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Occurrence, removal and risk assessment of emerging chemicals in selected rivers and wastewater treatment plants in western Kenya.

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Abstract

Water resources play a crucial role in sustaining life on earth yet chemicals of emerging concern (CECs) arising from extensive human applications are an increasing threat towards their existence. In this study, we examined the occurrence, removal and potential risk of CECs found in rivers and wastewater treatment plants (WWTPs) in western Kenya. Samples were prepared by solid-phase extraction and analysed using high performance liquid chromatography-mass spectrometry with a target list of 785 compounds. Out of these, 333 and 353 compounds were quantified in rivers and wastewater respectively, with pharmaceuticals, industrial compounds, and pesticides being frequently detected in both rivers and WWTPs. Compounds with highest concentrations included saccharin (9.9 µg/L), metformin (7.5 µg/L), and oxypurinol (6.5 µg/L) in rivers whereas caffeine (280 µg/L), deoxycholic acid (179 µg/L), 2-oxindole (10.9 µg/L) and ibuprofen (8.1 µg/L) were found at high concentrations in WWTPs. Based on the crop types, samples from maize growing regions recorded the highest number of pesticides (75) which coincided with the spraying season. The WWTP showed the capacity to eliminate some compounds although the removal efficiencies varied greatly with 204 compounds exhibiting an average removal efficiency exceeding 50%. Based on the risk assessment, crustaceans had the highest potential risk for toxicity with toxic unit (TU) values up to 5.4 driven primarily by diazinon and dichlorvos followed by algae (TU up to 0.07) and fish (TU up to 0.01) in rivers. A similar trend was observed in WWTP with diazinon (TU up to 5.5), diuron (TU up to 0.07) and carbendazim (TU up to 0.006) driving the risk for crustaceans, algae and fish respectively. These findings highlight the significance of surface water and WWTPs as sources and sinks of CECs in the environment translating to potential risks on aquatic organisms and humans.

Keywords: pharmaceuticals; pesticides; land use; removal efficiencies; toxicity

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7 treatment plants (WWTPs) in western Kenya. Samples were prepared by solid-phase extraction and
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9 compounds. Out of these, 333 and 352 (influent 322, effluent 265) compounds were quantified in rivers
10 and wastewater respectively, with pharmaceuticals, industrial compounds, and pesticides being
11 frequently detected in both rivers and WWTPs. Compounds with highest concentrations included
12 saccharin (9.9 µg/L), metformin (7.5 µg/L), and oxypurinol (6.5 µg/L) in rivers whereas caffeine (280
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14 high concentrations in WWTPs. Based on the crop types, samples from maize growing regions recorded
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17 compounds exhibiting an average removal efficiency exceeding 50%. Based on the risk assessment,
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21 and carbendazim (TU up to 0.006) driving the risk for crustaceans, algae and fish respectively. These
22 findings highlight the significance of surface water and WWTPs as sources and sinks of CECs in the
23 environment translating to potential risks on aquatic organisms and humans.

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1.0 Introduction

Globally, over 350, 000 chemicals have been licensed and approved for manufacture and sale (Brack et al., 2022). The production, use and disposal of these chemicals result in their occurrence in the environment. Additionally, these chemicals can be biologically metabolised within an organism or transformed in the environment forming products which consequently increases the number of contaminants in the environment. These chemicals of emerging concern (CECs) include a diverse class of chemicals such as pesticides and biocides, pharmaceuticals, personal care products, industrial chemicals, and human metabolites (Khan et al., 2019; Rasheed et al., 2019).

Wastewater treatment plants (WWTPs) are a major pathway of CECs into aquatic ecosystems (Luo et al., 2014) since they were initially designed to remove conventional pollutants (Ferreiro et al., 2020) and not CECs through primary, secondary, and tertiary treatment processes. These processes have been proven to be inefficient especially for compounds that are hydrophobic with high $K_{ow} > 5$ (Tadkaew et al., 2011) resulting in the release of CECs into the receiving rivers. Additionally, a common occurrence in developing countries is that not all the residents and industries are connected to a WWTP and therefore run off and direct discharge of domestic and industrial wastewater is a major source of CECs in the aquatic ecosystem. Storm water runoffs in residential, agricultural and industrial areas contribute significantly as a nonpoint water pollution source in rivers (Busch et al., 2016).

Several studies have reported CEC occurrence in surface water systems in developed countries (Löffler et al., 2023; Finckh et al., 2024) with limited information from developing countries especially in Africa (Aus der Beek et al., 2016; Fekadu et al., 2019; K'oreje et al., 2020; Okeke et al., 2022). Concentrations of reported CECs varied greatly and ranged from ng/L to as high as g/L (Vasilachi et al., 2021).

Exposure of these chemicals to aquatic organisms result in adverse toxicological effects (Gogoi et al., 2018; Mishra et al., 2023) including changes in ecosystem structure and function (Schuijt et al., 2021), endocrine disruption due to their deleterious effects on endocrine systems (Kumar et al., 2020), acute and chronic toxicity (Wollenberger et al., 2000) and antimicrobial resistance (Arguello-Pérez et al., 2020). Indirect and direct effects of CECs on human health have also been shown. As an example, a study by Becker et al.(2020) found that pesticides in surface water increases the transmission of

schistosomiasis resulting in high prevalence of the disease. Although there has been an increase in studies focusing on the occurrence and risk assessment of CECs in Kenyan aquatic ecosystems, only few compounds have been monitored, in addition, their removals in WWTPs have been limited. This study aimed to fill this knowledge gaps by focusing on i) the identification and quantification of CECs in rivers and wastewater treatment plants in western Kenya, ii) the removal efficiency of the WWTPs in eliminating CECs, and iii) the ecotoxicological risk assessment on three standard test organisms (algae, crustaceans and fish).

2.0 Materials and methods

2.1 Chemicals

Methanol (MeOH), ethyl acetate, water and formic acid (all LC grade) were sourced from Sigma Aldrich. Analytical standards were of highest purity (>98%) and were sourced from various suppliers. A list of internal and analytical standards used in the study is provided in the Supplementary Information (SI A, Table S1).

2.2 Description of study area

The study was conducted in western Kenya covering Trans Nzoia, Uasin Gishu, Kisumu and Nandi counties. The regions experience different agricultural and economic activities, forming the basis of our selection. Maize and wheat are extensively grown in Trans nzoia and Uasin-Gishu counties while tea and rice are predominantly grown in Nandi and Kisumu respectively. The prevalence of Malaria is high in Kisumu county and thus the application and consumption of anti-malarial drugs is expected to be high. Four WWTPs in the region including Nzoia Water Services Company (NZOWASCO), Eldoret Water and Sanitation Company (ELDOWAS), Moi University WWTP (Moi WWTP), and D.L. Koisagat WWTP were selected, and influent and effluent samples collected. A comprehensive description of the WWTPs is provided in the Supplementary Information B, section A. In addition, 6 rivers were selected based on the dominant land use representing five crops: maize (R. Chetoto), wheat (R. Chepkoilel), flowers (R. Marura), rice (R. Miriu) and tea (R. Ndururo) plantations, more information is provided in Supplementary Information B, section A. Water samples were collected from upstream and downstream of the plantation except for R. Sosiani which was sampled before, within and after the

Eldoret town. River Chetoto and R. Sosiani receive effluents from NZOWASCO and ELDOWAS WWTPs respectively.

