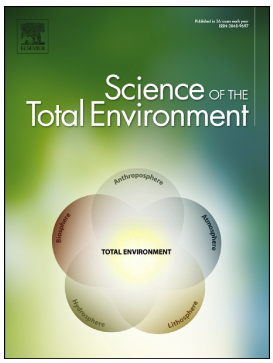

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Occurrence and risk assessment of organic micropollutants in freshwater systems within the Lake Victoria South Basin, Kenya

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Abstract

The unintended release of chemicals to the environment has led to global concern on water quality prompting widespread research on the occurrence of these compounds in water. While increasing information on organic micropollutants (OMPs) in European water resources is available, there is still limited information on the occurrence of OMPs in African water systems. In this study, a multi-residue analysis covering 428 chemicals using liquid chromatography coupled to high resolution mass spectrometry (LC-HRMS) was performed on water samples collected from 48 surface water sites within the Lake Victoria South Basin, Kenya. A total of 75 compounds including pharmaceuticals, personal care products (PPCPs), pesticides, and industrial chemicals were detected and an additional three compounds (nevirapine, lamivudine and adenosine) were identified through suspect screening. Four compounds including diphenhydramine, simazine, triethylphosphate and acetyl-sulfamethoxazole (A-SMX) were detected in more than 80% of the sites showing their ubiquitous nature in the study area. Individual compound concentrations were detected up to 24 µg L^{-1}. Concentrations above 1 µg L^{-1} were also reported for triethylcitrate, N-ethyl-o-toluenesulfonamide, hexazinone, nevirapine, adenosine and carbendazim. While crustaceans were potentially the taxon at risk for acute toxicity (toxic unit (TU) up to 2) with diazinon driving this risk, lower but substantial acute risk (TU 0.5) was observed for algae. Chronic risks were observed in 11 sites for algae (TU > 0.02) and in 5 sites for fish (TU > 0.01). A total of 16 compounds were prioritized based on frequency and extent of the exceedance of thresholds for acute and chronic risks to algae, crustaceans and fish and another 7 compounds prioritized by applying lowest Predicted No-Effect Concentrations (PNEC).

Based on these indicators, this study provides candidate priority compounds for monitoring, assessment and abatement in western Kenya.

Keywords: Emerging contaminants; Western Kenya; Risk assessment; Surface water; Prioritization

1. Introduction

The widespread and intensive use of chemicals such as pesticides, pharmaceuticals and personal care products (PPCPs) has given rise to concern on their occurrence in and impact on aquatic ecosystems (Posthuma et al., 2019). There has been an increase in the use of pesticides and PPCPs due to the increasing population and diseases especially in developing countries (Bernhardt et al., 2017; Peng et al., 2018). In this context, Kenya being a developing country, faces great challenges to cater for food, clean water and health needs of its growing population. Agriculture is a main economic branch contributing more than 70% of Kenya's foreign trade which increases 10% on average annually (Moya et al., 2019). This has led to an increased demand for plant protection products. Between 2006 and 2010, the Ministry of Environment, Water and Natural resources reported approximately 36 thousand tons of pesticide importation into Kenya which increased to 54 thousand tons by 2013 (Loha et al., 2018). In addition, (re)emergence of diseases and epidemics (Berger et al., 2010) has led to increased use of pharmaceutical products in the country and to an increased release of these compounds into the environment. Many organic micropollutants (OMPs) are persistent in the environment including carbendazim, clothianidin, diuron and atrazine with several studies showing that exposure to these compounds results in acute and chronic effects to aquatic organisms (Ccanccapa et al., 2016; Liess & Von Der Ohe, 2005; Shahid et al., 2018; Velki et al., 2019).

Monitoring of emerging OMPs has been increasingly done in the western world; however, there is still a big lack of data for Africa (Aus der Beek et al., 2016; Fekadu et al., 2019; Madikizela et al., 2017). Most studies on water quality monitoring in Africa are

based on environmental or drinking water guidelines which cover only few OMPs (Gwenzi & Chaukura, 2018). The lack of state-of-the-art analytical equipment to detect concentrations in the ng L^{-1} range is a major obstacle to monitoring of hazardous environmental contamination in many developing countries. Although the occurrence of some pesticides in environmental matrices in Kenya has been monitored since 1987 (Kahunyo et al., 1988), the compounds analyzed were generally low in number. Only very few studies have been performed in Kenyan water systems characterizing pharmaceutical pollution patterns in surface waters. These studies focused on a few pharmaceuticals (Bagnis et al., 2020; K'oreje et al., 2018; 2016; 2012; Kimosop et al., 2016; Ngumba et al., 2016) and only three studies (Bagnis et al., 2020; K'oreje et al., 2018; Ngumba et al., 2016) reported potential risks on aquatic organisms based on the measured environmental concentrations.

To reduce this knowledge gap, the present study focused on the assessment of surface waters including rivers, drainage channels and dams to obtain information on the extent of pesticides, PPCPs and industrial compound pollution within the Lake Victoria South Basin (LVSB) in Kenya. The aim of this study was to (1) determine the level of OMPs pollution in various surface water systems within LVSB (2), to perform suspect screening for a comprehensive characterization of multi-residue pollution, (3) to undertake risk assessment on aquatic organisms based on toxic units (TU) and (4) for the first time, to prioritize compounds for regulation and monitoring in Kenya.

2. Materials and methods

2.1 Chemicals

LC-MS grade methanol, formic acid and ammonium formate were obtained from Honeywell, while LC-MS grade water was purchased from Thermo-Fisher. Analytical standards were obtained from various suppliers and at least of 97% purity. More information on the compounds analyzed is presented in supplementary information (Table SI-1).

2.2 Study area and sampling

The study was performed within the LVSB, Kenya (Figure 1) covering Kericho, Kisumu, Kisii, Nyamira, Migori, Narok and Homabay counties. LVSB has an estimated area of 21,720 km². A total of 48 sites were sampled including main rivers (11), tributaries (20), dams (8), irrigation field channels and associated rice fields (6), and ox-bow lakes (3). The study sites were selected to cover various types of surrounding land use including agricultural (tea, sugarcane, maize and rice plantations), industrial (sugarcane factory), natural (grassland) and mixed urban and residential areas. Variations in compound detections and concentrations is hypothesized to be related to these different land use systems within the study area.

Sampling was done between September and October 2017. This coincides with the short rainy season in western Kenya and thus with expected peaks in surface runoff and washout of pesticides. Detailed site descriptions are given in the SI (Table SI-2). Where feasible, samples were taken upstream and downstream of each land use type in a river system.

At each site, a 500-mL grab sample was taken in a pre-cleaned glass beaker and solids were allowed to settle for 1 minute. An aliquot of 1 mL was transferred to a 2-mL amber auto sampler glass vial (Phenomenex) for chemical analysis. To check for contamination during sampling, a total of 15 trip blanks and 95 sampling blanks (1 mL LC-MS grade water) were taken for all sampling trips and sites, respectively. All samples were stored immediately in a portable freezer at below -4 $^{\circ}$C and transported to the laboratory . Once in the laboratory, they were stored at -20 $^{\circ}$C until analysis.

In-situ physico-chemical characterization (flow, temperature, total conductivity, dissolved oxygen (DO), phosphates, pH, and turbidity) was performed during sampling. Additional water samples were collected in pre-cleaned 500-mL Nalgene bottles for further physico-chemical analysis. Laboratory measurements of nitrate, nitrite, ammonium and carbonate hardness were performed using Merck test kits (Merck KGaA, Darmstadt Germany) at the laboratories of the International Centre of Insect Physiology and Ecology (Icipe), Thomas Odhiambo Campus, Mbita, Kenya.

2.3 Target and suspect chemical analysis

Due to limited data availability on contaminants in Africa, the selection of compounds for chemical analysis was based on their occurrence in European surface waters and on local use. A target list of 428 compounds (Table SI-1) including pesticides, PPCPs and industrial compounds covering a wide range of physico-chemical properties were selected for chemical analysis.

In order to allow for a more comprehensive analysis, a suspect screening on additional 233 compounds including pesticides and pharmaceuticals (Table SI-3) known to be

used in Kenya was conducted. Candidate pesticides for suspect screening were selected based on a published list of pesticides registered for use in Kenya by the Pest Control Products Board (PCPB, 2018). A suspect list for pharmaceuticals was compiled based on a list from the Ministry of Health on essential pharmaceuticals for use in Kenya (Ministry of Health, 2016). The compounds were characterized based on log K_{ow}, log D and compound structure (Chemaxon, Budapest, Hungary). Based on their functional groups according to Moschet et al.(2013), the suspect list was filtered for liquid chromatography-electrospray ionization (LC–ESI) amenable compounds. Since water samples were analyzed, the focus was on hydrophilic organic compounds excluding any compound above log K_{ow} 5 (Moschet et al., 2013). Only $[M+H]^+$ and $[M-H]^-$ adducts were included in the screening workflow.

