprint sources of contaminants and flow pathways in the groundwater and as a tracer to provide information on catchment pathways and groundwater-surface water interaction (Stuart et al., 2014), a tracer of wastewater (White et al., 2019) and groundwater residence time (Lapworth et al., 2018).

In Africa, these organic compounds are mainly observed in areas where there are poorly protected wells, poor sanitation, and poor household waste disposals (Ngumba et al., 2016; Sorensen et al., 2015), although there have been relatively few studies Africa to date. Some pharmaceuticals used to treat HIV and malaria are more frequently detected in some regions in Africa (K'oreje et al., 2016).

The location of this research is the Awash River basin up to Werer town located in central Ethiopia. With a significant number of small, medium and large-scale irrigation schemes and hosting about 65 % of the country's industries, the Awash River is the most utilized river and the most polluted river in the country (Hague, 2013). The irrigation schemes in the region predominantly utilize

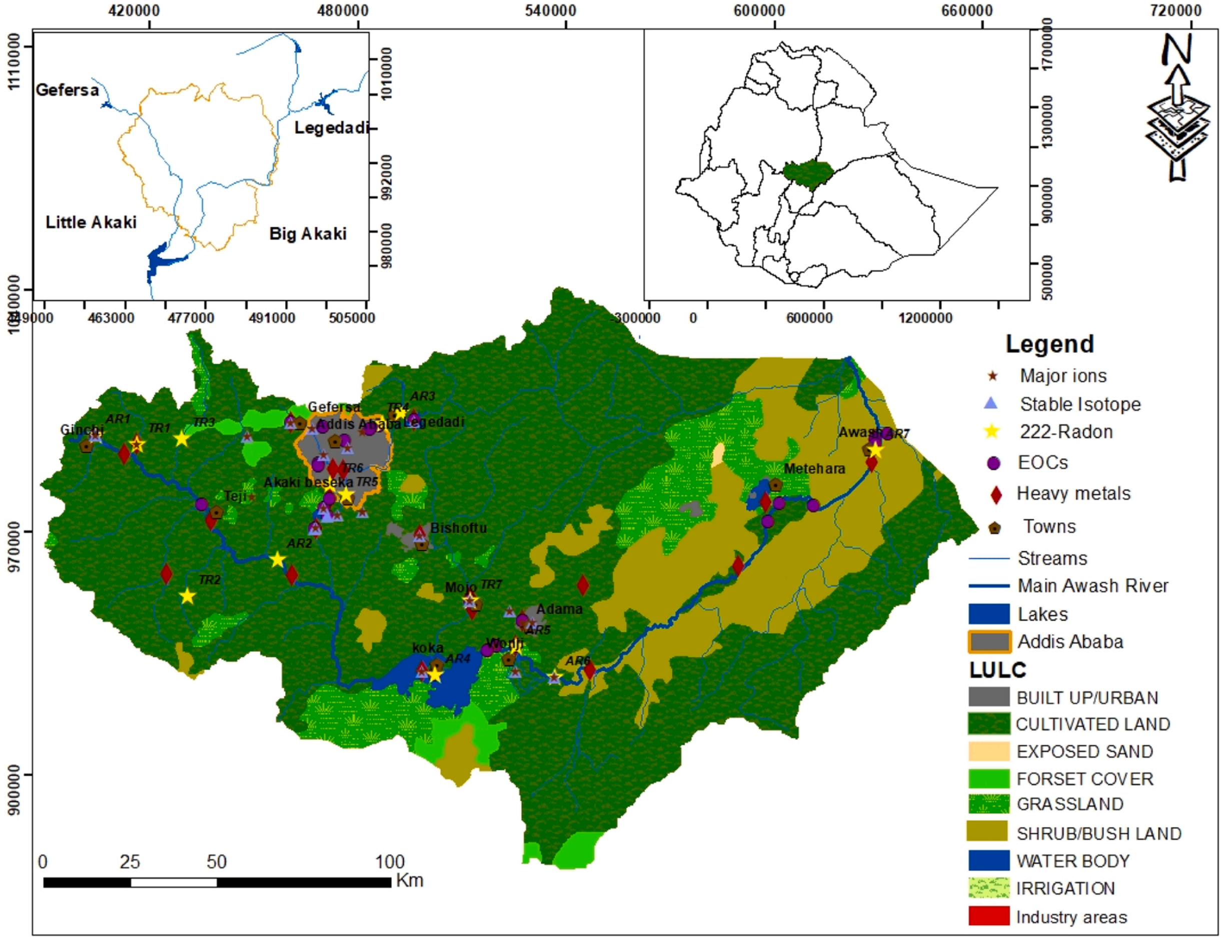

Fig. 1. Location map of the study area with EOCs, Chemical, Isotopes (δ ^{2}H, δ ^{18}O), and ^{222}Rn sampling points (a) and Land use/Land cover map (b).

water diverted from the Awash River. Industries in the area primarily rely on both groundwater and surface water for their water supply. Furthermore, major urban settlements also depend on these sources, utilizing both surface and groundwater for their drinking water needs (Birhanu et al., 2021). However, the water quality in these areas has been significantly compromised. This decline is attributed to several factors: the discharge of untreated industrial wastewater, seepage from agricultural practices, and contamination from urban activities (Colombani et al., 2018; Dessie et al., 2022; A. Keraga et al., 2017; A. S. Keraga et al., 2017; Sonder, 2015; Yohannes and Elias, 2017).

Particularly in Addis Ababa, the capital city of Ethiopia which is situated within the upper reaches of the Awash River Basin (ARB) and upstream of the area under study, the situation is more pronounced. Over 90 % of these industries in Addis Ababa discharge their waste directly into nearby rivers without adequate wastewater treatment processes (Eliku and Leta, 2018; Yohannes and Elias, 2017). This practice contributes significantly to the deteriorating water quality in the region, posing a serious environmental and public health challenge.

Several studies have been done to map the relationship between the Awash River and the groundwater using hydrochemistry, isotopes, and numerical modeling approaches (Ayenew et al., 2008; Azagegn et al., 2015; Birhanu et al., 2021; Demlie et al., 2008; Kebede et al., 2021; Kebede and Zewdu, 2019; Yitbarek et al., 2012). The studies show the Awash River is intimately linked with the groundwater system. Where groundwater-surface water interactions have been observed it is apparent that the pollution of either surface or groundwater resources affects the quality of the other. In some settings surface water bodies gain water and solutes from groundwater systems, in others, the surface water body is a source of groundwater recharge and causes changes in groundwater quality (Winter et al., 1998).

The objective of this study is to undertake a systematic analysis of emerging organic contaminants within the supply sources (both surface and groundwater) and the drinking water taps in the Awash River basin for the first time. In addition to emerging contaminants, analyses of the chemical parameters (major cation, anion, and heavy metals) were done. Integrated approaches of ^{222}Radon and stable isotopes of water molecules (δ^2H, δ^{18}O) were used to track the exchange of contaminants between the surface and groundwater. The results will be used to develop an understanding of EOCs occurrence and fate, the impact of surface-groundwater interactions on pollution fate and inform future water quality monitoring initiatives to protect human and environmental health.