2.3 Sampling and sample preparation

Sampling was done in May 2022 and a total of eight WWTP samples and 13 river samples collected. In each sampling site, 500 mL grab water samples were collected in pre-cleaned Nalgene bottles and in addition, 1 mL sample water pipetted into a 2 mL amber autosampler vials. For quality control, a trip blank and a sample blank consisting of 1 mL LC grade water was taken as described in Kandie et al. (2020). Samples were transported to the lab at $< 4^{\circ}\text{C}$ in a cool box containing ice packs and transferred to -20°C freezer awaiting sample preparation the following day. The samples were filtered through 50 mm glass fibre filters (Whatman GF/F) with a pore size of $0.7\ \mu\text{m}$ using a vacuum filtration pump (Rocker Chemker). Prior to solid-phase extraction (SPE), HR-X cartridges containing 200 mg sorbent (Milford, USA) were conditioned using 5 mL of MeOH, 5 mL of ethyl acetate and rinsed with 10 mL of water (all LC grade). Thereafter, 350 mL of river samples and 400 mL of WWTP samples were extracted at a flow rate of 5 mL/min. After extraction, the cartridges were air dried for 30 minutes using the vacuum manifold and stored at -20°C awaiting elution. Elution of the samples was carried out into 20 mL amber glass vials using solvents starting with 5 mL of ethyl acetate, followed by 5 mL of MeOH, 4 mL of MeOH containing 1.0 vol% of formic acid, and 4 mL of MeOH containing 2.0 vol% of 7N ammonia. The eluate was thereafter evaporated using a gentle stream of nitrogen gas (99% purity) to a final volume of 1 mL. The samples were then filtered through $0.2\ \mu\text{m}$ PTFE syringe filters (Whatman) into 2 mL amber glass vials, dried using nitrogen stream and then reconstituted with methanol (LC-MS grade) to a volume of 350 μL and 400 μL for river and wastewater samples, respectively (enrichment factor (EF-1000)). The samples were finally vortexed for 2 minutes to ensure thorough mixing prior to instrumental analysis.

2.4. Instrumental analysis

2.4.1 Solid Phase Extracted samples

Instrumental analysis was performed as described in Finckh et al. (2022). Briefly, 50 μL of the enriched sample extract (EF1000) was taken and MeOH (15 μL), water (30 μL) and 5 μL of an internal standard

(1 µg/mL, containing 48 isotope-labelled compounds) added prior to instrumental analysis. Eleven matrix-matched calibration were prepared by spiking Wormsgraben water obtained from the Harz Mountains, Germany with isotope labelled compounds from levels of 0.5 ng/L to 1000 ng/L, before extracting in the same procedure as the samples. An aliquot (5 µL) of the sample was injected into the Thermo Ultimate 3000 LC system coupled to a QExactive Plus high-resolution mass spectrometer (LC-HRMS, Thermo) with separate runs in negative and positive electrospray ionization modes. Chromatographic separation in both modes utilized a Kinetex Biphenyl LC column (100 x 2.1 mm, 2.6 µm particle size Phenomenex) equipped with an inline filter and a pre-column (5x 2.1 mm) at a temperature of 40 °C. The HRMS analysis involved a full scan acquisition (m/z 80-1200) at a nominal resolving power of 70,000 along with six data-independent acquisition scans (m/z 80-182, 178-282, 278-382, 378-482, 478-682, 682-1200) at a nominal resolving power of 35,000.

2.4.2 Direct injection samples

This was performed for the 1 mL water samples and quality control samples. Methanol (25 µL), internal standard containing 48 isotope labelled standards (40 ng/mL; 25 µL) and 10 µL buffer (2M ammonium formate of pH 3.5) was added to the samples prior to instrumental analysis. Thirteen matrix-matched calibration standards spiked at levels ranging from 1-10,000 ng/L were prepared using 1 mL aliquots of the Wormsgraben water and processed the same way as samples. Aliquots of 100 µL were injected into the LC-HRMS (QExactive Plus, Thermo) and analysed the same way as SPE extracted samples described above.

2.5. Data analysis

Peak detection and identification of target compounds was done using MZmine (Version 2.38, Pluskal et al., 2010) and MSconvert by first converting the raw data to mzML format (Proteowizard version 3.0.18265) (Chambers et al., 2012). Subsequently, the detected target compounds were processed using MZquant (R Package, version 0.8.3) and Trace Finder 5.1 (Thermo Scientific) as performed by Beckers et al. (2020). Method detection limits (MDLs) were established based on replicate injection of the calibration standards as outlined in U.S EPA guidelines (U.S. EPA, 2016). Graphical representation

132 and statistical analysis were performed using R Software version 4.2.1 and Origin2024 SR1 version
133 10.10.178.

134 **2.6 Removal efficiency**

135 Removal efficiency was calculated using Equation 1, as applied by (Golovko et al., 2021; Khasawneh
136 & Palaniandy, 2021; Li et al., 2019).

137
$$Removal\ efficiency = \frac{([C_{influent}] - [C_{effluent}])}{[C_{influent}]} \times 100$$
 Equation 1

138 Where, $C_{influent}$ and $C_{effluent}$ represents the concentration of compound detected in the influent and
139 effluent respectively for each WWTP.

140 **2.7 Risk assessment**

141 To assess the potential risk of the detected compounds on organisms, Toxic Unit (TU) approach was
142 used for each trophic level (fish, crustaceans and algae). TU is defined as a ratio obtained by dividing
143 the measured environmental concentration (MEC) of a specific compound by the effect concentration
144 values (EC_{50}) (Equation 2). The effect values were extracted from ECOTOX database and applied as
145 described by Finckh et al. (2022) . All used EC_{50} values are provided in Supplementary Information A
146 (Tables S6, S7 and S8)

147
$$TU = \frac{MEC}{EC_{50}}$$
 Equation 2

3.0 Results and discussion

3.1 Compound detection frequencies in rivers

A total of 333 compounds were detected in rivers (SI A, Table S2). Eight compounds namely; trimethoprim, amantadine, atrazine, quinoline n-oxide, tetrabutylammonium, 2-amino-3-methylpyridine, zearalenone, and octyl-methoxycinnamate were detected in all the sites (Figure 1).

Among the pharmaceuticals, anti-hypertensives (bisoprolol and pravastatin) and antibiotics (trimethoprim, acetyl-sulfamethoxazole and sulfamethoxazole) were detected up to 100% (Figure 1).

The frequent detection of bisoprolol could be attributed to the prevalence of hypertension in Kenya which has been detected in frequencies up to 50% (Syed et al., 2018). Pesticides including imidacloprid, atrazine, terbuthylazine and metolachlor, and the transformation products of metolachlor (metolachlor OA and metolachlor ESA) were detected in more than 60% of the sites. The frequent detection of herbicides could be linked to the extensive application within the study area which also coincided with the sampling time. Industrial compounds such as quinoline N-oxide, tetrabutylammonium and 2-amino-3-methylpyridine were ubiquitously detected (up to 100% detection) and in high numbers (146). To the best of our knowledge, this study reports for the first time the presence of human metabolites (bile acids) in the study area and these included 7-oxolithocholic acid, cholic acid, deoxycholic acid, and chenodeoxycholic acid with frequencies up to 92%. These compounds are used as a biomarkers of faecal contamination in rivers (Elhmmali et al., 2000).

3.2 Compound concentrations in rivers

Individual pharmaceutical concentration ranged from below method detection limit ($< \text{MDL}$) to 7.5 $\mu\text{g/L}$ and this was reported for the antidiabetic drug metformin (Figure 2). This compound is commonly used in the management of diabetes and is excreted in its parent form (Bradley et al., 2016). The antifungal fluconazole and antibiotic oxytetracycline had maximum concentrations of 306 ng/L and 260 ng/L respectively (SI A Table S2). Fluconazole exceeded the predicted no effect threshold (250 ng/L) for antimicrobial resistance (Bengtsson-palme & Larsson, 2016) suggesting the potential development of resistance. To the best of our knowledge, we report for the first time the antiviral emtricitabine (856 ng/L) in Kenyan surface water.