2.4 Instrumental analysis

The 1-mL water aliquots were spiked with 25 µL of an internal standard mixture containing 40 isotope-labelled compounds at 40 ng mL^{-1}, 25 µL of methanol and 10 µL of a 2 M ammonium formate buffer at pH 3.5. Chemical analysis was performed by direct sample injection (100 µL) into a high performance liquid chromatography system (Thermo Ultimate 3000 LC) coupled to a high resolution mass spectrometer (QExactive Plus ,Thermo). Chromatographic separation was done at 40°C using a C18 column (Phenomenex Kinetex C18 EVO, 50 x 2.1 mm, 2.6 µm particle size), equipped with a pre-column (5.0 x 2.1 mm) and 0.2 µm in-line filter. The mobile phase comprised water (A) and methanol (B) both with 0.1% v/v formic acid. Analytes were ionized using a heated electrospray ionization (ESI) source with separate runs in positive and negative

ion mode. Details on the elution gradient and the mass spectrometer set up are shown in the SI (Table SI-4, SI-5).

Matrix-matched calibration standards were prepared using filtered water from a pristine reference stream (Wormsgraben) without anthropogenic pollution from the Harz Mountains (Germany), standards of the target substances dissolved in methanol and isotope-labelled internal standards. Eleven calibration levels ranging from 1 to 2000 ng L^{-1} were used. Analyte concentrations were determined using internal quantification against internal standards. Due to a limited number of isotope labeled standards, internal quantification was performed using the internal standard whose retention time was closest to that of the analyte. For concentrations > 2000 ng L^{-1}, samples were re-run after appropriate dilution with LC-MS grade water.

Raw data files were first converted into mzML files using ProteoWizard (mscovert frontend version 2.1.0) and processed using MZmine (Version 2.38, Pluskal et al., 2010) including the ADAP chromatogram builder module (Myers et al., 2017). The settings used for MZmine data processing are included in the supplementary information (Table SI-6). Target compounds were annotated in MZmine (Version 2.38) using a custom database search. Target compounds detected in MZmine were further confirmed and quantified using TraceFinder 4.1 (Thermo, Table SI-7). Method detection limits (MDLs) were determined based on a replicate analysis of calibration standards based on US EPA (2011).

For suspect screening, peaks were tentatively annotated using MZmine (Version 2.38). A peak intensity threshold of 10^5 was set in both modes and any peak below this

threshold was excluded from the subsequent data processing. In total, 79 peaks were tentatively annotated in positive and 50 peaks above 10% a.u. intensity in negative mode. Based on the peak shape and baseline noise, the candidate list contained 38 compounds (24 in positive and 14 in negative ionization mode). Data dependent acquisition was then performed on the environmental samples using the LC-HRMS to obtain mass fragments in both ionization modes in separate runs. The MS/MS spectra were extracted in XCalibur (Thermo) and ions with an intensity below 5000 were omitted before further processing. Extracted accurate masses where checked for plausible fragment ion molecular formulas using SIRIUS (V4.0.1, (Böcker et al., 2009; Böcker & Rasche, 2008; Dührkop & Böcker, 2016)). For compound identification, MS/MS spectra were searched against the MassBank (Horai et al., 2010) and mzCloud (www.mzcloud.org) spectral libraries and matched to *in-silico* predicted spectra of the compounds using the MetFrag (Ruttkies et al., 2016) and CFM-ID (Dührkop et al., 2015; Shen et al., 2014; Heinonen et al., 2012) software. In MetFrag (settings: search ppm: 5, PubChem, KEGG and CompTox search) compounds were considered as a plausible candidates based on fragment match and spectral similarity (above 0.5, maximum 2). If a match was obtained between the measured spectrum, predicted spectrum (MetFrag and CFM-ID) and spectral libraries (MassBank and mzCloud) a reference standard was acquired to confirm the identity with MS/MS and retention time. Six out of the 38 compounds were tentatively identified and reference standards were acquired for confirmation. The confirmed compounds in the samples were quantified (retrospective analysis) using 12-level standard calibration solutions (1-5000 ng L^{-1}) spiked with internal standards.

2.5 Risk assessment

In order to assess the toxic risks posed by the compounds detected, toxic units (TU) (Sprague, 1970) were calculated for three different trophic levels (fish, crustaceans and algae). The measured environmental concentrations (MEC) were normalized by lethal and sublethal concentrations causing effect in these organisms (Equation 1). The effect values were retrieved from the ECOTOX database and selected as described by (Beckers et al., 2018; Busch et al., 2016). Where ECOTOX data was not available, the values were predicted from Structure Activity Relationships models using the ECOSAR database as described in Busch et al. (2016) (SI Table SI-8).

Equation 1:

$$TU = \frac{MEC(mg\ L^{-1})}{EFFECT\ CONCENTRATION\ (mg\ L^{-1})}$$

Mixture risks in environmental samples were calculated using the model of concentration addition (CA) (Loewe and Muischnek, 1926) as the sum of TUs (TU sum, Equation 2). This model is designed for compounds with similar modes of action, while mixture effects of dissimilarly acting compounds are better described with the model of independent action (IA). However, it has been shown that CA and IA predictions do not differ by more than a factor of 2 in almost 90% of the cases (Belden et al., 2007). Thus, using the more conservative CA model has been suggested to give good predictions in most environmental mixtures irrespective of the modes of action of the components

(Backhaus and Faust, 2012) since full concentration-response data as required for IA are available only for a limited number of compounds.

Equation 2:

$$TU\ sum = \sum TU$$

2.6 Prioritization of pollutants based on potential risk

Compounds of particular concern for monitoring and regulation in western Kenya were prioritized based on exceedance of risk threshold values calculated using two methods: (i) based on toxic units (TUs) and (ii) based on risk quotients (RQs). Based on TUs, compounds were prioritized according to the exceedance of the risk threshold values suggested by (Malaj et al., 2014): acute toxic risk (0.1 TUs) for all organisms and chronic risk for fish (0.01 TUs), *Daphnia*, (0.001 TUs) and algae (0.02 TUs). The second method was applied by calculating the RQ derived by normalizing concentrations to the lowest Predicted No-Effect Concentration (PNEC) across three trophic levels available from the NORMAN network (www.norman-network.net). Here, the risk threshold value was 1. Using these two methods independently, prioritization was based on two indicators: (i) the frequency of exceedance of TU and RQ-based thresholds (Equation 3 with n as the number of sites (*n*) where the TU or RQ of a specific compound exceeded the risk thresholds and N as the total number of sites sampled) and (ii) the maximum extent of exceedance (Equation 4) of these thresholds ranking compounds addressing the maximum intensity of the risk (von der Ohe et al., 2011).

Equation 3:

$$Frequency\ of\ Exceedance = \frac{\sum n}{\mathrm{N}}$$

The extent of exceedance was calculated by normalizing the maximum toxic unit (TU_{max}) or risk quotient (RQ_{max}) per compound across all sites to the respective threshold (Equation 4). Results were then scaled from 0 to 1 as proposed by (von der Ohe et al., 2011). Results from the two indicators were summed up (maximum is 2) resulting in a priority score which was the basis of the compound ranking.

Equation 4:

$$Extent\ of\ Exceedance = \frac{\mathrm{TUmax}}{\mathrm{Threshold\ Value}} \quad or \quad \frac{\mathrm{RQmax}}{\mathrm{Threshold\ Value}}$$

2.7 Data analysis

Data analysis and visualization was performed using Microsoft Excel 2013, R version 3.5.0 and R studio (version 1.1.383). For reporting concentrations, data below the method detection limits (<MDLs) were considered as zeros. Cluster analysis was used to determine spatial pollution patterns. Due to variations in the concentration of detected compounds, the data was log transformed and scaled to reduce skewedness prior to analysis as performed by Beckers et al. (2018). Heatmaps (R package 'gplots', function heatmap.2, linkage = "complete", dist= "euclidean") were used to display spatial patterns of the detected compounds in the study area (Beckers et al., 2018).

3. Results and discussion

The results from the analysis of general water quality parameters are given in the supplementary information (Table SI-9).