2. Methodology

2.1. Study area

The Awash River Basin (ARB) has a total areal coverage of more than 110,000 km^2 (Hague, 2013; Hemel and Loijenga, 2013). The focus of this study is located within the geographic coordinate of 385384–658532 Easting and 871282–1038597 Northing, with total aerial coverage of about 25,671 km^2 and elevation ranging from 700 to 4150 m.a.s.l (Fig. 1). The land use and land cover is characterized mainly by rain-fed farmland (68 %) and the remaining 32 % by irrigated area, forest cover, shrubland, grassland, and built-up areas (Fig. 1). The rapid expansion of urbanization, population growth, and industrialization observed are the main factors for water quality deterioration in the basin (Assegide et al., 2022; Mcgrane, 2016).

The rainfall pattern is predominantly bimodal, with the heaviest rains beginning in July and continuing through September, while the light rains occur from March to May. Fifteen years of meteorological data (2000–2015) from eighteen stations (Fig. 2) show that the

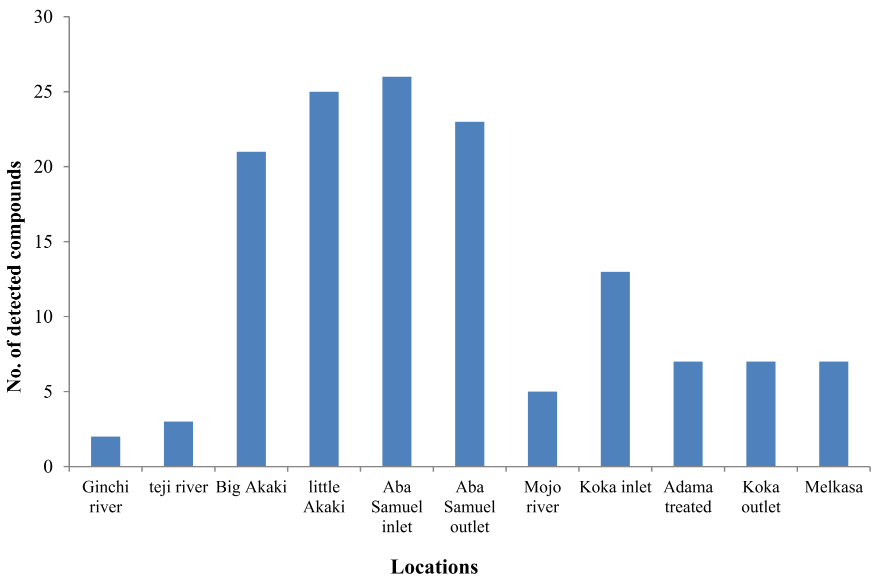

Fig. 2. Number of EOCs detected in the main Awash River and its tributaries using qualitative analytical method.

average annual rainfall and temperature in the upper part of ARB is 994.5 mm and 17° C and the downstream of the study area is 761 mm and 24 °C, respectively.

2.2. Methods

2.2.1. Sampling

Samples from groundwater, Awash River, tap water, and surface water reservoirs were collected for emerging contaminants and chemical analysis. In-situ measurements of electrical conductivity, temperature, and pH were measured at each point where the samples for laboratory analysis were taken. Readings for field parameters (Electrical conductivity, pH and temperature) were obtained prior to sampling groundwater sites. Moreover, samples for stable isotope analysis ($\delta\,^{2}H$, $\delta^{18}O$) from boreholes, river, and surface water reservoirs were collected, and in-situ measurements of a radioactive isotope (^{222}Rn) were done along the course of the Awash River. River water samples were collected by grab sampling from a flowing section of the river. Groundwater samples were collected from existing abstraction boreholes which are in continual use. Tap water samples were collected from the main tap in the building following extensive flushing to ensure to minimize effects of 'standing' water in the pipe network.

Spatial distribution and variety of water sample sources (Awash River, tributaries, shallow and deep groundwater, tap water and surface water reservoirs (Legedadi and Gefersa) were taken into consideration while choosing the sample points. Additionally, due to the vulnerable locations caused by the disposal of wastes from municipality and industries to the river, the sample sites were purposely chosen to represent the major urban settlements (Addis Ababa, Mojo, Adama, Wonji, Metehara, and Awash).

Samples for EOCs were collected using pre cleaned amber glass bottles. The samples were collected in November 2019. Samples were kept in ice box during their transport and sent to the UK for analysis. The analysis was conducted at Agilent laboratories and at the NLS Environment Agency Laboratory (Starcross, UK) using two methods detailed in the following section.

2.2.2. Analysis for emerging organic contaminants

Qualitative non-target screening was undertaken at Agilent laboratories (Cheadle, UK) using an Agilent 1290 Infinity II LC coupled with 6546 LC-QTOF. 900 μL of each sample was added to 100 μL methanol in sample vials to prevent hydrophobic analytes like long chain PFAS sticking to vials, the direct injection volume was 100 μL. Each sample was analyzed twice: once with a positive mode method and once with a negative mode method. Both methods used All Ions, a data-independent acquisition mode with no quadrupole filtering and several different collision energies, including 0 V. Blank samples of ultrapure water from the lab were analyzed alongside each batch. All reported compounds should be considered suspect screening hits. Suspect screening was performed by searching against PCDLs (Personal Compound Databases and Libraries) in the MassHunter Qualitative Analysis (Qual) software using the Find-by-Formula feature.

Positive and negative data files were searched against a large database of all classes of potential contaminants (pesticides, drugs, E+Ls, known water contaminants etc). Positive mode data files were also searched against a smaller plasticisers PCDL, and negative mode data files against a smaller PFAS PCDL. Requirements for suspect hits in Qual were as follows: i) EIC abundance filter – 5000 counts for general screen in positive mode; 2000 counts for targeted plasticizers PCDL and in negative mode, ii) Mass error $<$ 5 ppm, iii) At least one qualifier ion was required (hits with no library spectrum were ignored), iv) Overall score (mass accuracy, isotope pattern + isotope spacing) $>$ 90 %. For each group of samples (tap water, groundwater, river), any compounds that was a suspect hit were added into a method in MassHunter Quantitative Analysis to show the relative abundances of the primary peak in the different samples at the retention time of the suspect hit.

Semi-quantitative analysis was undertaken at the National Laboratory Service (NLS). Solid phase extraction (SPE) was conducted with an automated extraction system using waters Oasis HLB SPE cartridges, which had been conditioned with 6 ml of methanol followed by 6 ml of ultra-high purity water. A 1000 ml water sample was loaded onto the cartridge at a flow rate of 10 ml/min. An isotopically labeled internal standard (Carbutamine-d9) was added to each of the pre-conditioned SPE cartridges to assess instrument performance. After loading, the cartridge was washed with 6 ml of ultra-high pure water and sorbent dried fully with high purity nitrogen, followed by elution first with 6 ml of 0.1 % formic acid in methanol: acetonitrile (1:1) and then with 6 ml of dichloromethane. The eluted fractions were collected in separate vials; with the dichloromethane elute evaporated to incipient dryness under a gentle stream of nitrogen. The corresponding methanol: acetonitrile elute was transferred to the dry dichloromethane vials and evaporated to 100 μL. Ultra-high purity water (900 μL) was added to each vial to a total volume of 1000 μL. The sample was vortex mixed, filtered and transferred to a salinized screw top vial for analysis. Ultra-High Definition Liquid Chromatography / Quadruple-Time-of-Flight Mass Spectrometry (LC/Q-TOF-MS) analysis was performed using a semi-quantitative method on an Agilent Q-TOF (model 6545). This broad screening approach allows for semi-quantitation of $>$ 750 compounds. The compounds were identified by compounds matching database such as Pharmaceutical drugs, pesticides, veterinary drugs, insecticides, herbicides, artificial sweeteners, surfactants, personal care products, plasticizers, flame retardants, and volatile solvents. Hits were confirmed manually by checking retention times and mass fragments. A two-point calibration procedure was used to semi-quantify hits.