Pesticide concentrations ranged from <MDL to 1521 ng/L with amitrole and metolachlor being reported above 1 µg/L (Figure 2). Carbendazim, carbofuran, and diazinon were detected with maximum concentrations of 134 ng/L, 47 ng/L and 54 ng/L respectively. These compounds have been banned in Europe (Pesticides Action Network Europe, 2020) but still find their way to the Kenyan markets and are frequently detected in the Kenyan aquatic environment (K'oreje et al., 2020; Kandie, et al., 2020). Artificial sweeteners (AS) including saccharin, cyclamate, acesulfame and sucralose were detected with concentrations of up to 9.9 µg/L, 4.0 µg/L, 3.1 µg/L, and 0.6 µg/L respectively. High concentrations of AS were detected in two of our study sites (Rivers Sosiani and Chetoto) and could be linked to effluent discharges from WWTPs which drain into the rivers. Similar trend in concentration of AS were reported in Nairobi river (Sumida et al., 2024). Other industrial compounds included lubricants such as methyl diethanolamine (2.8 µg/L), perfluoropropanoic acid (2.4 µg/L), TMDD, perfluorobutanoic acid (2.3 µg/L), 2,2,6,6-tetramethylpiperidin-4-ol (1.9 µg/L) and triethylene glycol monobutyl ether (1.1 µg/L) which could be attributed to the indiscriminate washing of motorcycles and cars along the rivers and storm water drain from urban areas.

3.3 The influence of crop type in contamination of rivers by pesticides

Based on the crop types, the maize growing regions had the highest median concentrations of pesticides in the upstream (2.7 µg/L) and downstream (4.9 µg/L) of R. Chetoto with herbicides (41) and insecticides (24) being mostly detected. Amitrole had the highest concentration in the upstream (1521 ng/L) whereas metolachlor (1069 ng/L) was detected downstream of R. Chetoto (SI A, Figure S1). These compounds were previously reported to have positive correlation between their use and concentrations in surface water (Stackpoole et al., 2021). River Miriu, which is in rice growing fields, had upstream and downstream sum concentrations of 66 ng/L and 374 ng/L respectively, which was greatly contributed by concentrations of imidacloprid, metalaxyl and carbendazim. The river is a source of drinking water for the local community and yet concentrations of metalaxyl (130 ng/L) and imidacloprid (148 ng/L) exceeded the threshold for water quality for human consumption set at 100 ng/L (Manjarres-López et al., 2021). Contrary to maize and rice plantations, River Ndururo located in the tea plantations had the least (6) number of compounds and sum concentration up to 8 ng/L. This is

in line with the findings from Kandie et al. (2020) who found surface water in tea growing areas less polluted. This could be attributed to the lower utilization of pesticides among tea growers and the presence of buffer zones between tea plantations and the rivers. Similarly, lower concentrations were found in wheat areas as the wheat growing season had not started thus a mismatch between sampling and spraying season. The upstream notable concentration could be linked to other agricultural practices and untreated household waste connected to the rivers upstream.

The hierarchical clustering revealed several clusters (Figure 3) based on the compounds that were commonly detected in more than three rivers. The first cluster (a) comprised of metolachlor, terbuthylazine, atrazine and transformational product desethylatrazine which were detected in three rivers (R.Chetoto, R.Chepkolel and R.Sosiani). These rivers are situated in maize and wheat growing areas where metolachlor and terbuthylazine are predominantly used (Karlsson et al., 2020; Kruć-Fijałkowska, 2022). Metolachlor and terbuthylazine easily degrade to their transformation products (metolachlor ESA (ethanesulfonic acid) and terbutylazine-2-hydroxy) respectively forming (cluster b), are weakly adsorbed into the soil, increasing their mobility to surface water (Nagy-Kovács et al., 2018) were detected in R.Chetoto, R.Chepkolel and R. Marura. Another interesting cluster was that of insecticides carbendazim and imidacloprid (cluster c) that were detected in R. Chetoto, Miriu and Sosiani. The presence of these insecticides can be linked to their extensive use in rice and maize growing farms (Negi et al., 2014; Singh & Kaur, 2018)

3.4 Compound detections in WWTPs

Pharmaceuticals, personal care products, and industrial chemicals were detected in the WWTP samples with pharmaceuticals having the highest number of compounds detected (102 compounds, SI A Table S3). Two hundred and fifty-one (174) of the detected compounds were found in more than 50% of the influent samples and included TMDD, 2-oxindole, dichlorvos, atrazine, diazinon, diuron, carbendazim, trimethoprim which were detected in all the WWTPs (SI A Table S4).

The high detection of trimethoprim could be linked to its use in management of a broad spectrum of bacterial infections, as well as daily prophylaxis in HIV-infected adults (K'oreje et al., 2018; Chiller et al., 2009). Trimethoprim is commonly used in combination with sulfamethoxazole to treat various

bacterial infections (K'oreje et al., 2018). Sulfamethoxazole, which is normally administered in combination with trimethoprim as co-trimoxazole was detected at a lower frequency (75%) compared to trimethoprim and could be attributed to sulfamethoxazole metabolism to acetyl-sulfamethoxazole which also had a detection frequency of 75%. The high frequency of detection of antibiotics (up to 100%) and NSAIDs (up to 88%) (SI A Table S4) can be attributed to their easy accessibility as an over the counter drug and have been frequently detected in African wastewater (K'oreje et al., 2020; Necibi et al., 2021). The low detection of psychiatric drug flupentixol can be associated with the low prevalence rate of schizophrenia in sub-Saharan Africa, and its low daily dosage (maximum. 3mg daily) prescription (Mamah et al., 2021).

For pesticides, atrazine, diazinon, dichlorvos, imidacloprid-urea, metolachlor, and terbutylazine registered 100% detection frequency (Figure S4). The presence of pesticides in WWTPs is could be due to their use in households for pest control (Powell & Cuthbertson, 2013). Furthermore, WWTPs receive wastewater from sources such as slaughterhouses, where residues from veterinary medicines and products used in animal husbandry (Kolar et al., 2015). The neonicotinoids acetamiprid, imidacloprid and thiamethoxam registered a considerable high detection frequency >50% which could be attributed to their extensive use in the region (PCPB 2018). Industrial chemicals 2,2-dihydroxybiphenyl, 2-hydroxyquinoline, 2-oxindole, 4-(4-hydroxyphenyl)-butan-2-one, quinoline N-oxide, TMDD and Triethylene glycol monobutyl ether were detected in all the WWTPs showing their ubiquitous nature.

High detection (100%) of CECs in the WWTP effluent was observed for compounds including, carbendazim, diuron, TMDD, diazinon, trimethoprim, cetirizine, 2-oxindole, triethylene glycol monobutyl ether, and terbutylazine (SI B, figure S2). The low log K_{ow} (2.8) and biodegradability of 15.7% after 57 days and retention time of 10 days (Guedez et al., 2010; Blum et al., 2018) could explain its high detection frequency of TMDD in the effluents. The pesticide imidacloprid undergoes biodegradability in WWTPs treatment processes to form imidacloprid-urea, and imidacloprid-guanidine (Gautam & Dubey, 2022), which had 75% detection frequency in this study. Low detection

frequency (25%) was also observed for venlafaxine-o-desemethyl, clarithromycin, bisphenol B,1-naphthol, diclosan, fipronil and its metabolites fipronil desulfinyl, and fipronil sulfide.

