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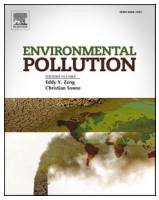

Septic tanks as a pathway for emerging contaminants to the aquatic environment–Need for alternative rural wastewater treatment?☆

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ABSTRACT

Septic tanks (STs) as a decentralised approach to community wastewater treatment were investigated as a pathway for emerging contaminants (ECs) entering the aquatic environment. A broad range of ECs were examined in five community STs (population equivalents 217–475) and receiving rivers in Scotland over 12 months. All 68 studied ECs were detected at least once in ST influent or effluent at a broad concentration range from ng L^{-1} – μg L^{-1} which can surpass freshwater predicted no-effect concentrations. Pharmaceuticals with acute use, such as antibiotics and antifungals, had high monthly variability and concentrations can exceed those previously found in centralised wastewater treatment works. Differences between the STs demonstrate the impact of localised prescription and population behaviour on EC concentrations. The similarities in concentrations between influent and effluent, suggest limited or no removal of ECs in STs. Hence, dilution of the discharges is required to mitigate environmental risk. Although the contribution of ECs sorbed to suspended solids to the total EC concentration was generally small (<10%), higher contributions (>30%) were observed for fluoroquinolone antibiotics (ofloxacin and ciprofloxacin), antidepressants (fluoxetine), and antifungals (clotrimazole). A wide range of ECs were also detected in rivers upstream and downstream of the ST discharge points, and concentrations increased by up to 95% downstream. In general, risk quotients (RQs) in the rivers were low, indicating small risk for the environment. However, higher RQs (>1) were found for ibuprofen, diclofenac and ciprofloxacin in a few samples. Therefore, reducing their concentration by improving ST performance or through sustainable medicines use may be needed at low dilution locations to mitigate any risk.

1. Introduction

Rural wastewater treatment often requires decentralised approaches due to the costs of building and operating centralised wastewater treatment works (WWTWs) and pipe networks in low-density population areas (Massoud et al., 2009). Historically in Scotland, a septic tank (ST) is used in rural and semi-urban areas to treat wastewater from individual houses and small communities (up to 2000 people) (Richards et al., 2016; Scottish Water, 2021). Conservative estimates suggest 9% of the Scottish population use a public or privately owned ST (Ramage et al., 2019; Richards et al., 2016; Scottish Water, 2021). In a watertight underground tank, heavy solids settle as sludge to the bottom and a top layer (scum) is formed of oil, grease and low density solids (Richards et al., 2016). Before being discharged into the ground or a nearby water body, the ST effluent may undergo additional treatment, such as being processed through a subsoil infiltration system (Dubber and Gill, 2014; Richards et al., 2016).

Centralised WWTWs and STs effluents contribute to an array of emerging contaminants (ECs), such as prescription or over-the-counter pharmaceuticals and related metabolites, natural and synthetic

Abbreviations: BOD, Biochemical oxygen demands; COD, Chemical oxygen demands; CAR, Controlled Activity Regulation; EC, Emerging contaminant; GF/F, Glass fibre filter; MQL, Method quantification limit; PVDF-HL, Polyvinylidene fluoride hydrophilic; PE, Population equivalents; PNEC, Predicted no-effect concentration; RQ, Risk quotient; SEPA, Scottish Environment Protection Agency; ST, Septic tank; S/N, signal-to-noise-ratio; SPE, Solid phase extraction; TSS, Total suspended solids; UHPLC-MS/MS, Ultra-high-performance liquid chromatography coupled to tandem mass spectrometry; WWTW, Wastewater treatment work.

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hormones, and other human marker compounds (e.g., caffeine), present in rivers, estuaries and groundwater (Burns et al., 2018; Darwano et al., 2014; Petrie and Moffat, 2022; Scheurer et al., 2012; Wilkinson et al., 2022; Zhang et al., 2018). ECs are known for their potential adverse effects on the aquatic environment that include acute and chronic toxicities, as well as the promotion of antibiotic resistances and endocrine-disrupting properties (Bengtsson-Palme and Larsson, 2016; Caldwell et al., 2012; Comber et al., 2018).

The predicted no-effect concentration (PNEC), indicating the concentration below which no adverse effects are expected, is used in environmental risk assessment. The possible environmental impact of detected ECs can be further evaluated by calculating the risk quotient (RQ) from the measured concentration and the PNEC (Rapp-Wright et al., 2023). Wastewater discharges in Scotland are subject to the Controlled Activity Regulations (CAR) and require authorisation by the Scottish Environment Protection Agency (SEPA). While maximum concentration limits of more routinely measured sanitary determinands, such as biochemical and chemical oxygen demands (BOD, COD), total suspended solids (TSS), and ammonia, can be included in the CAR licence, no legislation for the discharge of ECs exists in Scotland (Comber et al., 2019; SEPA, 2014).