3.1 Chemical analysis

3.1.1 Target screening

A total of 75 out of 428 compounds were detected in the water samples. The full list of detected compounds and concentrations are presented in SI (Table SI-10). Figure 2 shows the detection frequency of the 75 compounds while figure 3 shows the 20 compounds with the highest concentrations.

Pesticides and biocides were the most frequently detected chemical classes with the highest number of compounds (26 parent compounds and 5 transformation products (TP)). Simazine was the pesticide with the highest detection frequency of 88% followed by dodemorph and bendiocarb with 65% and 60%, respectively (Figure 2). Individual pesticide concentrations ranged from non-detects to 1.5 µg L^{-1}. Highest concentrations were found for hexazinone and carbendazim with more than 1 µg L^{-1}. Hexazinone is a non-selective post emergence herbicide used for the control of grasses and broad leaf weeds in sugarcane plantations while carbendazim is a broad spectrum benzimidazole fungicide used for the control of blight and powdery mildew (PCPB, 2018). The presence of agro-industrial farms, particularly growing rice and sugarcane, could be a plausible reason for the high concentrations of pesticides detected. In addition, sampling was carried out when the sugarcane plants were at the growing stage and during the spraying season.

Additionally, the neonicotinoid imidacloprid and its TP imidacloprid-guanidine were detected at concentrations ranging up to 32 and 152 ng L^{-1}, respectively. The use of neonicotinoids has been increasing globally due to the ban on most organophosphates and organochlorine compounds with imidacloprid being the most widely used substance (Calvo-Agudo et al., 2019; Wood & Goulson, 2017). The concentrations of most pesticides in this study are within the range of concentrations reported by K'oreje et al. (2018).

PPCPs were reported with a detection frequency ranging from 2-90%. The most frequently detected compound was the anti-allergic drug diphenhydramine, which was detected in 90% of the sites. This could be attributed to the availability of several over the counter drugs that contain diphenhydramine as one of the main active ingredients. Such medications are cheap, readily available and widely used for treatment of coughs and cold (Kigen et al., 2015). Among the reported metabolites, acetyl-sulfamethoxazole (A-SMX) was the most frequently detected one (81%). This result is in agreement with previous studies carried out on water samples obtained from Lake Victoria North and Nairobi Basins, Kenya (K'oreje et al., 2016; 2018; Ngumba et al., 2016) and Lake Victoria Basin, Uganda (Nantaba et al., 2019) which reported sulfamethoxazole to be the most frequently detected pharmaceutical in surface water.

Individually, the PPCP concentrations varied from 0.001 to 24 µg L^{-1} (Table SI-10) with A-SMX exhibiting the highest maximum concentration (Figure 3). This concentration exceeds the European drinking water guideline values by a factor of 2800. A-SMX is a TP of sulfamethoxazole, an antibiotic used to treat various bacterial infections in both humans and livestock (Aus der Beek et al., 2016; Fekadu et al., 2019).

Sulfamethoxazole, usually used in combination with trimethoprim as co-trimoxazole, is of relatively low cost compared to other antibiotics. It is easily accessible over the counter and used as a first line treatment drug for several ailments including HIV opportunistic infections which are prevalent in Kenya (National AIDS Control Council (NACC), 2018). Noticeably, the highest A-SMX, sulfamethoxazole (297 ng L^{-1}) and trimethoprim (110 ng L^{-1}) concentrations were detected (PS16) at the same site. These concentrations were lower than those previously reported in cities in Kenya (K'oreje et al., 2016; 2018; Ngumba et al., 2016) but higher (factor of 8-14) compared to those reported in a review by Aus der Beek et al. (2016) for European waters. The common insect repellants DEET and icaridin were found at concentrations of 28 and 67 ng L^{-1}, respectively. The co-occurrence of pharmaceuticals and pesticides in agricultural sites is probably due to the influence of wastewater treatment plants, untreated wastewater and poor waste disposal (Gwenzi & Chaukura, 2018) with no clear demarcation between agricultural and residential areas in the study area.

To the best of our knowledge, we report for the first time concentrations of plasticizers (Figure 2, Table SI-10) in Kenya. The most frequently detected compounds include triethylphosphate (85%), N-ethyl-o-toluenesulfonamide (79%) and triethylcitrate (67%), detected at maximum concentrations of 0.3 µg L^{-1}, 2 µg L^{-1} and 6.5 µg L^{-1} respectively. These compounds have been recently found in high frequency but about one order of magnitude lower concentrations at sites along Yangtze River Delta in eastern China (Peng et al., 2018). Triethylphosphate is a multiple use industrial chemical applied in the plastics industry as a catalyzer, plasticizer, flame retardant, in polyester resins and polyurethane foam (Wei et al., 2015). N-Ethyl-o-toluenesulfonamide is of similarly wide

spread use in industrial products including plastics, inks and cosmetics but also as inert ingredient in pesticide formulations. Triethylcitrate is used as a plasticizer and replacement of phthalates but also used as a food additive. A probable source of these compounds would be from the traffic, waste dumpsites and car and motor bike washing activities at the river banks rampant in the area.

3.1.2 Suspect screening

Using the suspect screening workflow outlined in subsection 2.4, six compounds (rimantidine, adenosine, nevirapine, pencycuron, lamivudine and flupyradifurone) from the candidate list were tentatively identified and selected for further confirmation (Table SI-11). After instrumental analysis with respective standards, nevirapine, lamivudine and adenosine were confirmed (SI Figures SI-1, SI-2 and SI-3). Retrospective quantification revealed concentrations of up to 4 µg L^{-1} (adenosine), 0.5 µg L^{-1} (lamivudine) and 1 µg L^{-1} (Nevirapine). Nevirapine and lamivudine are anti-retroviral (ARV) drugs used in Kenya for the treatment of HIV/AIDS and to prevent mother-to-child transmission in pregnant infected females. The detection of these ARVs shows evidence of the national occurrence of the compounds in surface water as they had previously been reported in western (K'oreje et al., 2016; 2018) and central Kenya (K'oreje et al., 2016; Ngumba et al., 2016). This ubiquitous occurrence could be attributed to the relatively high national prevalence (4.9%) of HIV/AIDS in Kenya and specifically between 4 and 21% within the study area (NACC, 2018). In contrast to Europe, these compounds are frequently reported in African waters in line with the consumption pattern of the ARVs (Fekadu et al., 2019; Madikizela et al., 2019; Ncube et al., 2018;). Lamivudine and nevirapine are known to be rather photostable and poorly

biodegradable. Their detection in the water samples receiving treated wastewater suggest that they are poorly removed (11-59%) during wastewater treatment (K'oreje et al., 2018). Pencycuron and flupyradifurone had a high MetFrag score above 1 (Table SI-10), but the MS/MS of the reference standard and the measured spectrum did not match. Rimantidine had a hit in MassBank, MetFrag and mzCloud, however, the retention time differed from that of the reference standard. The software used for *in-silico* fragmentation and candidate identification are helpful to exclude candidates however, verification with reference standards was shown to be essential.

3.2 Spatial pattern analysis

We hypothesized that chemicals will group depending on land use cover. To determine the pollution patterns occurring in the LVSB, cluster analysis was computed in order to identify spatial patterns in chemical exposure. A hierarchical clustering was performed considering all compounds detected at every site. However, only limited grouping of compounds and sites could be obtained in the present study (Figure 4). This is due to the high and rather random variability in pollutant concentrations and mixed land use systems. No clear demarcation exists between agricultural and non-agricultural areas. The most interesting cluster comprises majorly pesticides including 2,4-D, diuron, diazinon, atrazine, hexazinone, ametryn and pirimiphos methyl. This group contains site-specific compounds which were detected at high concentrations in Uli9, PS16, PS17 and PS18 within Migori County. This could be attributed to the presence of large-scale agro-industrial sugarcane plantations within this county. Additionally, a cluster exists consisting of compounds which have been detected at similar concentrations in

all the sites. These compounds include imidacloprid, dodemorph, simazine, diphenhydramine and N-ethyl-o-toluenesulfonamide.

3.3 Risk assessment

The potential for risk was evaluated comparing the sum of TUs based on the measured concentrations of all contaminants and compared to acute and chronic risk thresholds for fish, crustaceans and algae as explained above (Figure 5, 6, 7 and SI-12).