3.5 Compound concentrations in WWTPs

Stimulants had the highest influent concentrations (up to 830 µg/L) across all the WWTPs, followed by industrial chemicals (up to 28 µg/L), pharmaceuticals (up to 8.9 µg/L) and pesticides (up to 5.6 µg/L). In the influent, caffeine registered the highest concentration at 830 µg/L, likely due to increased consumption of caffeinated beverages. Caffeine is a common active ingredient found in most soft and energy drinks including tea which is majorly consumed in Kenya with 41 million kilograms sold domestically in 2022 (Egunjobi & Asatsa, 2022). The human metabolites deoxycholic acid (179 µg/L), cholic acid (149 µg/L), 7-oxolithocholic acid (55 µg/L), and chenodeoxycholic acid (44 µg/L) were also detected at high concentrations in the influent (Figure 4, SI A Table S4).

Pharmaceuticals such as ibuprofen (8.1 µg/L), trimethoprim (5.7 µg/L), cetirizine (5.7 µg/L) and fluconazole (2.5 µg/L) also exhibited notable influent concentrations. Pesticides and biocides exhibited varying concentrations from <MDL to 5.6 µg/L across the WWTPs. Dichlorvos, an organophosphorus insecticide was detected at concentrations up to 5.6 µg/L and could be linked to its extensive utilization in pests control within households (USEPA, 2000).

In the effluent, caffeine concentration was the highest with 170 µg/L followed by sucralose (3.5 µg/L), TMDD (1.4 µg/L), dichlorvos (1.1 µg/L), and cetirizine (827 ng/L). TMDD has been reported in previous studies to be persistent during WWTP treatment processes resulting to its partial discharge into the environment in a concentration ranging from <MDL- 5.8µg/L (Blum et al., 2017; Guedez & Püttmann, 2011). High concentration of sucralose in the effluent has been linked with its high-water solubility, its chemical and biological stability (Yang et al., 2021). 10,11-dihydro-10,11-dihydroxycarbamazepine, a metabolite of carbamazepine utilized in the management of epilepsy and bipolar disorder, was found at high concentrations (1.5µg/L), along with acetyl-sulfamethoxazole (1.2 µg/L) usually excreted in urine (Göbel et al., 2004).

3.6 Removal efficiency of CECs in wastewater treatment plants

Removal efficiencies varied greatly with 204 compounds exhibiting an average removal efficiency above 50%, (SI A Table S5). Figure 5 shows removal efficiencies of selected compounds from each compound class.

Based on the removal efficiencies, the compounds were divided into two groups: positive removal efficiency for compounds with effluent concentrations lower than the influent concentrations and negative removal efficiency for compounds with effluent concentrations higher than influent concentrations. A total of 286 had positive removal efficiencies while 67 had negative removal efficiencies. (SI A Table S5). Positive removals above 80% were observed for NSAIDs (ibuprofen, diclofenac), antibiotics (trimethoprim, sulfamethoxazole), industrial chemicals (2-oxindole, TMDD, 4-chlorophenol), and pesticides (diazinon, methylparaben, and 4-(2,4-dichlorophenoxy) butyric acid) (Figure 5). Compounds such as diclofenac, methylparaben, ibuprofen, and trimethoprim displayed removal efficiencies exceeding 95% which was consistent with previous studies (Carazo-Rojas et al., 2018; Khasawneh & Palaniandy, 2021; Ofrydopoulou et al., 2022). Biosorption, bioaccumulation, photodegradation and biodegradation processes employed in the WWTPs aided their high removal efficiencies. Caffeine and nicotine exhibited high removal efficiencies up to > 99 % and could be attributed to their high biosorption and biodegradation abilities (Golovko et al., 2021; Rigueto et al., 2020). Negative removals were obtained for 67 compounds including 10,11-Dihydro-10,11-dihydroxycarbamazepine, 2-hydroxyatrazine, terbuthylazine-2-hydroxy, azithromycin, carbamazepine, primidone, and bisphenol Z. Increased compound concentrations in the effluent could be explained by their fate including transformation of metabolites excreted by humans (mainly conjugates) to parent compounds and partitioning from solid phase into the aqueous phase (Golovko et al., 2021; Jelic et al., 2011; Ofrydopoulou et al., 2022). It could also be attributed to the sampling time since the samples were taken at the same time hence representing different portions of wastewater and did not consider differences in residence time. Additionally, compound concentrations close to the method detection limits could introduce uncertainties in calculation of the removal efficiencies (Golovko et al., 2021; Ort et al., 2010).

306 Among the WWTPs, NZOWASCO had the highest (126) number of compounds which exhibited 100%
307 removal efficiencies, followed by ELDOWAS (105 compounds), Moi WWTP (60 compounds) and
308 D.L. Koisagat with (12 compounds). The high number of compounds with > 99% removal efficiencies
309 in NZOWASCO can be as a result of environmental factors such as sunlight and temperature in the
310 region which promotes photodegradation and biodegradation processes. Disparities in removal
311 efficiencies can also be attributed to differences in plant design, technologies, and treatment
312 methodologies employed across the various WWTPs (K'oreje et al., 2018; Ofrydopoulou et al., 2022).
313 For example, the high number of positive removal efficiency compounds in ELDOWAS could be
314 attributed to the implementation of trickling filters applied in the treatment process.

315 **3.7 Risk assessment**

316 **3.7.1 Risk assessment in rivers**

317 Among the organisms, crustaceans had the highest potential risk for acute toxicity (TU_{sum} 8.6), followed
318 by algae (TU_{sum} 0.29) and fish (TU_{sum} 0.03) (SI A, Table S9, S10 and S11). The TU values for
319 crustaceans ranged from 4.43×10^{-12} to 5.4 with diazinon being the compound driving this risk (Figure
320 6). Other compounds including dichlorvos, pirimiphos-methyl, imidacloprid and salicylic acid
321 exceeded the acute risk threshold (ART; TU 0.1) as set by Malaj et al. (2020). Diazinon has been
322 previously associated with adverse inhibition of cholinesterase enzyme activity (Santos et al., 2022;
323 Siregar et al., 2021) in *mytella charruana*. For algae, TU values ranged from 5.11×10^{-11} to 6.96×10^{-2}
324 with the herbicide diuron (TU 0.07) driving this risk. Terbutylazine (TU 0.06), triclosan (0.04),
325 dichlorvos (TU 0.04), and metolachlor (TU 0.03) exceeded the chronic risk threshold (TU 0.02). Diuron
326 and terbutylazine have been previously reported to be very toxic to algae causing inhibition of
327 photosynthesis (DeLorenzo & Fulton, 2012; Sbrilli et al., 2005). Unlike in crustaceans and algae, the
328 risk towards fish was considerably lower and ranged from 3.6×10^{-12} to 0.012. The risk towards fish
329 was found to be driven by carbendazim which also exceeded the chronic risk threshold (CRT, TU 0.01).
330 Carbendazim has been previously reported to induce indicative stresses and gulping of air in Zebrafish
331 (de Oliveira et al., 2024).