The removal and transformation of ECs in centralised WWTWs depends on the treatment type, wastewater composition and compound properties (Ghazal et al., 2022; Verlicchi et al., 2012). Typically, secondary WWTWs use activated sludge processes and trickling filters, where ECs are mainly removed through aerobic biodegradation and sorption (Verlicchi et al., 2012). While over 90% of the anti-diabetic metformin is transformed to guanylurea by aerobic biodegradation, the anti-convulsant carbamazepine is found to be persistent, with removal efficiencies mostly below 10% (Scheurer et al., 2012; Zhang et al., 2008). In STs, ECs are removed through anaerobic biodegradation, or sorption to particles and oil followed by the physical separation of sludge and scum (Schaider et al., 2017). When particles are not completely separated from the liquid phase, they can act as a vector for ECs into the environment (Baker and Kasprzyk-Hordern, 2011; Darwano et al., 2014; Schaider et al., 2017). Therefore, determination of ECs bound to TSS, as well as the liquid phase of the sample is important (Baker and Kasprzyk-Hordern, 2011; Costa Junior et al., 2022; Darwano et al., 2014), but has so far not been reported for STs.

Most studies have focused on centralised WWTWs and their receiving surface waters, as they are considered the main pathway of ECs into the environment (Baker and Kasprzyk-Hordern, 2011; Darwano et al., 2014; Kay et al., 2017; Paíga et al., 2019). STs have been less intensively studied, but effluents can contain ECs in higher concentrations than those from centralised WWTWs (Matamoros et al., 2009; Ramage et al., 2019). For instance, Matamoros et al. (2009) reported carbamazepine concentrations up to 13.8 μg L^{-1} in the effluent of one decentralised WWTWs with a drainfield. For comparison, the maximum concentration in a European Union-wide investigation of centralised WWTWs by Loos et al. (2013) was 4.6 μg L^{-1}.

So far, most research determining ECs in STs was conducted in the USA and focused on STs that discharge to the ground through subsoil infiltration systems (Conn et al., 2010, 2006; Del Rosario et al., 2014; Fisher et al., 2016; Phillips et al., 2015; Yang et al., 2017). However, in Scotland a significant number of STs discharge to surface waters (rivers, lochs, and transitional and coastal waters) with or without additional treatment. Furthermore, several studies on the fate and removal of ECs in STs was conducted under controlled conditions in pilot projects (Du et al., 2014; Garcia et al., 2013; Teerlink et al., 2012b), potentially due to the difficulties associated with sampling STs, such as their remote location, lack of suitable sampling points and confidentiality. However, the performance of a ST depends highly on its usage population and maintenance, such as emptying, and malfunctioning, e.g., caused by blockages (Du et al., 2014; Richards et al., 2016). Investigating different full-scale STs, by sampling influent, effluent, and river water will allow a more realistic estimate of their performance and their impact on the environment.

Therefore, the aim of the study was to understand the fate and removal of ECs in community STs, and the impact of a variety of ST discharges to water quality in Scotland. A broad range of ECs were analysed over 12 months in influent and effluent wastewater and TSS of five different community STs and in the receiving rivers.

2. Materials and methods

2.1. Materials

The study included the determination of 68 ECs taking their potential for posing a risk to the Scottish environment and existing prioritization and monitoring schemes into consideration (European Commission, 2018, 2019, 2022; Helwig et al., 2021; UKWIR, 2023; 2018). Selected ECs were prescription or over-the-counter pharmaceuticals and related metabolites from different classes, natural and synthetic hormones, and other human wastewater marker compounds (Table S1). Isotopically labelled ECs are used as surrogates (Table S2). Methanol (HPLC grade, ≥99.9%), glass fibre filter (GF/F) discs (0.7 μm, 47 mm) and formic acid (≥99.0%) were purchased from Fisher Scientific (Loughborough, UK); ammonium formate (≥99.0%) and ammonium fluoride (≥99.99%) from Sigma Aldrich (Gillingham, UK); and ammonium hydroxide (35%) from Fison Instruments Ltd (Glasgow, UK). Water was produced at ultra-pure quality in the laboratory (resistivity = 18.2 MΩ cm at 25 °C, PurA-Q18.2, LabPro, European Instruments, Oxford, UK). Oasis HLB solid phase extraction (SPE) cartridges (3 mL, 60 mg for water; 6 mL, 200 mg for filter paper retained solids) were purchased from Waters (Manchester, UK), and polyvinylidene fluoride hydrophilic (PVDF-HL) Q-Fil syringe filter (13 mm, 0.22 μm) from Greyhound (Birkenhead, UK).