The highest risk was found for invertebrates with 23 out of 48 sites (Figure 5) exhibiting acute toxic risk (TU > 0.1) for these organisms. Two of them even showed TU_{sum} > 1 indicating concentrations above the EC values. For 39 out of 48 sites, chronic toxic risks (TU > 0.001) are detected typically related to changes in the invertebrate communities and losses of sensitive species (Liess & Von Der Ohe, 2005, Malaj et al., 2014, Shahid et al., 2018). In all 23 sites exhibiting acute toxic risks these risks are predominated by the neurotoxic insecticide diazinon. At all other sites, diazinon fell below the MDL of 2 ng L^{-1} corresponds to 0.2 TU. Thus, diazinon probably causes acute and chronic toxic risks also at other sites, which is masked by the non-detectability at very low but biologically active concentrations. This high toxicity of diazinon is influenced by the low effect value of diazinon reported by (Bouldin et al., 2007) in their study performed on a constructed wetland. The results from this study are in agreement with several studies in Europe identifying diazinon as a major risk driver for invertebrates represented by the sensitive standard test organism *Daphnia magna* wherever the compound is applied. This has been reported by Ccanccapa et al. (2016) for the Ebro river basin. The compound was also shown to contribute greatly to the overall toxicity in waste and

surface waters in Germany and Switzerland (Beckers et al. (2018) and Munz et al. (2017)) despite diazinon being banned for use as a plant protection product in Europe. In Kenya, it is still sold legally over the counter (PCPB, 2018). In the 17 sites where a chronic risk to invertebrates was found while diazinon was not detected, the carbamates bendiocarb and carbendazim, pirimiphos-methyl (phosphoric ester insecticide) and the quaternary ammonium disinfection agent hexadecylpyridinium were major toxicity drivers for the standard test organism *Daphnia magna*.

For algae, the acute toxicity threshold (TU > 0.1) was exceeded by 4 out of 48 samples in Migori County (Figure 6). This could be attributed to the large-scale agro-industrial sugarcane plantations in this region. In all cases this risk was driven by the herbicide, hexazinone with TU up to 0.51 and TU_{sum} up to 0.55. At 11 out of 48 sites chronic risk was observed (TU > 0.02). In addition to hexazinone, the biocide triclosan, the photosynthesis inhibiting herbicides metribuzin, simazine, atrazine and its transformation product desisopropylatrazine and the pharmaceutical acetaminophen were compounds responsible for toxic risk to algae.

For fish, the overall risk for acute toxicity was low compared to crustaceans and algae. While no acute toxic risks were found, chronic toxic risks (TU > 0.01) were observed for 5 out of 48 sites (Figure 7). Risk drivers were the fungicide carbendazim with a maximum TU of 0.09 and the disinfectant hexadecylpyridinium with a maximum TU of 0.04. Despite the relatively low toxicity risk to fish based on the compounds analyzed in this study it should be mentioned that this assessment does not include the risk of endocrine disruption for example by steroid hormones, which are not detectable at effect concentrations in the applied screening analysis but require a more targeted

approach. It should be considered that the assessment was based on toxicity data for data rich test species used in European monitoring and assessment due to the lack of African species with a sufficient data basis. Thus, the actual risk to native species may deviate from the risk to the standard test species. It should also be mentioned that the involvement of toxicity to insects, which are for example particularly sensitive to neonicotinoids but are data poor in general and thus hard to use in a general assessment might unravel additional risky compounds.

Based on the acute and chronic thresholds, 16 compounds were ranked ranging from 0.1-1.5 (Table 1). Among the compounds with the highest ranking include diazinon, bendiocarb, hexazinon, carbandazim and pirimophos methyl. According to the PNEC criteria, 7 compounds were ranked ranging from 0.1 to 0.7 (Table 2). In addition to compounds already considered such as diazinon, three additional compounds are flagged as posing a significant risk including A-SMX, ametryn and terbuthylazine which had a priority score of 0.4, 0.3 and 0.2 respectively based on toxicity to the algae (*Selenastrum capricornutum*). Irrespective of the approach applied, diazinon ranked the highest in priority indicating a need for constant monitoring in order to protect aquatic ecosystems.

4. Conclusions

The present study has provided a comprehensive identification and risk assessment of emerging OMPs in freshwater systems in rural areas within the Lake Victoria South Basin for three representative organism groups including crustaceans, algae and fish. Particularly high concentrations (> 1 µg L^{-1}) were detected for some pharmaceuticals

and pesticides with A-SMX being reported at 24 µg L^{-1}. Suspect screening supported the detection of two common antiretroviral drugs used in the first line of treatment among HIV/AIDS infected individuals. Risk assessment revealed a high risk of acute and chronic toxicity for crustaceans while fish and algae experience majorly chronic risk. This risk was driven by a low number of strongly dominating pesticides including diazinon, bendiocarb, hexazinone, carbendazim, which should be highly prioritized for monitoring, regulation and abatement.

There is a potential risk on human health considering that the rivers and reservoirs are used by the local communities for daily household activities including source of drinking water. The maximum concentration of A-SMX reported in this study exceeds European drinking water guideline values by a factor of 2800. Thus, the assessment of contamination in Africa and other developing countries based on acute toxicity data for aquatic organisms as done in the present study is an important first step but demands for extension particularly with respect to endpoints and areas of concern as a basis for efficient abatement for a non-toxic environment in Africa for humans and ecosystems. Further research should focus on seasonal variability of contaminants within the region.

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Marvin/Jchem 17.21.0, 2019 ChemAxon (https://www.chemaxon.com). ArcMap 10.5.1 was used to map the sampling sites. The QExactive Plus LC-HRMS used is part of the major infrastructure initiative CITEPro (Chemicals in the Terrestrial Environment Profiler) funded by the Helmholtz Association.

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Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Figure captions

Figure 1: Map of the study area A) Kenya and B) Sampling area within the Lake Victoria South Catchment area. Data used for mapping was extracted from https://africaopendata.org.

Figure 2: Frequency of detection for target compounds in the Lake Victoria South Basin. 10,11-D-10,11-dihydroxyCBZ: 10,11-Dihydro-10,11-dihydroxycarbamazepine, 4-Amino-N,N-dimethylBSA: 4-Amino-N,N-dimethylbenzenesulfonamide, 10,11-D-10-hydroxyCBZ: 10,11-Dihydro-10-hydroxycarbamazepine, 2,4-D: 2,4-Dichlorophenoxyacetic acid, NETS: N-Ethyl-o-toluenesulfonamide.

Figure 3: Box plots of concentration ranges of twenty compounds detected with the highest concentration within the different study sites. ● outlier (Q1–1.5xIQR) with Q1: lower quartile and IQR: interquartile range. The center line is the median concentration of the individual compound."

Figure 4: Spatial pollution patterns in Lake Victoria South Basin based on compound concentrations (ng L^{-1}) detected in the study sites (data scaled and centered). 10,11-D-10,11-dihydroxyCBZ: 10,11-Dihydro-10,11-dihydroxycarbamazepine, 4-Amino-N,N-dimethylBSA: 4-Amino-N,N-dimethylbenzenesulfonamide, 10,11-D-10-hydroxyCBZ: 10,11-Dihydro-10-hydroxycarbamazepine, 2,4-D: 2,4-Dichlorophenoxyacetic acid, NETS: N-Ethyl-o-toluenesulfonamide.

Figure 5: Compounds driving acute and chronic risk on D. Magna in the Lake Victoria South Basin based on compound toxic unit value (TU). Figure A includes all sites sampled, Figure B shows the sites which are below the acute threshold but exceeded the chronic threshold. Figure C shows the compounds which exceeded the chronic threshold. The bold line (in Figure A) indicates the threshold for acute risk (0.1) and the dotted line (in Figure C) indicates the chronic threshold (0.001) for D. Magna

Figure 6: Compounds driving acute and chronic risk on algae in the Lake Victoria South Basin based on compound toxic unit value (TU). The bold line (in Figure A) indicates the threshold for acute risk (0.1) and the dotted line (in Figure B) indicates the chronic threshold (0.02) for algae.

Figure 7: Compounds driving chronic risk on fish in the Lake Victoria South Basin based on compound toxic unit value (TU). The bold line indicates the threshold for acute risk (0.1) and the dotted line indicates the chronic threshold (0.01) for fish.

Table captions

Table 1: Compounds prioritized based on acute and chronic risk thresholds, compound class, trophic level, threshold level (acute 0.1), frequency and extent of exceedance of the threshold, priority ranking.

Table 2: Compounds prioritized based on Predicted No-Effect Concentration (PNEC) threshold, compound class, trophic level, threshold level (acute 0.1), frequency and extent of exceedance of the threshold, priority ranking.