332

3.7.2 Risk assessment in WWTP effluents

Crustaceans had the highest potential risk of toxicity (TU_{sum} up to 9.6), followed by algae (TU_{sum} up to 0.5) and fish (TU_{sum} up to 0.06) (SI A, Table S12, S13 and S14). Diazinon (TU 5.5) and dichlorvos (TU 4.6) were responsible for the risk in crustaceans (Figure 7) and exceeded the acute risk threshold (TU 0.1) (Malaj et al., 2020). Diuron has been reported to cause changes in feeding behaviour and oxidative stress when exposed to *Tigriopus japonicus* (Yun et al., 2023). Dichlorvos (TU up to 0.07), diuron (TU up to 0.07), and terbuthylazine (TU up to 0.03) were driving the risk for algae and exceeded the CRT (0.02) whereas didecyldimethylammonium (TU up to 0.009), carbendazim (TU up to 0.006) and dichlorvos (TU up to 0.005) were driving the risk for fish but were below the CRT (0.01)

4.0 Conclusion

This comprehensive study shows that rivers and WWTPs are potential sources and sinks of emerging contaminants in the study area. Pesticides and biocides, pharmaceuticals and industrial compounds were frequently detected with concentrations up to 9.9 $\mu\text{g/L}$ (saccharin) in river samples and up to 280 $\mu\text{g/L}$ (caffeine) in WWTP influent. Antifungal fluconazole exceeded the predicted no effect threshold (250 ng/L) for antimicrobial resistance indicating potential risk for antibiotic resistance development within the aquatic ecosystem. The removal efficiencies of the WWTPs varied with ibuprofen, trimethoprim, and sulfamethoxazole being completely eliminated while others including 10,11-Dihydro-10,11-dihydroxycarbamazepine and cetirizine were recalcitrant. Diuron and diazinon were the risk drivers for algae and crustaceans respectively in both the rivers and the WWTPs. Lower but substantial risk was found towards fish in both surface water and WWTP effluent. This study aided to close the data gaps on emerging contaminants in Kenyan aquatic ecosystems and their elimination during WWTP treatment process. There is need for more studies to focus on antimicrobial resistance and effect of seasonal variation which will contribute towards data-based policy formulation and implementation in the region.

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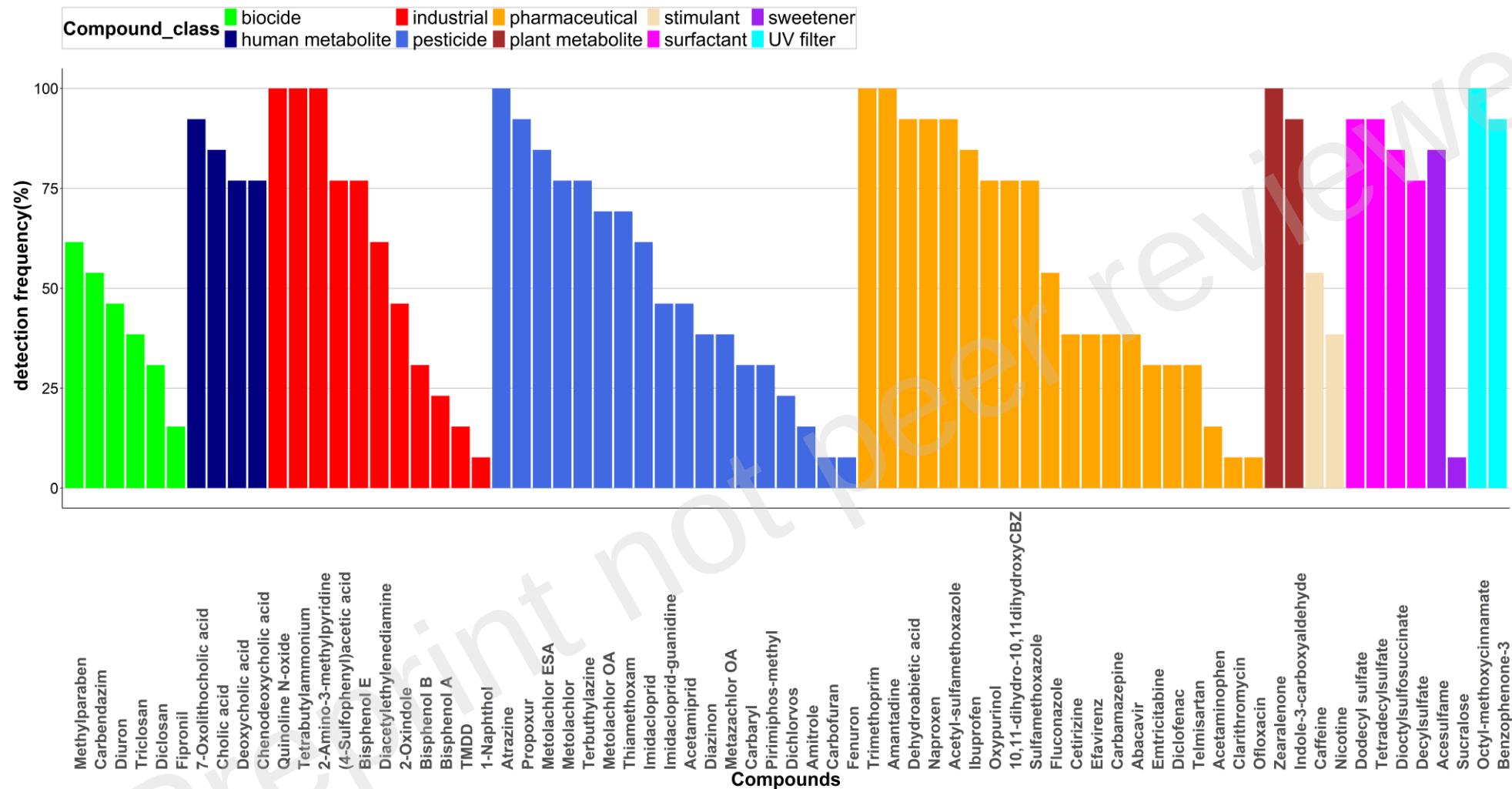


Figure 1: Detection frequencies of compounds found in the rivers. TMDD: 2,4,7,9-tetramethyl-5-decindiol; 10,11-Dihydro-10,11DCBZ: 10,11-Dihydro-10,11Dcarbamazepine.