2.2. Sampling of septic tanks and receiving surface waters

Five community STs serving 217–475 population equivalents (PE) were monitored between October 2021 and September 2022. They are concrete rectangular tanks between 75 and 225 m^3 that receive rainwater runoff in addition to wastewater. Hydraulic retention times (HRT) were estimated to be 5.5–23 h. The STs were emptied every 8–52 weeks, depending on the size of the tank, PE and existing concerns or compliance issues (Table 1). The STs were located in rural areas in the Central Belt and North-West Highlands in Scotland, and discharged to three different rivers and a small stream (Table 1). Distances from the STs to the rivers were estimated to be between 20 and 120 m. All receiving rivers mainly flowed through agricultural, wood- and grassland with little urban land use. There were single houses and smaller villages alongside the rivers that were served by public or privately owned STs. The total rain in mm day^{-1} and the river flow during sampling were received from SEPA (SEPA, 2022), and the monthly nominal dilutions of the ST discharges into the rivers were calculated from the river and the ST flows following industry practice (Table S3). Mean effluent dilutions were 96–18148 (Table 1).

Grab samples (1 L) were collected in polypropylene bottles at the influent and effluent point of the STs monthly, and in the river upstream and downstream of the ST discharge point at a minimum distance of five river widths every three months (Table S3).

2.3. Analytical methods

Initially, samples were filtered under vacuum through 0.7 μm GF/F membrane filters. Liquid samples were analysed by direct injection and following SPE using Oasis HLB cartridges (Details in S3). Ultrasonic extraction of TSS was performed at 50 °C using three extraction cycles with 2% NH_4OH in methanol, 2% formic acid in methanol and methanol. The combined supernatants were filtered, diluted and cleaned up by SPE. All extracts and direct injection samples were filtered through a PVDF-HL syringe filter prior to ultra-high-performance liquid

Table 1
Selected septic tanks (STs) with the respective population equivalents (PE) contributing to the ST, ST volume (V), estimated hydraulic retention time (HRT), emptying frequency, location in Scotland, the receiving river and dilution factors. The dilution factor is calculated from the mean river flow over 2 h at sampling time[a] or from the mean flow of the river[b], and the ST flow following industry practice (See Supplementary data). Monthly dilution factors are presented in Table S3. HRT was estimated by dividing the ST flow with ST volume.

ST	PE	V/m^3	HRT/h	Emptying frequency /weeks	Location	Receiving River	Mean dilution factor and observed range
1	308	75	7.6	8	Central Belt	Clyde	3189[a] (580–11990)
2	314	75	7.8	52	Central Belt	Clyde	3257[a] (592–12244)
3	475	75	5.5	8	Central Belt	Small tributary to Clyde	96[b]
4	314	100	10	17	North-West Highlands	Black Water	4808[b]
5	217	225	23	26	North-West Highlands	Glass	18148[a] (4276–35476)

[a] Mean calculated from observed dilution factors during sampling.
[b] No daily/hourly river flow data available: Mean calculated from historic mean daily flow.

chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS) injection.

Samples were analysed using an established and fully validated UHPLC-MS/MS methodology (Wilschnack et al., 2024) using an ACQUITY UPLC system from Waters (Waters Corporation, Milford, MA) with a Xevo TQ-XS Triple Quadrupole Mass Spectrometer. Two separate methods were applied to achieve maximum sensitivity of both acidic and basic ECs using methanol-water-gradients along with 5 mM ammonium formate and 0.1% formic acid in positive ionisation, and 0.5 mM ammonium fluoride in negative ionisation (Table S4). ECs were quantified using multiple reaction monitoring (MRM) transitions (Table S5). Ion ratios, retention times and signal-to-noise ratios (S/N) were monitored (European Commission, 2002).

Method quantification limits (MQLs) were 0.0001–1.2 μg L^{-1} in ST influent, effluent and river water, with ≤0.01 μg L^{-1} achieved for 60% of ECs in all three water matrices, and 0.1–49 μg kg^{-1} in solids (Table S6). For quality control, one influent and effluent, and two river water samples (upstream and downstream) were spiked with ECs (10 μg L^{-1}) and processed with each batch of environmental samples using both sampling preparation methods (Table S7). Method precision was <10% and method accuracy was 75–125% for the majority of studied compounds during the course of this study (Table S7). When accuracies were outside the acceptable range, environmental concentrations were corrected.