Eleven additional samples were collected on December 2022 from the Awash River and its tributaries. The analyses result have been done on LCMS methods and reported as presence or absence of EOCs (qualitative result).

For later comparisons between samples, we grouped organic chemicals into three broad categories; urban, agricultural and industrial sourced organic compounds. Urban contaminants: Pharmaceuticals (equine medications, endocrine disruptors, psychoactive stimulants, drug of abuse, antiviral, analgesic, bactericide, antibiotic, anti-inflammatory, antidepressant, and anticonvulsant) as well as personal care products and artificial sweeteners. Industrial contaminants: solvents, surfactants, plasticizers, and flame retardants are examples from this group. Agricultural contaminants: pesticides, plant growth regulators, fungicides, insecticide, veterinary drugs as well as herbicides and insecticides are included in this group.

2.3. Sampling for chemical analysis

Twenty-four spatially distributed samples for physicochemical analysis were taken from surface water, tap water, surface water reservoirs, and deep and shallow wells with 30 ml Nalgene sample bottles from 27th December to 4th January 2023. Before sampling, sample bottles were washed three times with the water to be sampled at each point. The 0.45-micron filter papers were used to filter the samples in situ and fill the bottles to separate the suspended particles from the samples. For heavy metal analysis, the samples were acidified with nitric acid to pH lower than 2. The samples were then labeled with the descriptive code and sent to the British Geological Survey laboratory, UK within an ice-box on 5th January 2023 for analysis. Major cations, anions, and metals (Cr, Pb, Cu, Ni, and Cd) were analyzed. Cations were analyzed by ICP-MS (Agilent 8900 Triple Quadruple), anions by ion chromatography (Dionex ICS5000 dual line IC). Anion and cation analysis was undertaken using UKAS accredited methods using NIST traceable standards and analysis checked with Certified Reference Materials.

The quality of the analysis was checked according to the principle of electro-neutrality (Cherry, 1979). To preserve electro-neutrality, there must be a balance between cations solution and anions (Hem, 1985). All the sample results are in the acceptable range with an ionic balance error of less than 10 % (Mageshkumar and Vennila, 2020).

2.4. Environmental isotopes (δ^2H, $\delta^{18}O$ and ^{222}Rn)

Twenty samples were collected from Awash River, surface water reservoirs, shallow and deep boreholes with 30 ml Nalgene sample bottles for stable isotope analysis of hydrogen (δ^2H) and oxygen ($\delta^{18}O$). The ^{18}O and ^2H samples were analyzed at the British Geological Survey laboratory using standard preparation techniques followed by isotope ratio measurement on a VG-Micromass Optima mass spectrometer. Measurement precision was within ± 0.1 ‰ for $\delta^{18}O$ and ± 1 ‰ for δ^2H. Stable isotope results are reported as a deviation from Vienna Standard Mean Ocean Water (vs. VSMOW) in per mil (‰) difference using delta (δ) notation.

^{222}Rn is a radioactive noble gas produced from Radium-226 as part of the decay series of Uranium-238 to lead-206 (Cook et al., 2008). ^{222}Rn naturally occurs in higher concentrations in groundwater. Since its half-life is only 3.82 days and degasses when exposed to the surface, it is found in low concentrations in surface water bodies. It is the most reliable radioactive isotope to investigate surface and groundwater interconnection (Cartwright et al., 2017; Cook et al., 2008; Dimova and Burnett, 2011; Freyer et al., n.d.; Kebede et al., 2021; Kebede and Zewdu, 2019; Schmidt et al., 2008). In this study, we used stable and radioactive isotopes to investigate the water and contaminant exchange between the surface and groundwater whenever interactions occur between the two systems.

The ^{222}Rn concentration was measured at 23 sites (tributary streams and main Awash River) (Hailu et al., 2023) with a RAD7 electronic radon detector, fitted with a big bottle system for high sensitivity (Durrige Company Inc 2020). The detection limit of the device is of the order of 40 Bq/m^3. Counting is based on the principle of liquid-gas-membrane extraction (Schubert et al., 2008). An extraction module, which consists of hollow vinyl fibers, allows radon stripping from the water of interest into a connected closed-air loop. The water temperature was measured to convert ^{222}Rn in the air to ^{222}Rn in water. The overall standard deviation varies between 25 % and 30 %, higher for low radon content. Radon counting was conducted for a period of 1 h in four cycles. The first two readings were discarded and the average of the last two readings was taken as the mean ^{222}Rn composition of the specific water point.

3. Result

3.1. Emerging organic contaminants (EOCs)

———— Samples were collected in December 2022 to characterize the contamination pattern in the Awash River and its tributaries. The number of organic compounds detected in the upstream of Addis Ababa at Ginchi area is lower than the downstream of Addis Ababa area (little Akaki, Big Akaki, inlet and outlet of Aba Samuel Lake). Tables of results for the qualitative and semi-quantitative screening are given in the supplementary information (Table S1). Overall, the number of compounds gradually decreased further downstream up to Melkasa except for a slight increase in compound detection at Koka inlet (Fig. 2). Using the qualitative screening method, there were no hits for groundwater samples that met the confirmation criteria.

For the semi-quantitative data analysis of EOCs, more than a hundred different compounds are identified in the seventeen collected samples. EOCs are detected in all water samples collected from all sources including tap water. Pharmaceutical drugs (Caffeine (0.01 μg/l), Atazanavir (0.001–0.0043 g/l), Carbamazepine (0.001–0.0058 μg/l), Cocaine (0.001 μg/l), Ibuprofen (0.001 μg/l), bactericide (0.001–0.0015 μg/l), disinfectant (0.001–0.0015 μg/l), and Acetaminophen (0.005 μg/l) were detected in the Awash River and the tap water samples. Pesticides, veterinary drugs, artificial sweeteners, and personal care products were detected in samples from all sources (surface, ground, and tap water). Endocrine disruptors and equine drugs were found in both surface and groundwater sources.

Several newly identified compounds from industrial uses and urban sourced compounds were identified. Melamine is a newly identified compound in Awash River and Akaki shallow well sourced from industries. Bromoacetonitrile, Dibromoacetonitrile, Acetonitrile, dichloro (industrial sourced compounds) and Iohexol (from urban source) were detected in Awash River samples. Amantadine, Azelaic acid (from urban source) and Benzoylecgonine 1,1-Dimethyle-3-chloropropanol, 2-Methyle-3-bromo-2-butanol, and 1-bromo-2-methyle-2-butanol (from industries) were detected in tap water samples at Addis Ababa condominium sites which sources its water from a self-supply borehole.