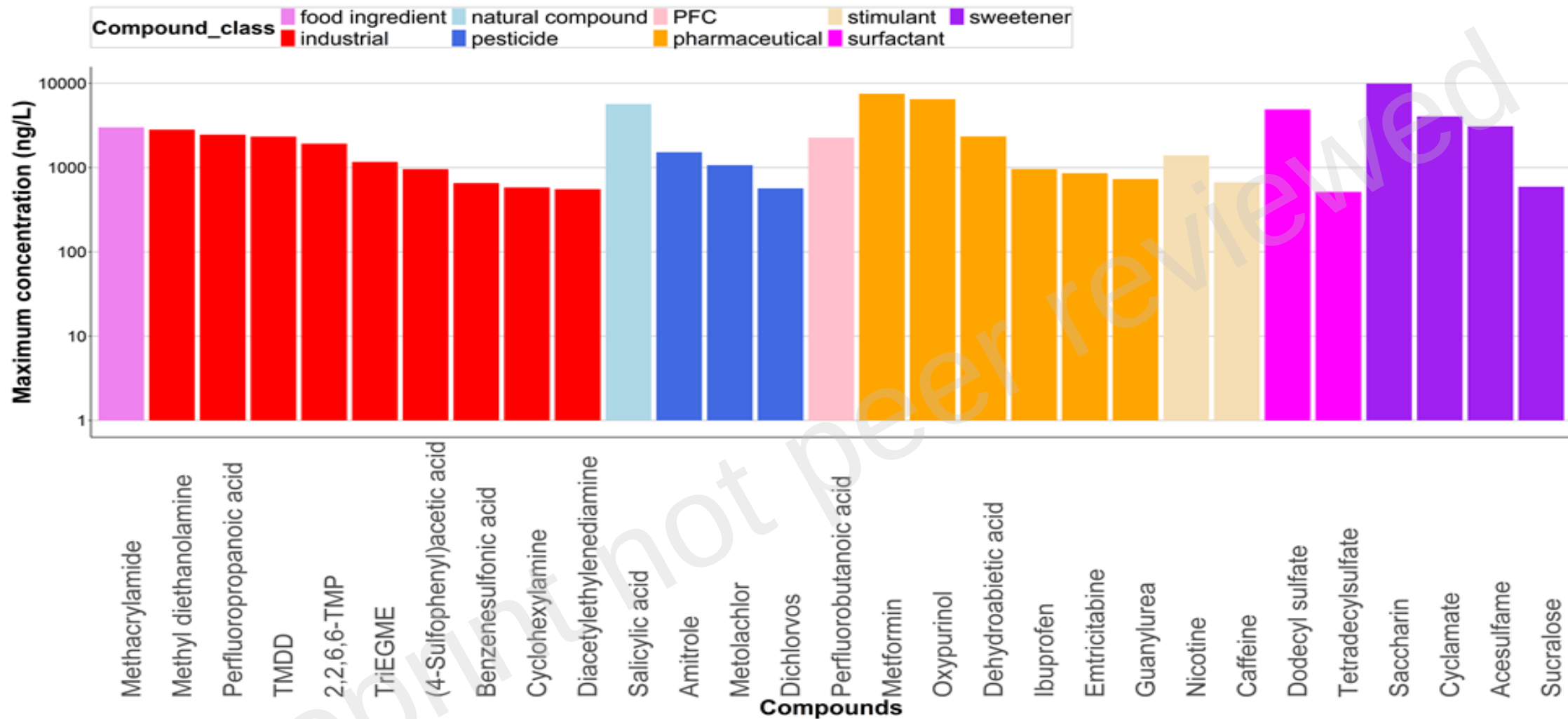


Figure 2. Compounds present at concentrations > 500 ng/L in river samples. TMDD: 2,4,7,9-tetramethyl-5-decindiol, TriEGME: Triethylene Glycol Monomethyl Ether, 2,6,6,6-TMP:2,2,6,6-tetramethylpiperidin-4-ol.

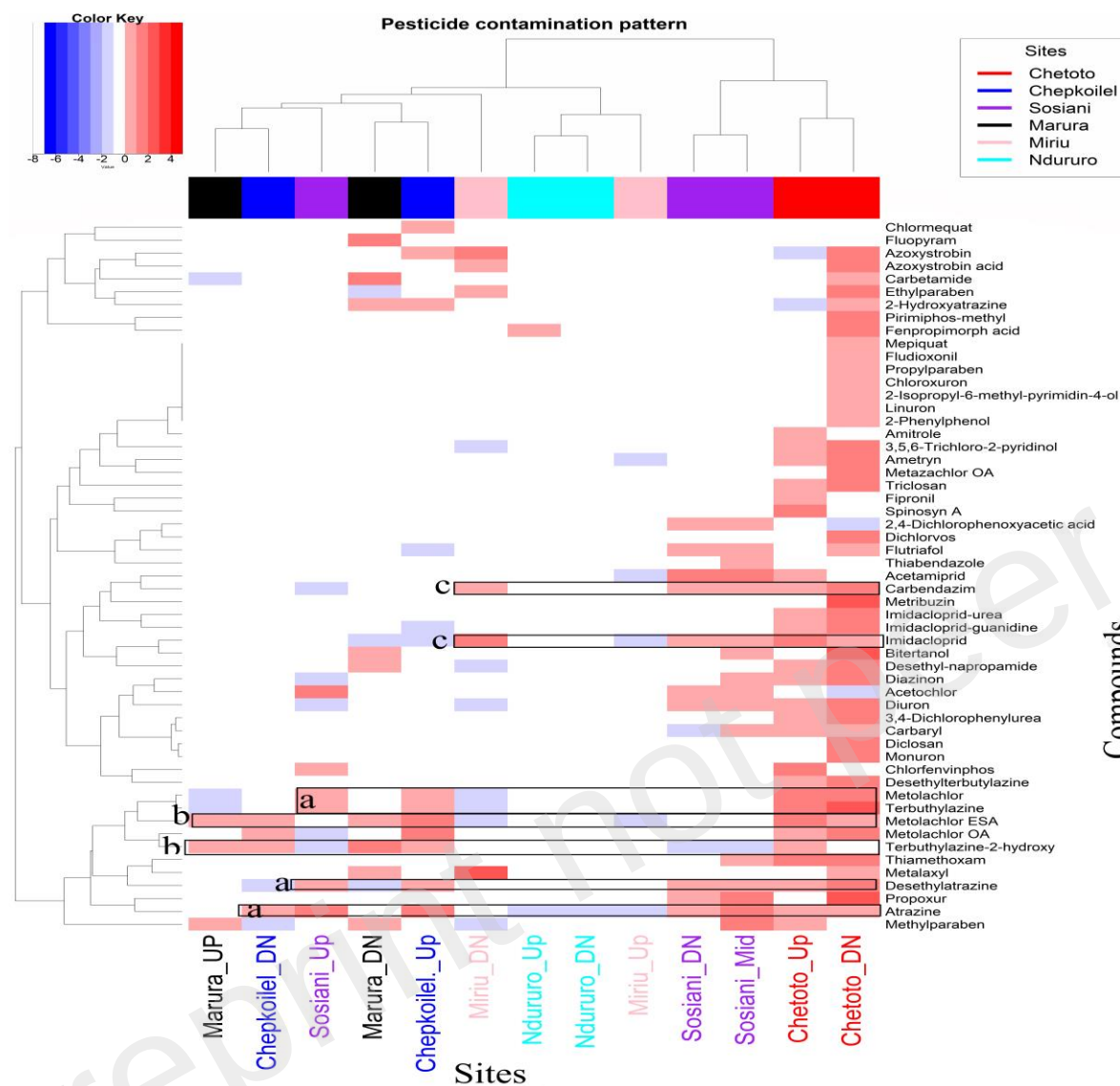


Figure 3: Spatial pesticide pollution patterns based on compound concentrations (ng/L) detected in the study sites (data scaled and centred). UP: Upstream; DN: Downstream