TP Pharma: Transformation product from pharmaceutical; *S. capricornutum: Selenastrum capricornutum; P. promelas: Pimephales promelas*

Table 3: Compounds prioritized based on acute and chronic risk thresholds, compound class, trophic level, threshold level (acute 0.1), frequency and extent of exceedance of the threshold, priority ranking.

Compound	Class	Organism	Level	Extent of exceedance	Frequency of exceedance	Priority ranking
Diazinon	Pesticide	*D. magna*	Chronic	1.0	0.5	1.5
Bendiocarb	Pesticide	*D. magna*	Chronic	0.2	0.5	0.7
Diazinon	Pesticide	*D. magna*	Acute	0.5	0.2	0.7
Hexazinone	Pesticide	Algae	Chronic	0.2	0.2	0.4
Carbendazim	Pesticide	*D. magna*	Chronic	0.2	0.1	0.3
Pirimiphos-methyl	Pesticide	*D. magna*	Chronic	0.2	0.1	0.3
Carbendazim	Pesticide	Fish	Chronic	0.2	0.1	0.3
Hexadecylpyridinium	Surfactant	*D. magna*	Chronic	0.2	0.0	0.2
Hexazinone	Pesticide	Algae	Acute	0.1	0.1	0.2
Triclocarban	Biocide	*D. magna*	Chronic	0.1	0.1	0.2
Hexadecylpyridinium	Biocide	Fish	Chronic	0.1	0.04	0.1
Acetaminophen	Pharmaceutical	*D. magna*	Chronic	0.1	0.02	0.1
Acetamiprid	Pesticide	*D. magna*	Chronic	0.1	0.02	0.1
Acetaminophen	Pharmaceutical	Algae	Chronic	0.1	0.0	0.1
Metribuzin	Pesticide	Algae	Chronic	0.1	0.02	0.1
Triclosan	Biocide	Algae	Chronic	0.1	0.02	0.1

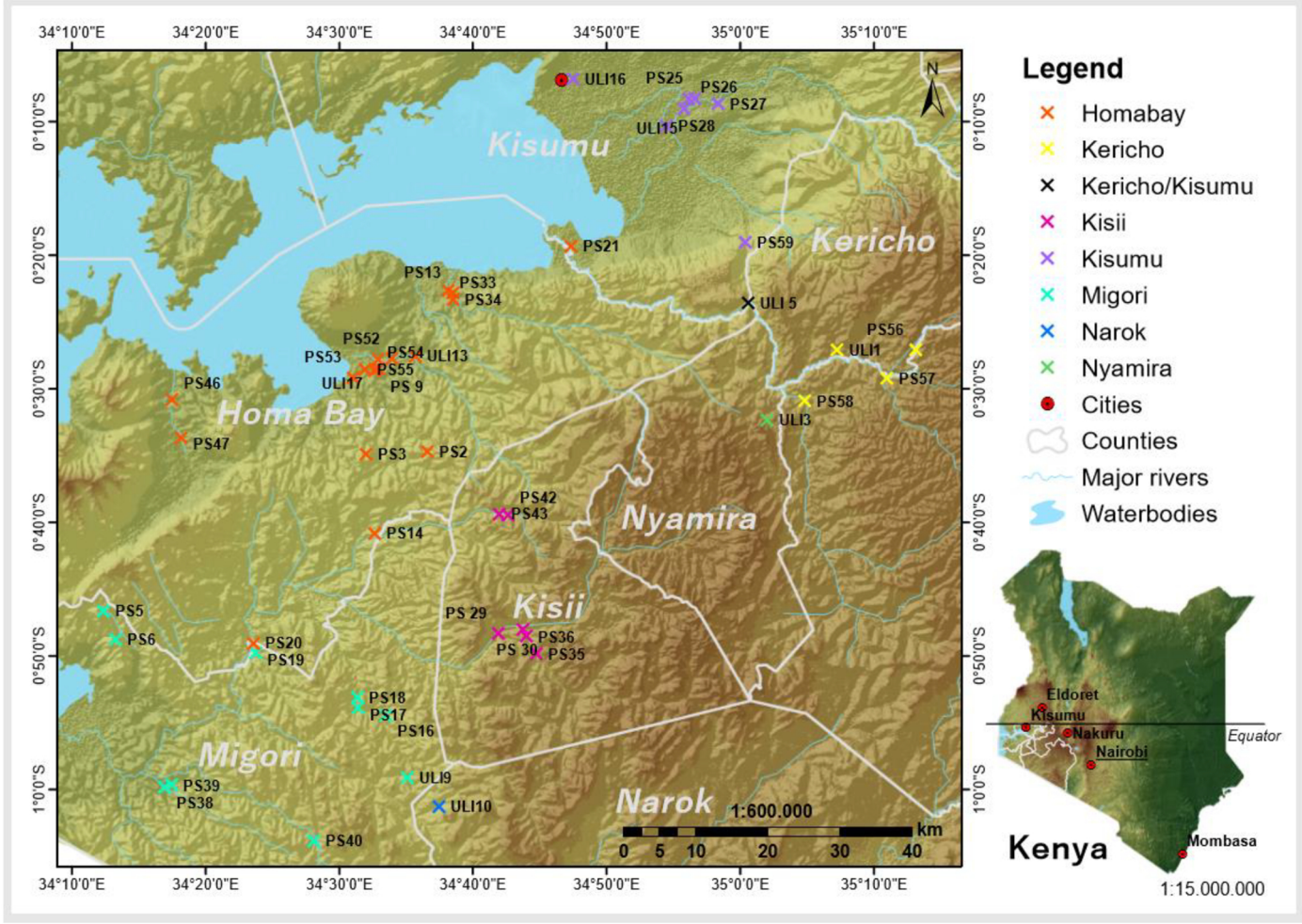
Table 4: Compounds prioritized based on Predicted No-Effect Concentration (PNEC) threshold, compound class, trophic level, threshold level (acute 0.1), frequency and extent of exceedance of the threshold, priority ranking.

Compound	Class	Organism	Extent of exceedance	Frequency of exceedance	Priority ranking
Diazinon	Pesticide	*D. magna*	0.2	0.5	0.7
A-SMX	TP Pharma	*S. capricornutum*	0.2	0.2	0.4
Ametryn	Pesticide	*S.capricornutum*	0.2	0.1	0.3
Pirimiphos-methyl	Pesticide	*D. magna*	0.2	0.1	0.3
Simazine	Pesticide	*S.capricornutum*	0.1	0.1	0.2
Hexadecylpyridinium	Surfactant	*P.promelas*	0.1	0.04	0.1
Terbuthylazine	Pesticide	*S.capricornutum*	0.1	0.02	0.1

TP Pharma: Transformation product from pharmaceutical; *S. capricornutum: Selenastrum capricornutum; P. promelas: Pimephales promelas*

Highlights

- First comprehensive identification of 78 OMPs in western Kenya
- Pharmaceuticals, pesticides and biocides most frequently detected
- First data on plasticizers in Kenyan surface water systems up to 6.5 µg L^{-1}
- High acute and chronic risk for toxicity in crustaceans
- Diazinon, bendiocarb and carbendazim prioritized for regular monitoring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Homabay
Kericho
Kericho/Kisumu
Kisii
Kisumu
Migori
Narok
Nyamira
Cities
Counties
Major rivers
Waterbodies
Eldoret
Kisumu
Nakuru
Nairobi
Equator
Mombasa
Kenya
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Figure 1