The shallow groundwater system is more contaminated with organic compounds than the deep groundwater system (Fig. 3). Atrazine, Boscalid, Dodecamethylcyclohexasiloxane (D6), Sulfamethoxazole, Trinexapac, Saccharin, Acesulfame (Acesulfame-K), Bisphenol S, Diphenhydramine, and Thiabendazole are found in shallow groundwater system whereas Trinexapac, Bisphenol S, and N, N-Diethyl-m-toluamide were found in the deep groundwater system. The number of emerging organic contaminants identified in the deep borehole samples was much lower than samples collected from shallow wells, tap water, surface water reservoirs, and Awash River. The Awash River has the highest number of organic compounds by a factor greater than 2 compared to other water types (Fig. 2). The semi-quantitative EOCs analysis result shows the similarity of detected EOCs at Adama towards Awash town.

At Addis Ababa tap water samples taken at Jemo-1 and Jemo-2 sites (low-cost housing area and sourced from shallow groundwater drilled within the condominium area), the impact of industry and urbanization is more pronounced than in the other tap water samples. Moreover, at Addis Ababa, Paulos tap water which is sourced from the Gefersa reservoir has contamination from a range of different potential sources including industrial, urban and agricultural. At Addis Ababa in the Kotebe and Bole tap water samples, only agricultural contaminants are observed.

EOCs linked to urban and industrial sources were detected in high total concentrations in all water samples as compared to total concentrations from agricultural sources. In the Awash River at Adama sample (31.3 μg/L) and in the tap water sample at Jemo 1

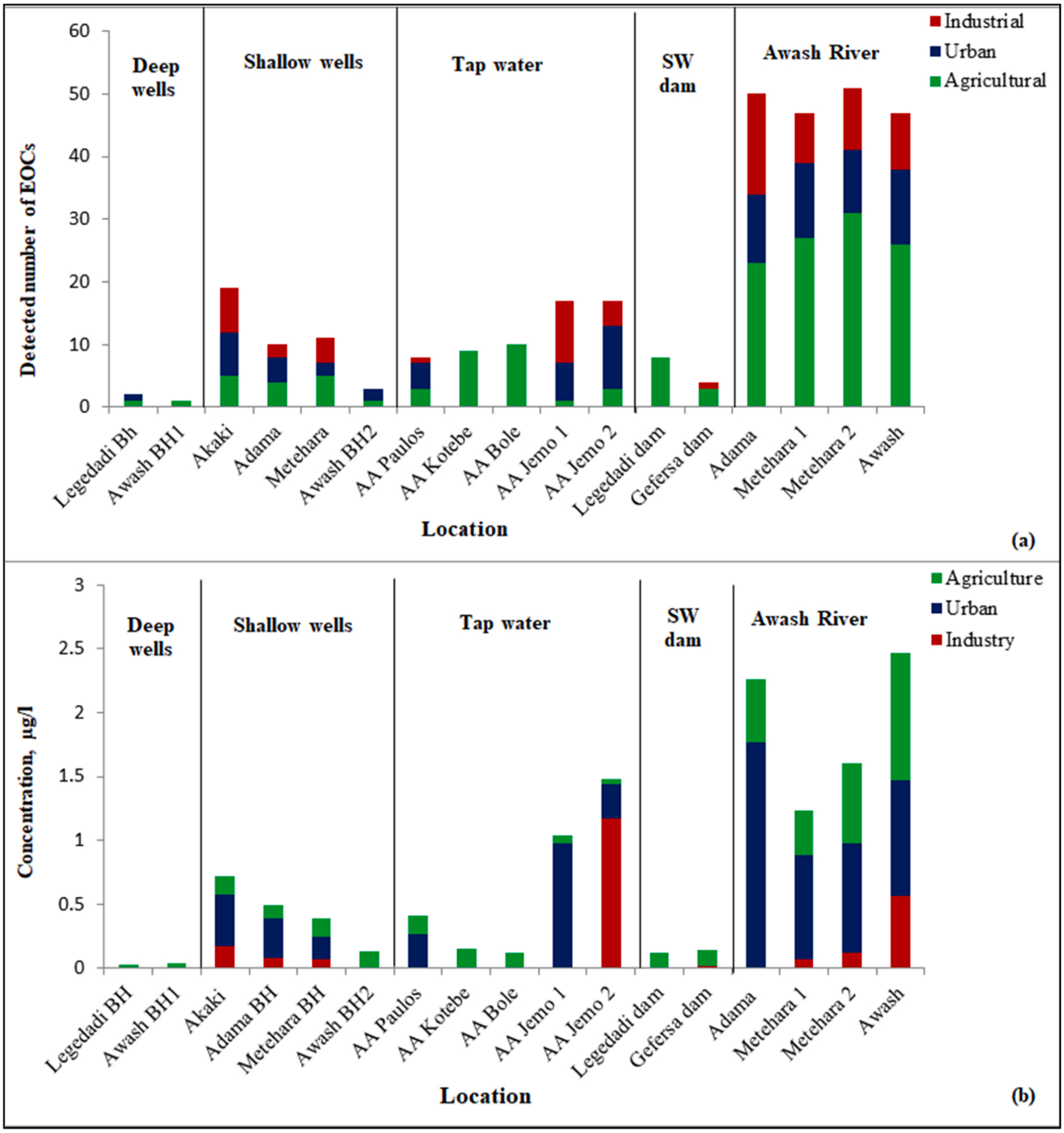

Fig. 3. Number (a) and Concentration (b) of EOCs in all water sample sources detected using the semi-quantitative LCMS method.