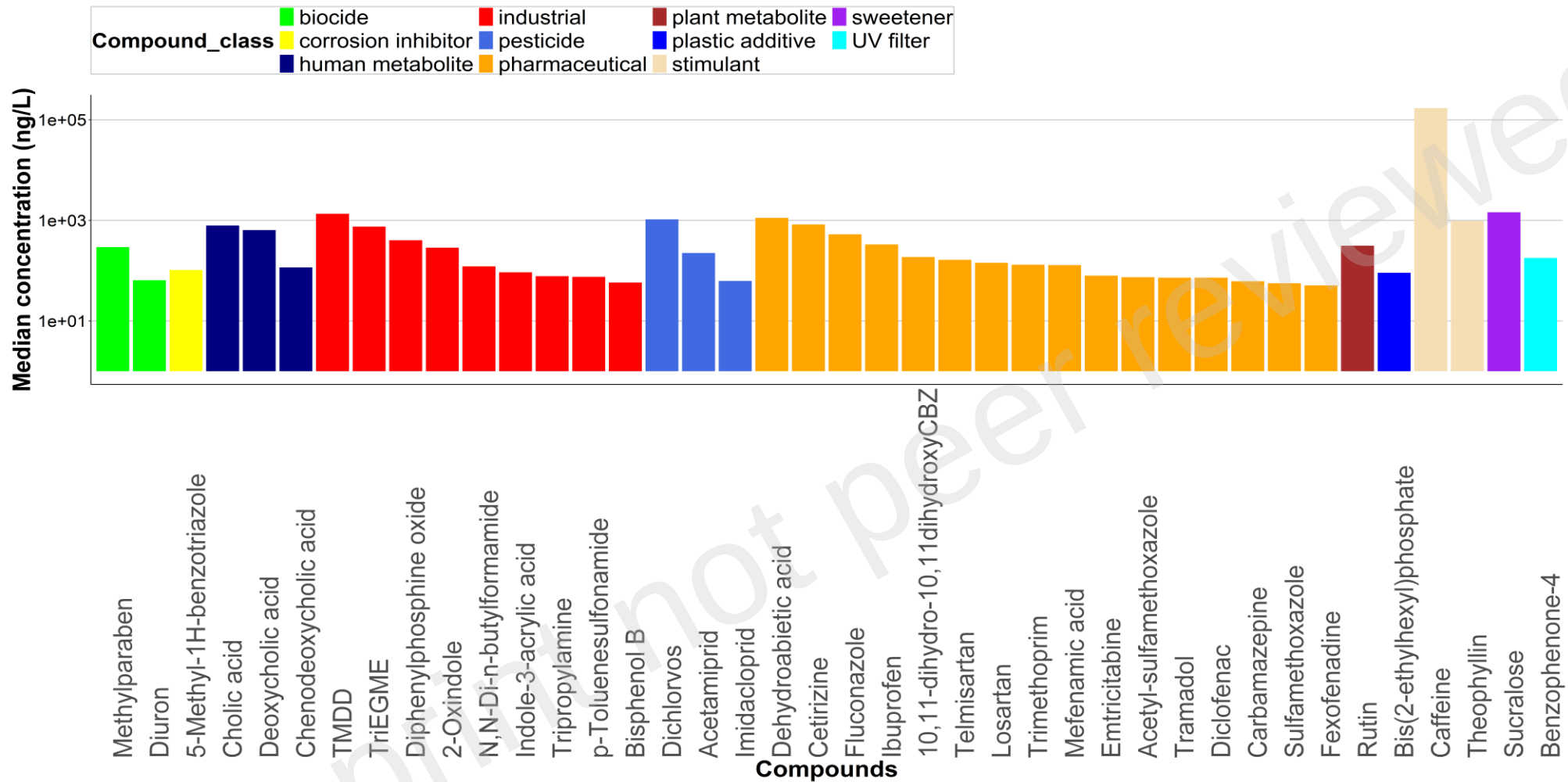


Figure 4: CECs found in the effluent of WWTPs with median concentrations > 200 ng/L. TMDD: 2,4,7,9-tetramethyl-5-decindiol; 2,4-DB: 4-(2,4-dichlorophenoxy) butyric acid; 10,11-dihydro-10,11-dihydroxyCBZ:10,11-dihydro-10,11-dihydroxycarbamazepine; TriEGME: Triethylene Glycol Monomethyl Ether.

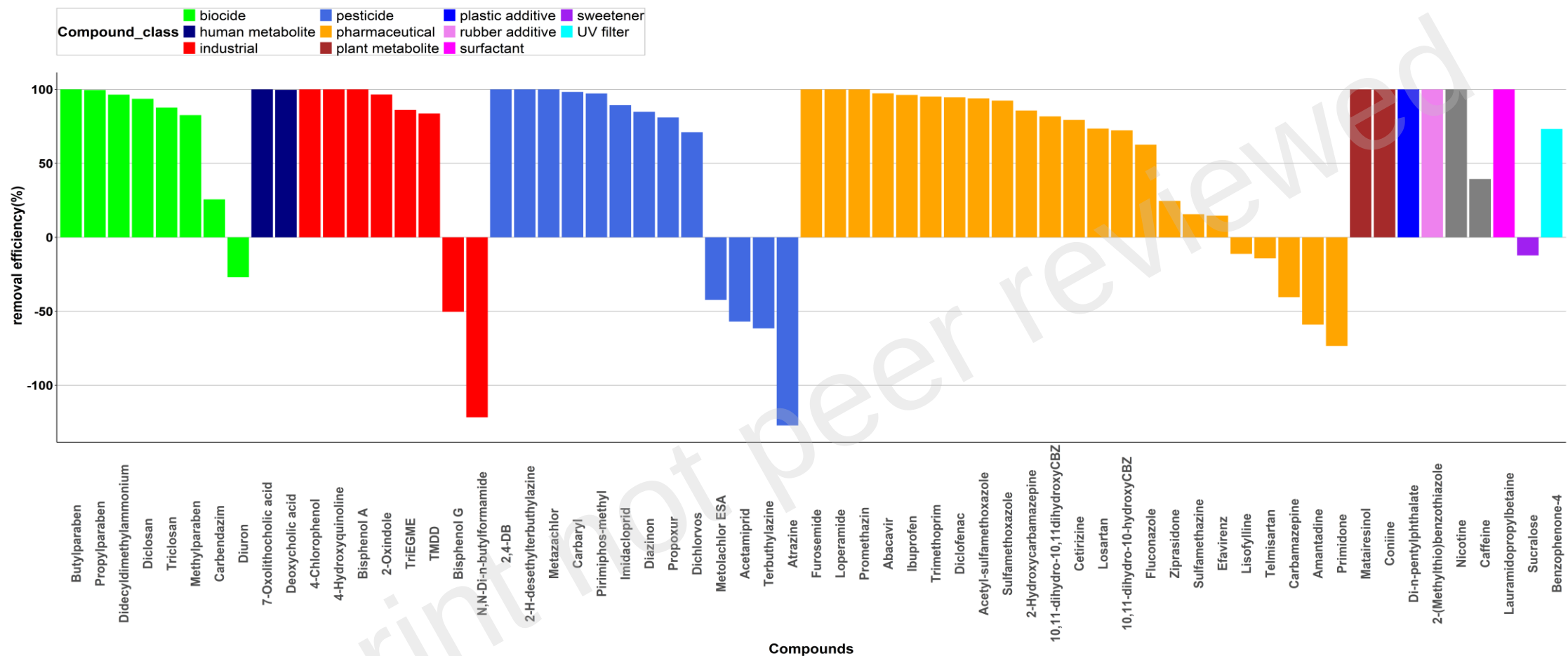


Figure 5: Removal efficiencies of selected CECs in WWTPs in western Kenya. TMDD: 2,4,7,9-tetramethyl-5-decindiol; 2,4-DB: 4-(2,4-dichlorophenoxy) butyric acid; 10,11-dihydro-10,11dihydroxyCBZ: 10,11-dihydro-10,11dihydroxycarbamazepine; TriEGME: Triethylene Glycol Monomethyl Ether; TXIB: 2,2,4-trimethyl-1,3-pentanediol diisobutyrate; 10,11-dihydro-10-hydroxyCBZ: 10,11-dihydro-10-hydroxycarbamazepine.