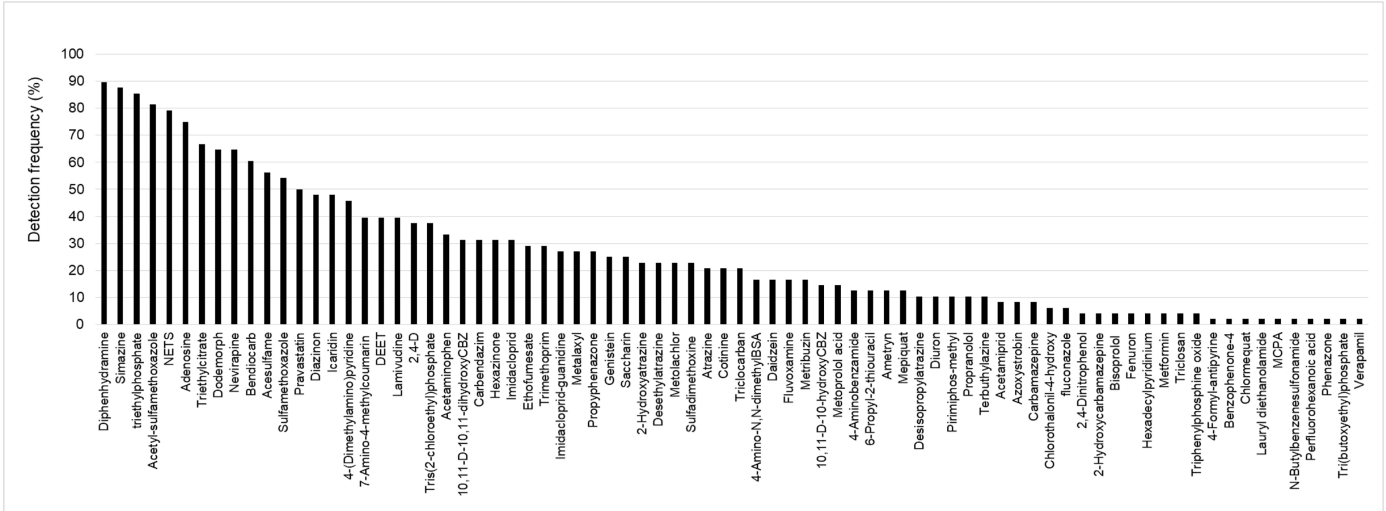
Detection frequency (%)
100
90
80
70
60
50
40
30
20
10
0
Diphenhydramine
Simazine
triethylphosphate
Acetyl-sulfamethoxazole
NETS
Adenosine
Triethylcitrate
Dodemorph
Nevirapine
Bendiocarb
Acesulfame
Sulfamethoxazole
Pravastatin
Diazinon
Icaridin
4-(Dimethylamino)pyridine
7-Amino-4-methylcoumarin
DEET
Lamivudine
2,4-D
Tris(2-chloroethyl)phosphate
Acetaminophen
10,11-D-10,11-dihydroxyCBZ
Carbendazim
Hexazinone
Imidacloprid
Ethofumesate
Trimethoprim
Imidacloprid-guanidine
Metalaxyl
Propyphenazone
Genistein
Saccharin
2-Hydroxyatrazine
Desethylatrazine
Metolachlor
Sulfadimethoxine
Atrazine
Cotinine
Triclocarban
4-Amino-N,N-dimethylBSA
Daidzein
Fluvoxamine
Metribuzin
10,11-D-10-hydroxyCBZ
Metoprolol acid
4-Aminobenzamide
6-Propyl-2-thiouracil
Ametryn
Mepiquat
Desisopropylatrazine
Diuron
Pirimiphos-methyl
Propranolol
Terbuthylazine
Acetamiprid
Azoxystrobin
Carbamazepine
Chlorothalonil-4-hydroxy
fluconazole
2,4-Dinitrophenol
2-Hydroxycarbamazepine
Bisoprolol
Fenuron
Hexadecylpyridinium
Metformin
Triclosan
Triphenylphosphine oxide
4-Formyl-antipyrine
Benzophenone-4
Chlormequat
Lauryl diethanolamide
MCPA
N-Butylbenzenesulfonamide
Perfluorohexanoic acid
Phenazone
Tri(butoxyethyl)phosphate
Verapamil

Figure 2

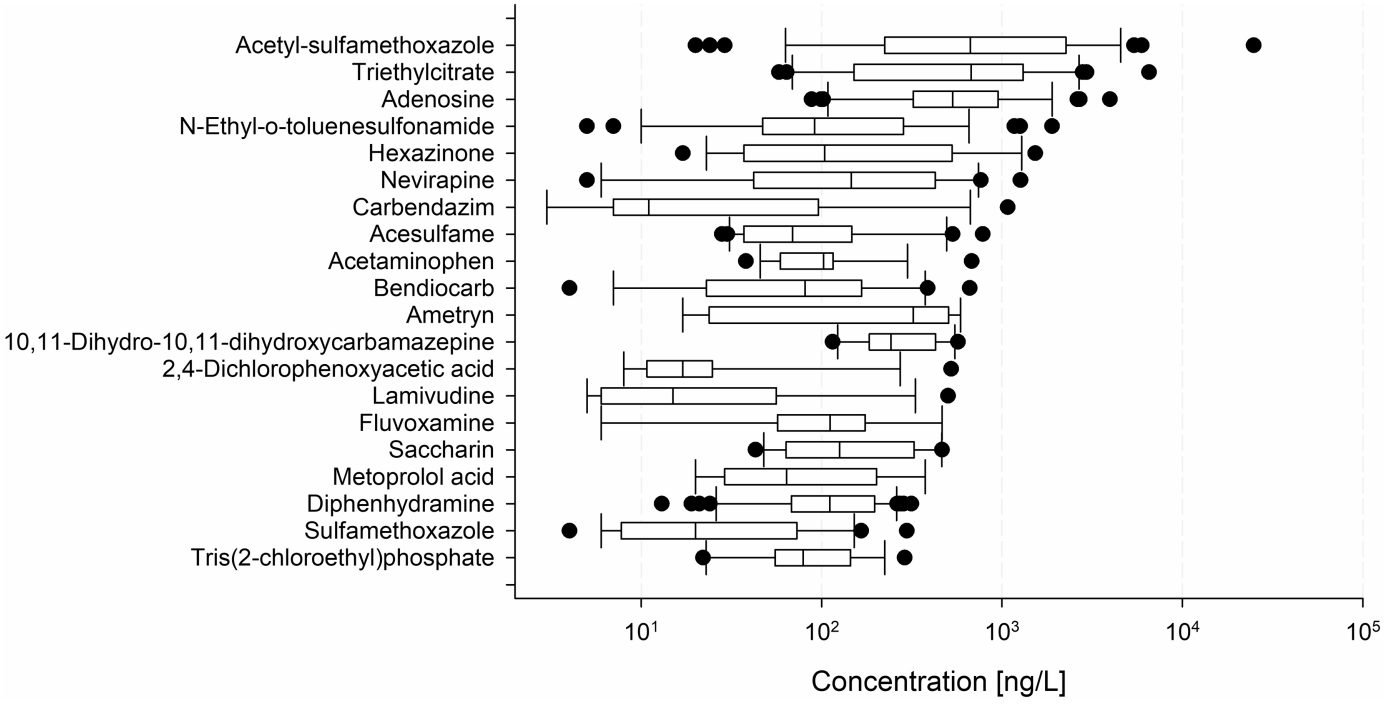
Acetyl-sulfamethoxazole
Triethylcitrate
Adenosine
N-Ethyl-o-toluenesulfonamide
Hexazinone
Nevirapine
Carbendazim
Acesulfame
Acetaminophen
Bendiocarb
Ametryn
10,11-Dihydro-10,11-dihydroxycarbamazepine
2,4-Dichlorophenoxyacetic acid
Lamivudine
Fluvoxamine
Saccharin
Metoprolol acid
Diphenhydramine
Sulfamethoxazole
Tris(2-chloroethyl)phosphate
10^1
10^2
10^3
10^4
10^5
Concentration [ng/L]