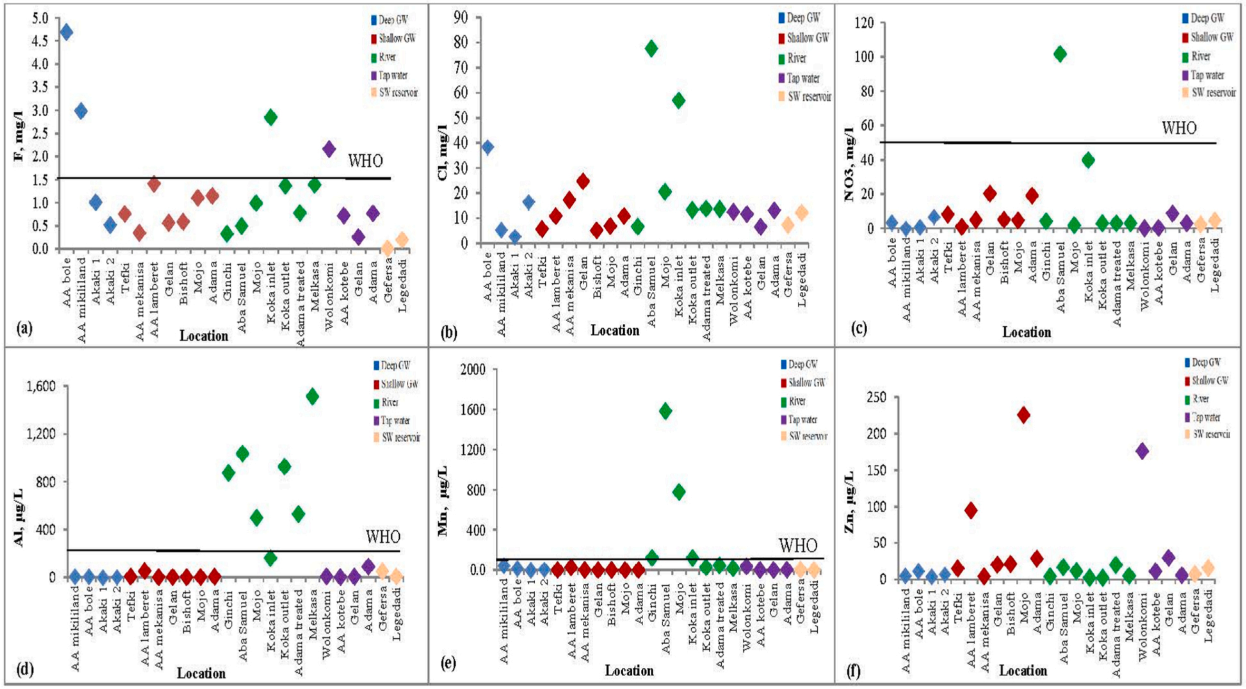

Fig. 4. Concentration of Fluoride(a), Chloride(b), Nitrate(c), Aluminum(d), Manganese(e) and Zinc(f) in different sources (deep, Shallow, River, Tap water, and surface water reservoirs).

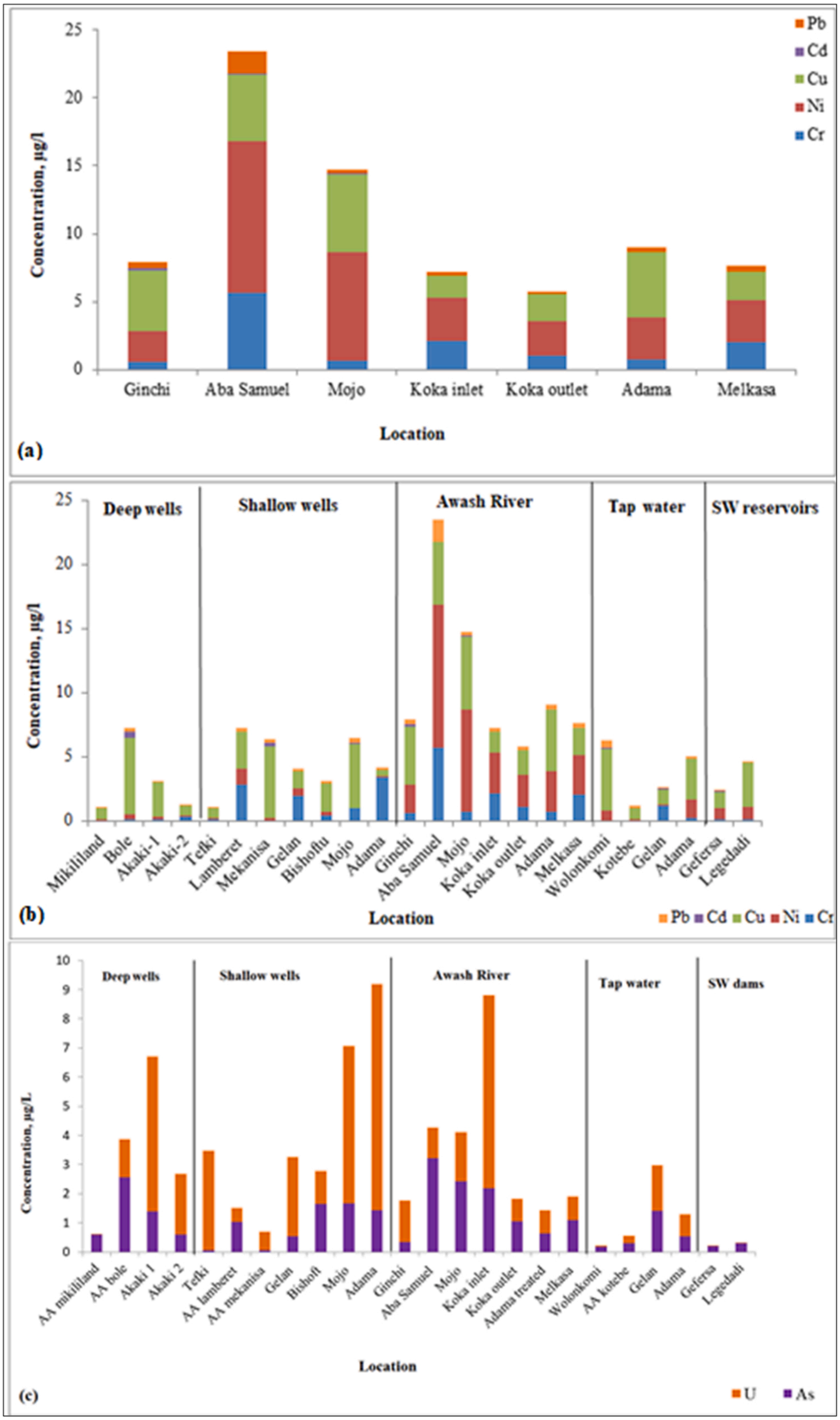

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Fig. 5. Heavy metals concentrations in the Awash River (a), heavy metals concentrations in all water supply sources (b), Uranium and Arsenic concentrations in all water supply sources(c).

(22.2 μg/L) exceptionally high concentration industrial EOCs were detected (Fig. 2b).

The highest concentration of total emerging contaminants from urban sources was observed in Awash River sample at Adama 1.7 μg/L. The concentration of emerging contaminants associated with agricultural usage ranges from 0.03 μg/L at Legedadi reservoir to 0.9 μg/L at Downstream of Awash River (Awash town) (Fig. 2b).

3.2. *Major ion and trace element chemistry*

3.2.1. *Fluoride, chloride, and nitrate*

The concentration of fluoride along the Awash River from upstream to downstream shows an increasing trend except for the relatively high value recorded at the inlet of Koka Dam (2.85 mg/l). In the shallow groundwater system, relatively high concentrations of fluoride are observed in the major cities (Addis Ababa, Mojo and Adama range 1.11–1.41 mg/L) compared to the other shallow groundwater samples (0.35–0.76 mg/L). The deep groundwater samples (2.99–4.69 mg/L) at Addis Ababa City exceeded WHO standard guidelines of 1.5 mg/L. Except for the tap water sample taken upstream of the study area (Wolenkomi: 2.16 mg/L), both surface water reservoirs and tap water had fluoride concentrations that are within WHO permissible limits (Fig. 4a).

The Awash River samples taken at the inlets of Aba Samuel Lake and Koka Dam show higher Chloride concentrations than the other samples. A deep groundwater sample from the Addis Ababa Bole area shows a relative increase in chloride. Chloride concentrations are lower in the other sample sources, which include shallow groundwater systems, tap water, and surface water reservoirs (Fig. 4b).

Nitrate concentrations in the Awash River sample taken at the inlet of Aba Samuel Lake is 102 mg/L, exceeding the permissible limit of WHO guideline (50 mg/L), and a relative increase in nitrate concentration was also noted at the inlet of Koka Dam (39.8 mg/L), compared to the other sample sources (0.02–20.3 mg/L) (Fig. 4c). Shallow groundwater nitrate concentrations were found to be higher compared to deep groundwater (mean 9.05 mg/L and 3.73 mg/L respectively).