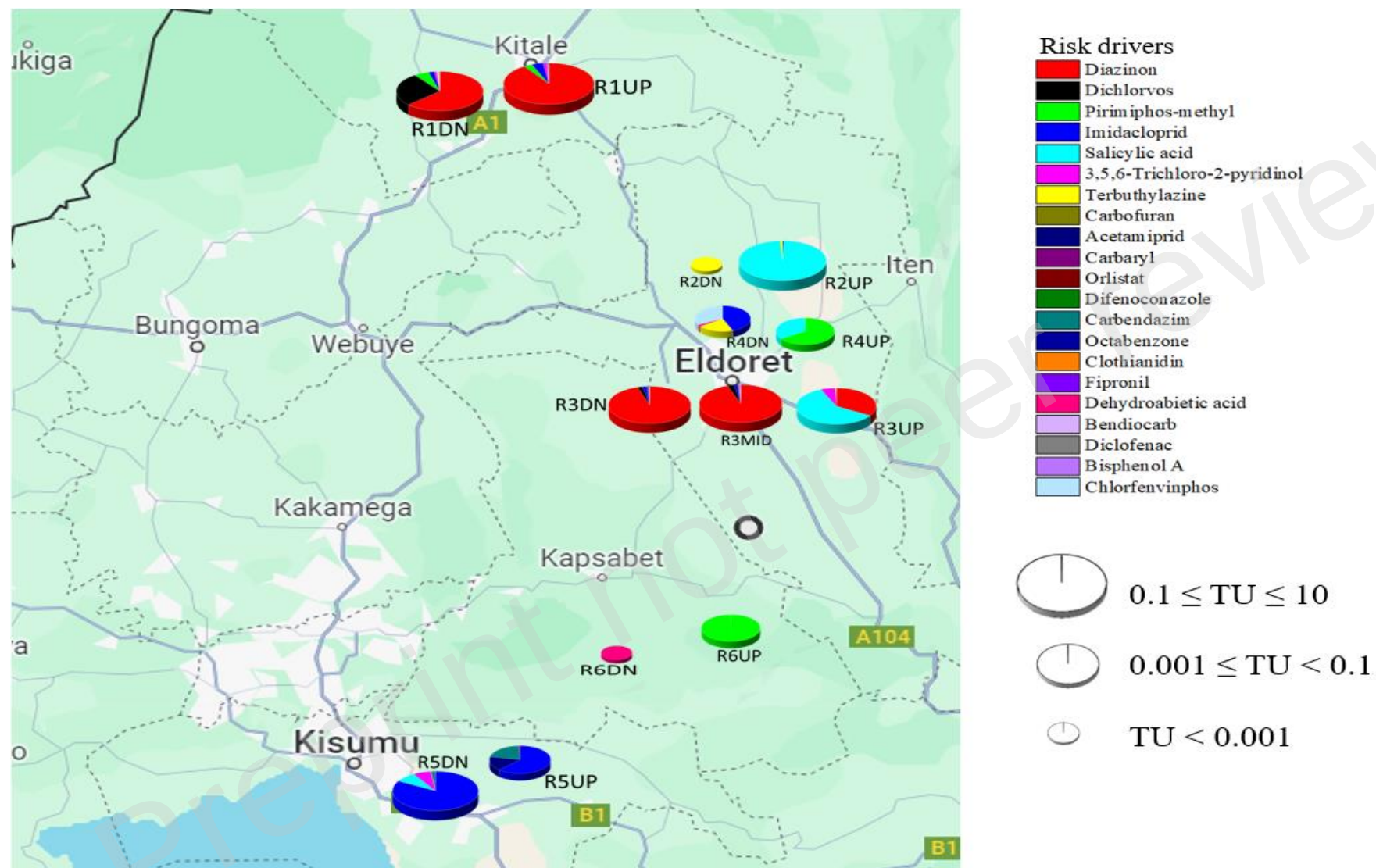


Figure 6: Risk assessment for crustaceans in rivers. R1, R2, R3, R4, R5, and R6 are R. Chetoto, R. Chepkoilel, R. Sosiani, R. Marura, R. Miriu and R. Ndururo respectively; UP, DN and MID are upstream, downstream and midstream respectively.

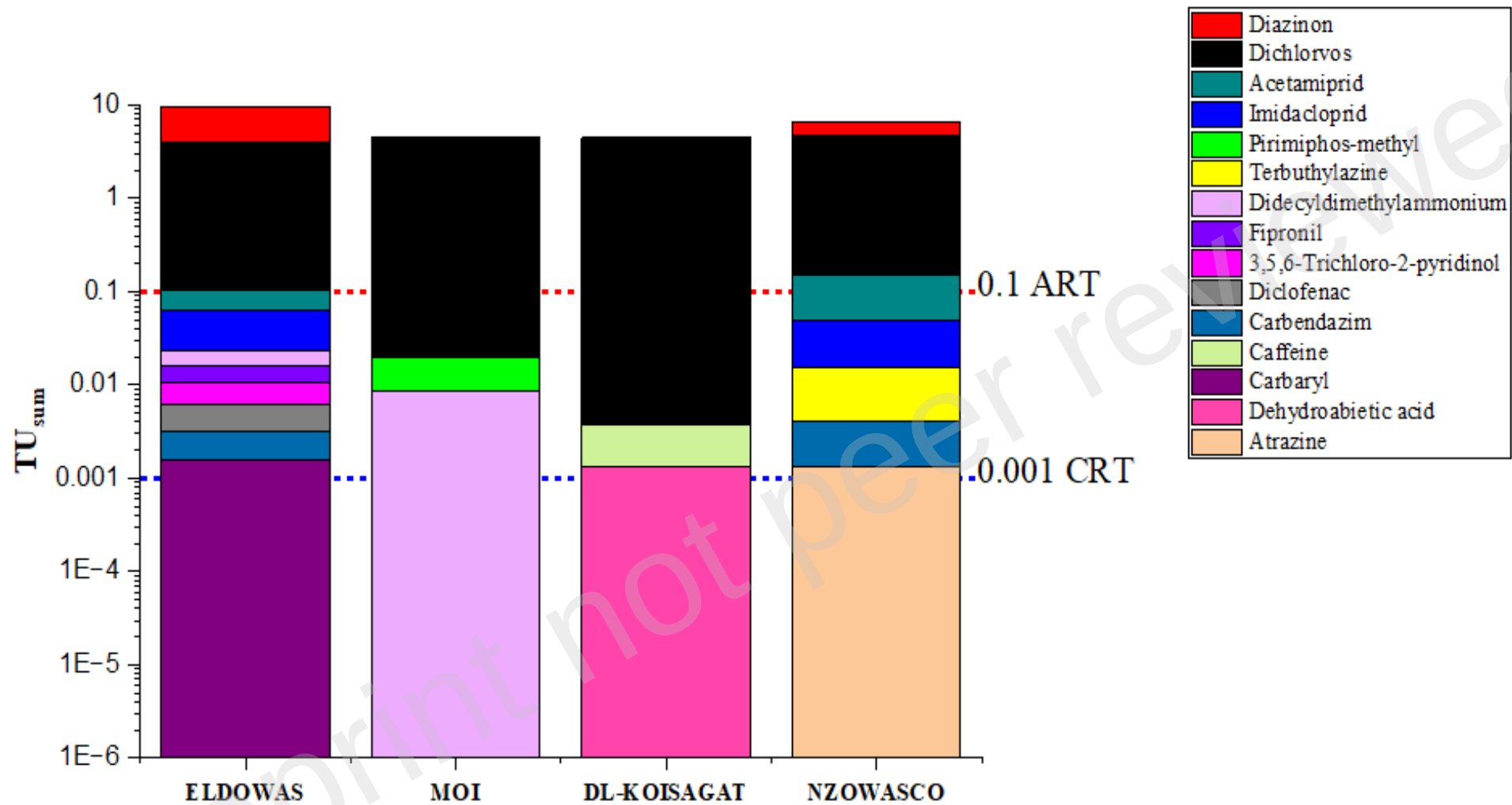


Figure7: Compounds driving the toxicity risk to crustaceans based on the effluent concentrations from the four selected WWTPs