Figure 3

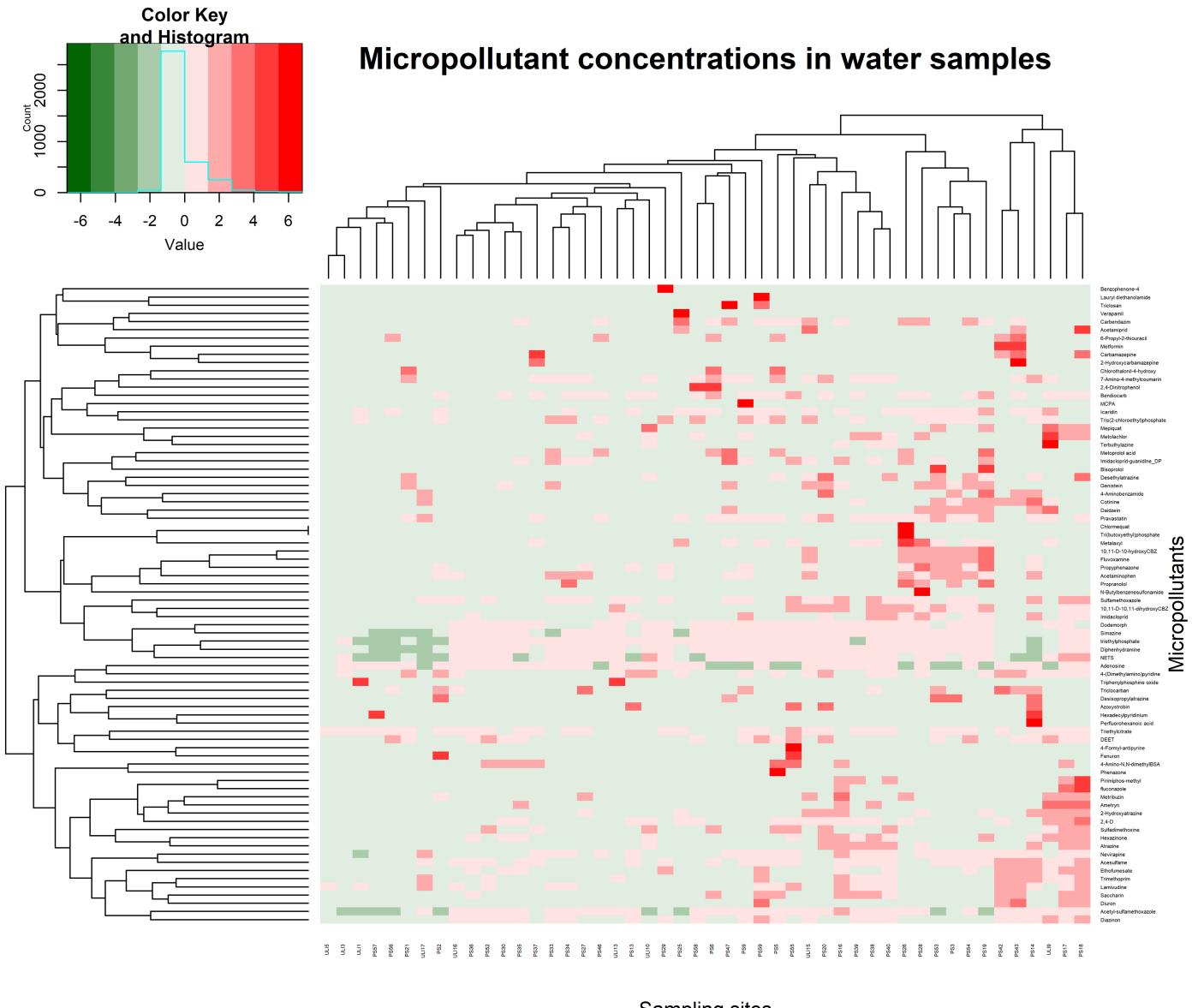
Color Key
and Histogram
Count
0
1000
2000
-6
-4
-2
0
2
4
6
Value
Micropollutant concentrations in water samples
Micropollutants
Benzophenone-4
Lauryl diethanolamide
Triclosan
Verapamil
Carbendazim
Acetamiprid
6-Propyl-2-thiouracil
Metformin
Carbamazepine
2-Hydroxycarbamazepine
Chlorothalonil-4-hydroxy
7-Amino-4-methylcoumarin
2,4-Dinitrophenol
Bendiocarb
MCPA
Icaridin
Tris(2-chloroethyl)phosphate
Mepiquat
Metolachlor
Terbuthylazine
Metoprolol acid
Imidacloprid-guanidine_DP
Bisoprolol
Desethylatrazine
Genistein
4-Aminobenzamide
Cotinine
Dietzein
Pravastatin
Chlormequat
Tri(butoxyethyl)phosphate
Metalaxyl
10,11-D-10-hydroxyCBZ
Fluvoxamine
Propyphenazone
Acetaminophen
Propranolol
N-Butylbenzenesulfonamide
Sulfamethoxazole
10,11-D-10,11-dihydroxyCBZ
Imidacloprid
Dodemorph
Simazine
Triethylphosphate
Diphenhydramine
NBTS
Adenosine
4-[Dimethylamino]pyridine
Triphenylphosphine oxide
Triclocarban
Desisopropylatrazine
Azoxystrobin
Hexadecylpyridinium
Perfluorohexanoic acid
Triethylcitrate
DEET
4-Formyl-antipyrine
Fenuron
4-Amino-N,N-dimethylBSA
Phenazone
Pirimiphos-methyl
fluconazole
Metribuzin
Ametryn
2-Hydroxyatrazine
2,4-D
Sulfadimethoxine
Hexazinone
Atrazine
Nevirapine
Acesulfame
Ethofumesate
Trimethoprim
Lamivudine
Saccharin
Diuron
Acetyl-sulfamethoxazole
Diazinon
ULI5
ULI3
ULI1
PS57
PS56
PS21
ULI17
PS2
ULI16
PS36
PS62
PS30
PS35
PS37
PS33
PS34
PS27
PS46
ULI13
PS13
ULI10
PS29
PS25
PS58
PS6
PS47
PS9
PS59
PS5
PS55
ULI15
PS20
PS16
PS39
PS38
PS40
PS26
PS28
PS63
PS3
PS54
PS19
PS42
PS43
PS14
ULI9
PS17
PS18
Sampling sites

Figure 4

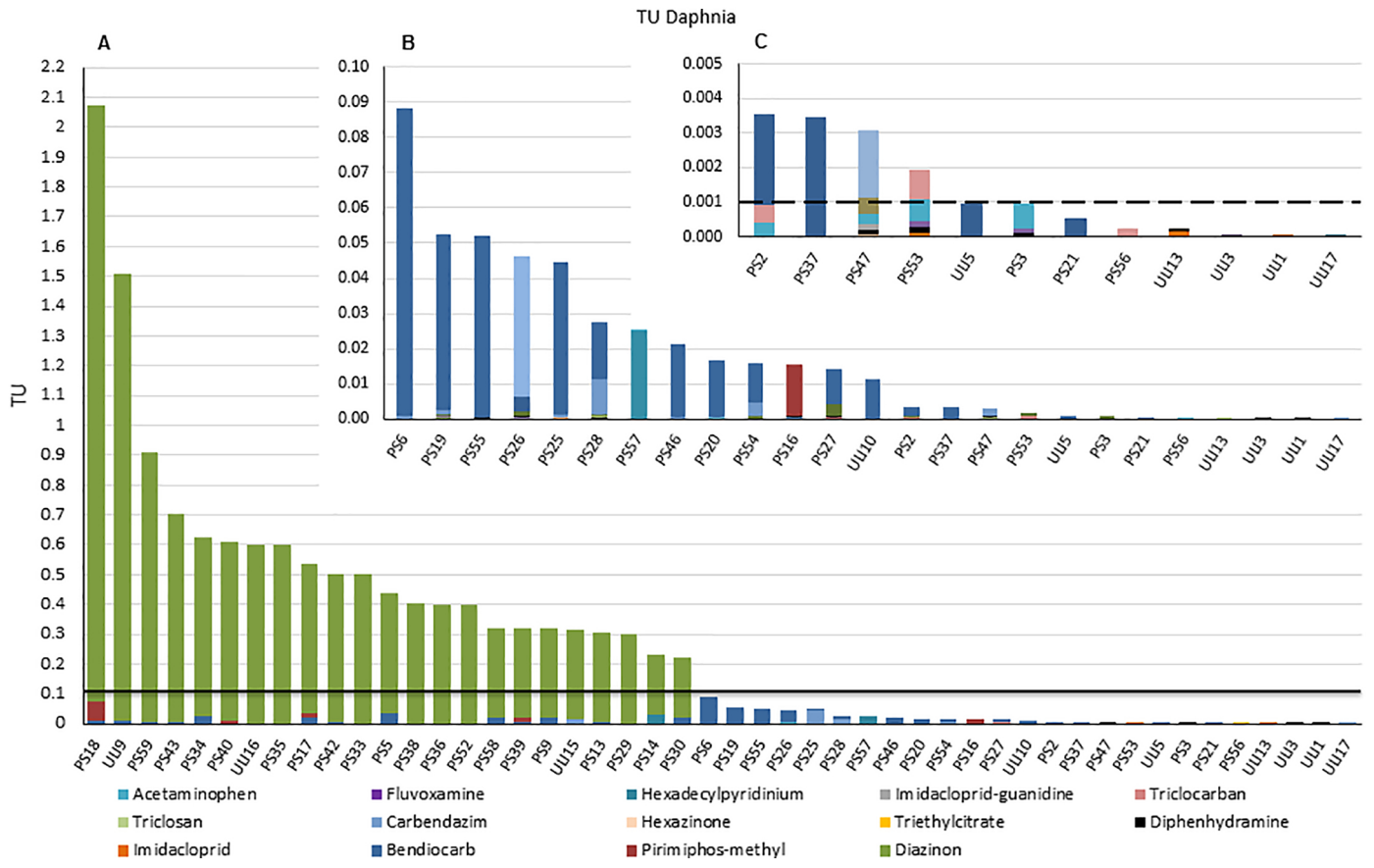
TU Daphnia
A
B
C
TU
PS18 UU9 PS59 PS43 PS34 PS40 UU16 PS35 PS17 PS42 PS33 PS5 PS38 PS36 PS52 PS58 PS39 PS9 UU15 PS13 PS29 PS14 PS30 PS6 PS19 PS55 PS26 PS25 PS28 PS57 PS46 PS20 PS54 PS16 PS27 UU10 PS2 PS37 PS47 PS53 UU5 PS3 PS21 PS56 UU13 UU3 UU1 UU17
Acetaminophen
Fluvoxamine
Hexadecylpyridinium
Imidacloprid-guanidine
Triclocarban
Triclosan
Carbendazim
Hexazinone
Triethylcitrate
Diphenhydramine
Imidacloprid
Bendiocarb
Pirimiphos-methyl
Diazinon