The upstream of Awash River samples shows a higher concentration of Mn (122–1583 μg/L) which is above the limit of the new provisional health based guideline value for Mn (80 μg/L) (WHO, 2021), whereas, the samples taken downstream of Awash River from Koka outlet to Melkasa area are under the limit (17.3–47.3 μg/L) (Fig. 6e). Aluminum concentrations in all Awash River samples, with the exception of the inlet of the Koka Dam, are higher value than the WHO allowable limit (200 μg/L) with a range between 499 and 1516 μg/L (Fig. 6d). Zinc concentrations are all below the limit of WHO guideline (5 mg/L), the shallow groundwater system has a substantially higher concentration of Zinc (4.2–226 μg/L) compared to the Awash River samples (2.4–19.9 μg/L) (Fig. 6 f).

3.2.2. *Heavy metals*

Ten heavy metals (Cr, Pb, Cu, Ni, Cd, U, As, Mn, Al and Zn) were selected to be analyzed for this study. Along upstream to downstream of Awash River samples, the concentration of metals increased from Ginchi (upstream) site to Aba Samuel Lake (downstream of Addis Ababa city). Then, a decreasing trend is observed from Addis Ababa to Melkasa, except for the higher concentration of metals observed at the Adama site (the Adama River sample was taken from the Awash River treatment plant from treated water) (Fig. 5a). Comparing the shallow groundwater system with the other sources (surface water reservoirs, Tap water, and deep groundwater system), the concentration of heavy metals is higher in shallow groundwater systems (Fig. 5b).

Except for the higher Awash River uranium concentrations at the inlet of the Koka Dam (6.62 μg/L), the groundwater has a higher concentration of uranium (mean 2.7 μg/L) than the surface water sources (mean 1.88 μg/L, Fig. 6c), but all are below the WHO guideline value of 30 μg/L. The surface water reservoirs (Gefersa and Legedadi dam) that provide water to Addis Ababa city have a

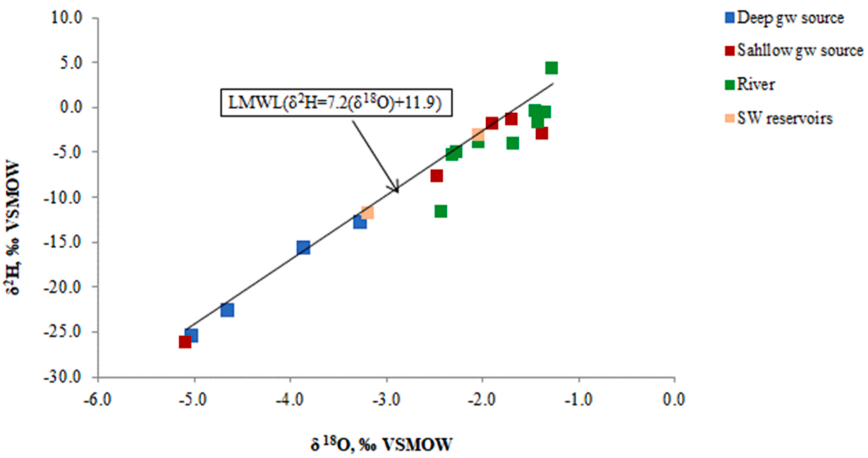

Fig. 6. δ^2H and δ^{18}O plot of samples taken from Deep wells, shallow wells, and surface water reservoirs.

very low uranium concentration (0.008 μg/L and 0.024 μg/L respectively), as shown in Fig. 6c.

Arsenic levels in the Awash River range from 0.032 μg /L to 3.22 μg /L, which is significantly higher than those in the other water sample sources, but below the WHO drinking water limit of 10 μg/L. The surface water reservoirs exhibited reduced arsenic contents (Fig. 6c).

3.3. Environmental isotopes (δ^2H, $\delta^{18}O$ and ^{222}Rn)

3.3.1. Stable isotopes (δ^2H, $\delta^{18}O$)

The isotopic composition of all samples fall close to the Local Meteoric Water Line (LMWL, D=7.2*^{18}O+11.9). Shallow wells and surface water samples showed similar isotopic signatures with high ^{2}H and ^{18}O values for most sites and are enriched (more positive) compared to the isotopic compositions of deep wells (Fig. 6). The ^{222}Rn concentration measured along the Awash River ranges from 20 Bq/L at downstream of the basin up to 1467 Bq/L at upper upstream of the basin (Hailu et al., 2023). Indicating, Awash River and its tributaries in upstream of Addis Ababa city is gaining river, whereas, it is losing downstream of the basin (Fig. 8).

4. Discussion

4.1. Occurrence of emerging organic contaminants and trace elements

EOCs concentration and detection frequency is very high in rivers and the shallow groundwater system of the ARB, but very low in deep wells and surface water reservoirs. The disposal of industrial and municipal wastes without adequate treatment results in a higher number of emerging organic contaminants in the Awash River samples (Fig. 3a).

At Addis Ababa, tap water samples taken at Jemo-1 and Jemo-2 sites (the tap water is coming from shallow groundwater wells drilled within the condominium area) showed the impact of urbanization due to the dense population in the low-cost houses and the industries located nearby. Moreover, at Addis Ababa, the Paulos tap water sample sourced from the Gefersa reservoir is affected by pollutants from urban, industry, and agriculture. As this tap water is sourced from the Gefersa reservoir, it is expected to have the same organic compounds. However, the urban sources of organic compounds are observed due to the pipe network on the path from its source to the tap. At Addis Ababa, the Kotebe sample sourced from the shallow groundwater has only organic compounds sourced from agriculture. Given the area is residential currently; the detected organic compound from the agricultural source can be legacy pollution from agricultural applications because the area has been agricultural land for many years. For the Bole tap water, only agricultural contaminants are observed as its source (Legedadi reservoir) comes from an upstream area surrounded by agricultural land. (Fig. 3a)

Comparing the concentration of EOCs, it can be seen that the Awash River in Adama has a very high concentration of emerging contaminants, likely associated with industrial sources (Total EOCs: 31.3 μ g/L), which is brought on by a number of industries located in the town of Adama. Similar to this, the factories in the immediate vicinity of Jemo area are also a potential source for the higher level of EOCs (Total EOCs: 22.2 μg/L) observed in the tap water at Jemo1. As evidenced by the concentration of EOCs predominately connected to urban sources in the remaining water samples collected from urbanized areas (shallow groundwater samples and tap waters) (Fig. 3b). The Metehara sugar plantation may also be the source of agricultural EOCs, resulting in higher concentrations in the Awash River samples in the Metehara area and Awash town (downstream of Metehara) (Demissie and Gheewala, 2019).

Fluoride and Chloride concentrations are higher in deep groundwater systems due to geogenic sources (Ayenew, 2008; Tekle-Haimanot et al., 2006). Higher measurements were also recorded in rivers and shallow groundwater systems in major cities like Addis Ababa, Mojo, and Adama likely as a result of anthropogenic water pollution (Colombani et al., 2018). A recent study in Addis Ababa city also revealed anthropogenic sources of fluoride intake through food or drinks, which led to significantly raised concentrations of fluoride in urine and in human slurry waste which was linked to higher concentrations of fluoride in the tributary streams of Awash River (Colombani et al., 2018).