Figure 5

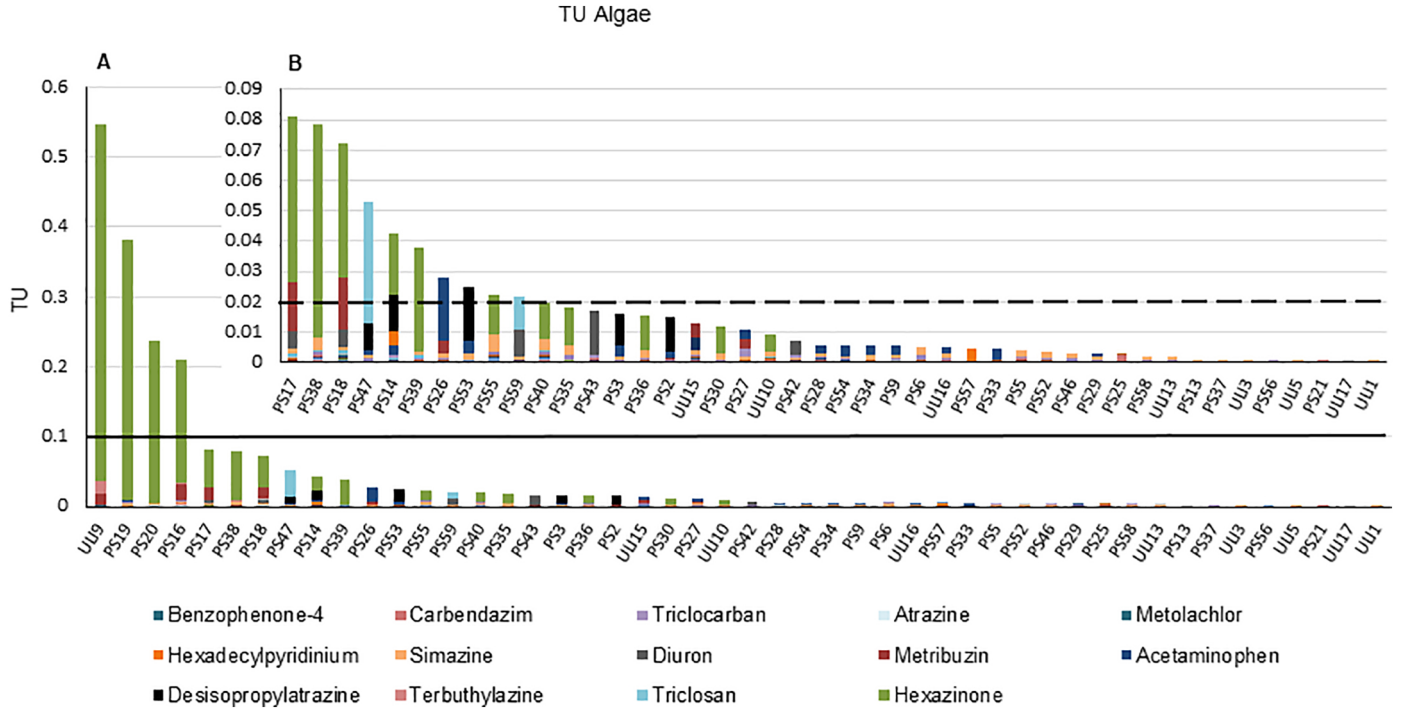
TU Algae
A
B
TU
0.6
0.5
0.4
0.3
0.2
0.1
0
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
UU9 PS19 PS20 PS16 PS17 PS38 PS18 PS47 PS14 PS39 PS26 PS53 PS55 PS59 PS40 PS35 PS43 PS3 PS36 PS2 UU15 PS30 PS27 UU10 PS42 PS28 PS54 PS34 PS9 PS6 UU16 PS57 PS33 PS5 PS52 PS46 PS29 PS25 PS58 UU13 PS13 PS37 UU3 PS56 UU5 PS21 UU17 UU1
PS17 PS38 PS18 PS47 PS14 PS39 PS26 PS53 PS55 PS59 PS40 PS35 PS43 PS3 PS36 PS2 UU15 PS30 PS27 UU10 PS42 PS28 PS54 PS34 PS9 PS6 UU16 PS57 PS33 PS5 PS52 PS46 PS29 PS25 PS58 UU13 PS13 PS37 UU3 PS56 UU5 PS21 UU17 UU1
Benzophenone-4
Carbendazim
Triclocarban
Atrazine
Metolachlor
Hexadecylpyridinium
Simazine
Diuron
Metribuzin
Acetaminophen
Desisopropylatrazine
Terbuthylazine
Triclosan
Hexazinone

Figure 6

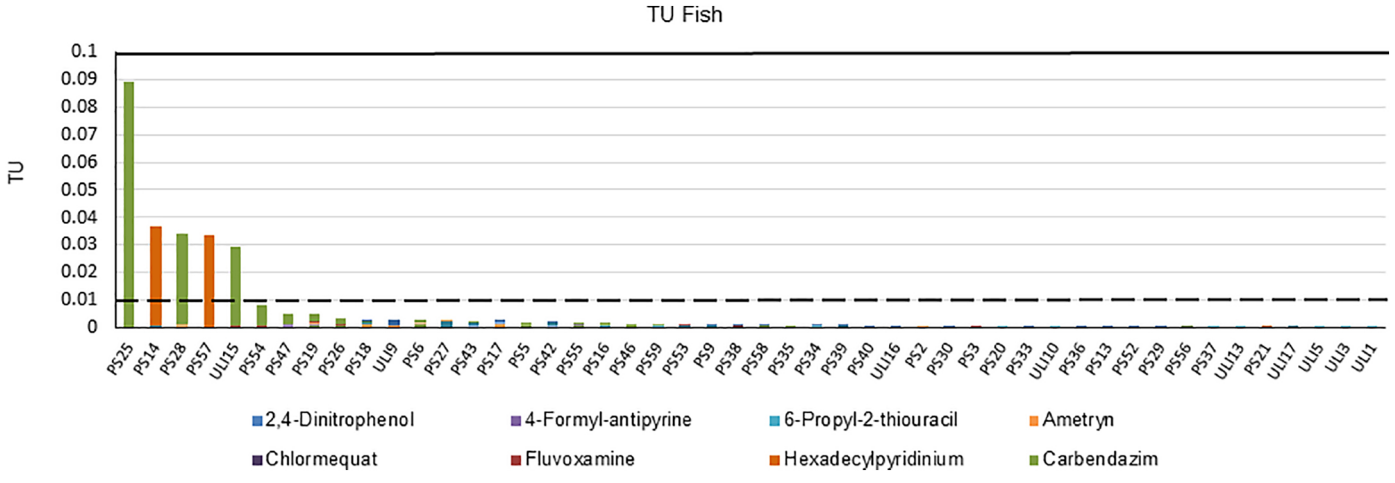
TU Fish
TU
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
PS25 PS14 PS28 PS57 ULI15 PS54 PS47 PS19 PS26 PS18 ULI9 PS6 PS27 PS43 PS17 PS5 PS42 PS55 PS16 PS46 PS59 PS53 PS9 PS38 PS58 PS35 PS34 PS39 PS40 ULI16 PS2 PS30 PS3 PS20 PS33 ULI10 PS36 PS13 PS52 PS29 PS56 PS37 ULI13 PS21 ULI17 ULI5 ULI3 ULI1
2,4-Dinitrophenol
4-Formyl-antipyrine
6-Propyl-2-thiouracil
Ametryn
Chlormequat
Fluvoxamine
Hexadecylpyridinium
Carbendazim

Figure 7