Major cations and anions, and some heavy metals, decrease along the Awash River from Addis Ababa city towards downstream settlements, which may have been caused by dilution from several tributary streams (Figs. 6a, 7 and 8a). Other recent studies have shown that stream flows from the escarpment have relatively freshwater quality with low TDS value (Degefu.. and Tigabu, 2013; Kassegne and Leta, 2020; Kebbede, 2016)

4.2. Spatial variation of emerging organic contaminants and heavy metals

The qualitative EOCs results in the Awash River show that there were more organic compounds found in the area downstream of Addis Ababa (n=23) compared to the area upstream of the capital (n=2, Fig. 2), which is related to contamination from municipal and industrial waste discharged into the river in Addis Ababa and neighboring towns. The number of EOCs decreases beyond Aba Samuel Lake, likely due to the lake's attenuation effect for some EOCs.

Similarly, the Koka dam also served to attenuate organic compounds. Higher numbers of organic compounds are present in the Koka Dam inlet than at its outlet. Industrial wastes to the Mojo River contribute to the detection of a greater number of EOCs at the inlet of Koka dam, and declining of EOCs at the outlet of the dam is as a result of the attenuation effect of the dam due to the fact that the dams act as a trap for pollutants in the sediment that accumulated inside the reservoir (Maavara et al., 2020; Watkins et al., 2019), dilution and degradation may also play role.

The semi-quantitative result of EOCs reveals that from upstream to downstream of Awash River (Adama to Metehara towns), the overall number of emerging organic contaminants appeared more or less similar, with observed variation in the sources of organic compounds (industrial, urban and agricultural). Organic compounds associated with industry decreased from Adama towards Metehara because more industries are located in Adama than downstream, while the impact of agricultural contaminants increases at Metehara, which is related to sugar plantations in Metehara. This impact of sugar plantation is also observed in the local shallow groundwater system in the Metehara area, in part due to the connection between surface and shallow groundwater systems (Hailu et al., 2023; Kebede et al., 2021).

With the exception of the low concentrations in the River Awash at Ginchi (Upstream of Addis Ababa) the concentration of heavy metals also displays a general decreasing pattern from upstream to downstream sites. The trend of heavy metal concentration and EOC results are similar; upstream locations (such as Addis Ababa and Akaki) are more heavily contaminated by anthropogenic pollutants than downstream areas. These overall trends broadly reflect the land use changes as you move down the catchment (Fig. 2 and Fig. 6a).

The concentration of heavy metals in the River Awash in the Mojo area is higher, this is likely due to the influence of industry in this region (the Mojo area is known for its extensive industries). Heavy metal concentrations then gradually decrease until Adama (the Adama sample was taken from the Awash River treatment plant, which provides drinking water for Adama city). However, the higher concentration at Adama may be related to the chemicals used to treat the Awash River (Fig. 6a).

The number of detections of EOCs and other chemical parameters upstream of the study area is relatively higher than downstream of the study area. This is likely linked to the expansion of urbanization and industries found in the upstream area which dispose of waste without proper treatment, leading to surface water contamination (Dinka et al., 2015).

4.3. Surface-groundwater Interactions and fate of anthropogenic pollutants

The similarity in emerging contaminant loads between the river and shallow groundwater is attributed to the strong connectivity between the two systems, as evidenced by enriched water isotope signatures (Fig. 7) and ^{222}Rn results (Fig. 8). The shallow well located in Mojo area shows a depleted isotopic signature due to the connection with the regional groundwater recharge system (Hailu et al., 2023). Tap water samples from shallow groundwater sources also had high concentrations of emerging organic contaminants as a result of surface-groundwater interactions. Because of its connection to extensively polluted surface water, the shallow groundwater system typically shows higher concentrations of anthropogenic pollution than the deep groundwater system. This has implications for the vulnerability of shallow groundwater sources, particularly those in hydraulic connection to rivers and suggests that there is minimal EOC attenuation within the shallow groundwater system in close proximity to rivers in alluvial plains; this is consistent with other studies in Africa and elsewhere (Richards et al., 2021; Sorensen et al., 2015).

The shallow groundwater system in Akaki is considerably contaminated with organic pollutants from urban and industrial activities, as depicted in Fig. 2. This contamination is more severe in the Akaki River and its adjacent shallow groundwater within the catchment area than in the downstream locations of Adama and Metehara. The primary cause of this heightened pollution level is the disposal of waste from municipal and industrial sources in Addis Ababa city, which exceeds that in the downstream areas. This situation leads to a direct exchange between the polluted surface water and the shallow groundwater system (Hailu et al., 2023; Kebede et al., 2021), further exacerbating the pollution problem.

The conceptual schematic diagram (Fig. 8) illustrates how urbanization and industry impact the sources of water supply and the flow of contaminants from upstream to downstream. The exchange of contaminants between surface and shallow groundwater systems is verified by the converged evidence by the EOCs and ^{222}Rn values.

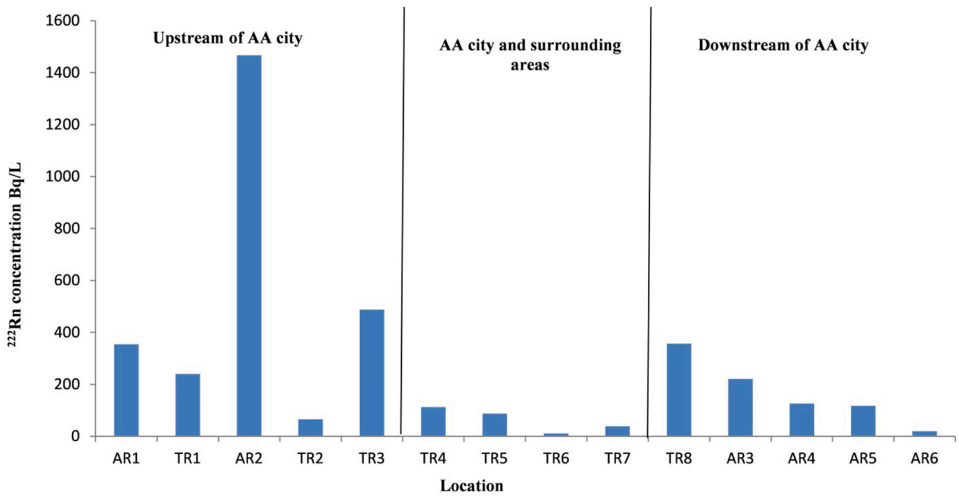

Fig. 7. ^{222}Rn concentration in the main Awash River and its tributary streams from upstream towards downstream of the study area (AR: Main Awash River and TR: Tributary streams).

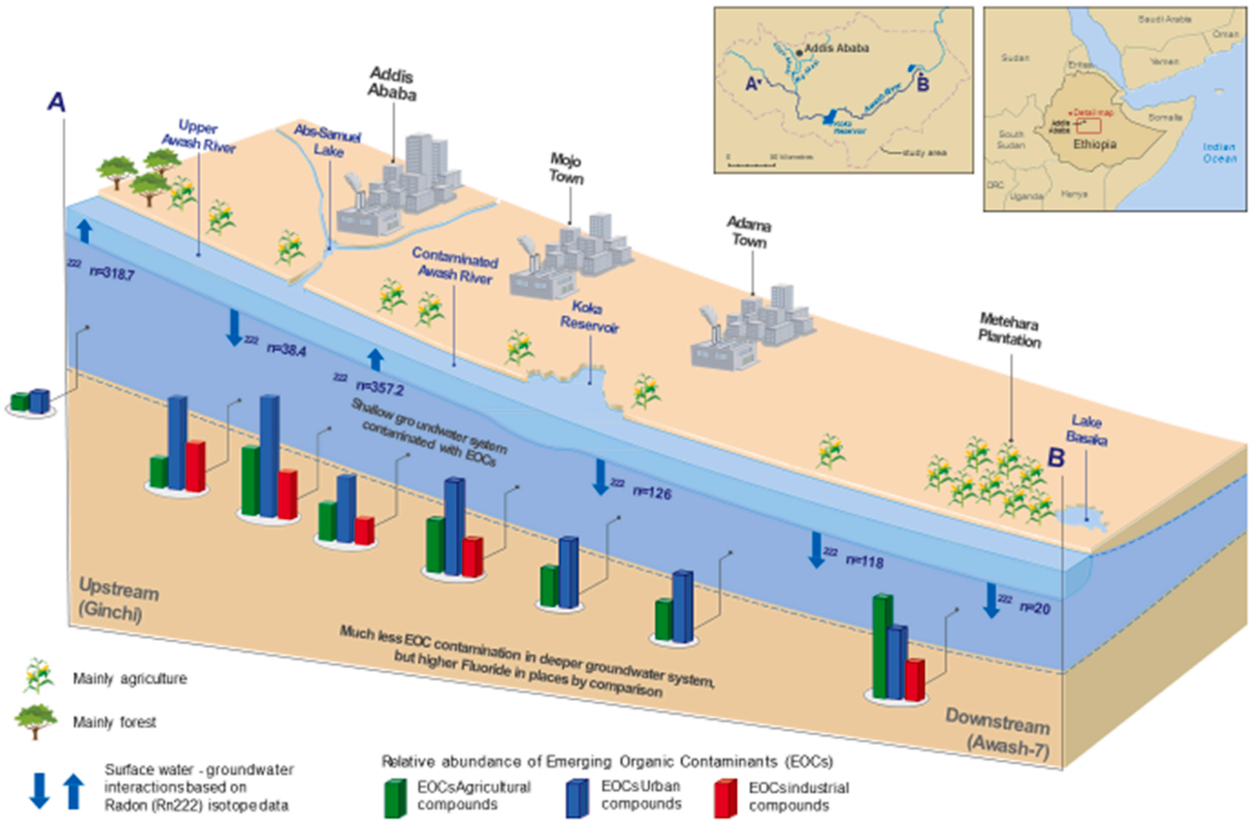

Fig. 8. Conceptual diagram showing pollutions sources (urban, industrial, and agricultural), surface-groundwater interaction (indicated by ^{222}Rn measurements) along the Awash River main course, and relative abundance of EOCs Kidist Hailu, Seifu Kebede, Behailu Birhanu and BGS © UKRI 2023.

4.4. The fate of EOCs and heavy metals

Due to inappropriate industry and municipal waste disposals in Addis Ababa and its suburbs, the little and big Akaki Rivers are well known for being extremely polluted (Assegide et al., 2022; Dessie et al., 2022). Furthermore, the big and little Akaki Rivers converge directly at Aba Samuel Lake, which is where a significant concentration of contaminants is anticipated to be present (Assegide et al., 2022; Dessie et al., 2022; Yohannes and Elias, 2017). As a result, the number of EOCs, the heavy metal concentration and other chemical parameters like nitrate at the Aba Samuel Lake and at Big and Little Akaki Rivers increased significantly (Fig. 2 and Fig. 6).

Besides, artificial infrastructures (such as Koka Dam and Aba Samuel Lake) appear to act as places of attenuation for compounds sourced upstream. Higher numbers of EOCs are observed at the Little and Big Akaki River and Inlet of Ababa Samuel Lake, with the number of EOCs decline at the outlet of Ababa Samuel Lake. A similar pattern is observed at the inlet and outlet of Koka dam. Both infrastructures (Aba Samuel and Koka) have similar impact on other chemical parameters including nitrates (Fig. 5). The higher residence times of surface waters in the dams and physical-chemical and biochemical (sorption and degradation) processes may act to reduce the concentrations and numbers of compounds detected at outlet points.

5. Conclusion

The main objective of this research is to characterize EOCs in the water supply sources (boreholes, river, and surface water reservoirs) and tap water in upstream and downstream of the study area. Chemical parameters are used to validate the water quality status. Environmental isotopes of ^{2}H, ^{18}O, and ^{222}Rn were applied to track the exchange of contaminants between surface and groundwater systems

More than 100 emerging organic contaminants were detected in all water sources (Awash River, tap water, and surface water reservoirs, shallow and deep groundwater). High EOCs are detected in the river and shallow groundwater systems and tap water originated from shallow groundwater systems than the deep groundwater system. The shallow groundwater system is polluted due to the direct connection with the river which is highly contaminated with anthropogenic contaminants from municipalities, industries, and agriculture. The analysis of chemical parameters (major ions and heavy metals) concentration also follows the same pattern as the EOCs, showing that the shallow groundwater system is more contaminated than the deep groundwater system and that this exchange of contaminants between surface and groundwater system is confirmed by the environmental isotope analysis.

Due to the increasing urban population and buildup of industries, the upstream of the area is more contaminated than the downstream sites. Conversely, contamination from agricultural uses is more frequently seen downstream as a result of extensive Metehara plantations. The Koka dam and Aba Samuel Lake seem to serve as points of pollution attenuation. Due to the artificial infrastructures, the downstream of the area is relatively less contaminated than the upstream.

The characterization of EOCs in the water supply sources revealed new organic contaminant concentrations with potential health implications in the water supply sources that have not been previously tested. The contaminants may be associated with hazardous substances for the environment and human health. Therefore, assessing the health effect of EOCs is important for regulating water quality. Moreover, many self-supplied water sources are being used in the ARB due to the rising demand for water that only consider safe water in customary hydro-chemical parameters. However, this research reveals how it's crucial to raise awareness on these emerging organic contaminants. Additional samples for emerging contaminant analysis with seasonal variation will help to identify more organic compounds and be used to understand the seasonal variability impact on loads of EOCs. Furthermore, it will be helpful to collect a sample at the inlet, inside and outlet of the dam (Aba Samuel and Koka dam) and analyze the concentration of the organic compounds to clearly demonstrate how the concentration of organic compounds is affected by the infrastructure due to sedimentation in the dam.

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CRediT authorship contribution statement

Kidist Hailu: Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Seifu Kebede:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Formal analysis, Conceptualization. **Behailu Birhanu:** Writing – original draft, Supervision, Methodology, Formal analysis, Data curation, Conceptualization. **Dan Lapworth:** Writing – review & editing, Resources, Methodology, Formal analysis, Conceptualization.

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. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ejrh.2024.101869.

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