Sanitary determinands: TSS, COD, BOD and ammonia were analysed by Scottish Water using accredited standardised methods.

2.4. Data analysis

Statistical analysis was performed with R (version 4.2.2–4.3.1) and RStudio (2022.12.0 and 2023.09.01) using the packages dplyr, openxlsx, readxl, tidyverse and rstatix for data manipulation and statistical analysis, and the packages ggplot2, patchwork and ggpubr for graph creation. Relative standard deviations and arithmetic means were determined for all replicates. For concentrations below the MDL or MQL limit, half of the value was used. Detections < MDL were excluded from calculating the sum of EC concentrations (European Commission, 2009) and in risk calculations. Statistical analysis for significant difference ($p < 0.05$) was determined for ECs with detection frequencies >40% (Burns et al., 2018) using nonparametric Wilcoxon and Kruskal-Wallis tests, due to the non-normality and unequal variance of the data. Correlations of ECs and sanitary determinands were assessed with ggcorrplot and psych using Spearman correlation coefficients (r), a nonparametric measure of monotonic, possibly non-linear, statistical dependence between two variables. Correlations were strong $|r| \geq 0.60$, moderate $0.40 \leq |r| < 0.60$, and weak $0.20 \leq |r| < 0.40$ (Gazzaz et al., 2013; Zhao et al., 2022), and statistically significant for $p < 0.05$.

To determine environmental risks, RQs were calculated in wastewater and river water by dividing the measured EC concentration by the lowest PNEC obtained from the NORMAN ecotoxicology database (NORMAN Ecotoxicology Database, 2023). Risks were categorised as RQ < 0.1 = insignificant risk; 0.1–1.0 = low risk; 1.0–10 = medium risk; and >10 = high risk (Rapp-Wright et al., 2023).

3. Results and discussion

3.1. Occurrence and removal of emerging contaminants in septic tank wastewater

Influent and effluent wastewater from the five STs were analysed. Overall, all 68 ECs were detected at least once, many of which are reported in ST wastewater for the first time. Detection frequencies varied from once to present in all influent and effluent samples (Table S8). Among the most detected compounds were the human discharge markers caffeine and cotinine, different analgesics, antihistamines, antidepressants, betablockers and the antidiabetic drug metformin. Overall, sum of EC concentrations were found at mean concentrations of 981 μg L^{-1} in influent and 762 μg L^{-1} in effluent (Fig. 1). For individual ECs, concentrations ranged from 0.016 ng L^{-1} – 2605 μg L^{-1} (Fig. 2). Wastewater commonly shows a wide concentration range for different ECs (Oertel et al., 2018; Rapp-Wright et al., 2023). Paracetamol was found at the highest individual concentration of up to $2.6 \cdot 10^3$ μg L^{-1} in influent and 720 μg L^{-1} in effluent in June, and mean concentrations of 400 μg L^{-1} and 340 μg L^{-1} in influent and effluent, respectively (Table S8). Maximum and mean EC concentrations were higher than typically reported for centralised WWTWs (Du et al., 2014; Kasprzyk-Hordern et al., 2009; Niemi et al., 2020), but lower than found in individual household STs (Ramage et al., 2019).

Overall, the differences in the sum of EC concentrations, concentrations of individual ECs and number of ECs detected across the 12 months between the five STs was small. Only the sum of EC concentrations in both influent and effluent was higher in ST 5 than in the other locations (Fig. 1). This is driven by the higher metformin concentration, mean concentrations of 823 μg L^{-1} in influents and 413 μg L^{-1} in effluents, respectively, which is higher than in the other STs (127–314 μg L^{-1} in influents and 125–195 μg L^{-1} in effluents), and centralised WWTWs (Helwig et al., 2022; Scheurer et al., 2012). At the same time, propranolol and atenolol were highest in ST 2 and clopidol was only detected in ST 3 in influent and effluent (Fig. S1). As STs are used by smaller groups than centralised WWTWs, localised prescription behaviour has a significant impact on ECs concentrations (Schaider et al., 2017). Hence, targeting influent concentrations through sustainable medicines use, such as green prescription, whereby pharmaceuticals with less environmental impact are selected for use, or non-pharmacological interventions could be especially effective in rural areas.

In both influent and effluent, the number of ECs and sum of EC concentrations detected were lowest in February in ST 4 and 5, and lowest in February and March in ST 1–3 (Fig. 1), in line with high rainfall (Table S3). Dilution of the wastewater with surface water runoff can reduce EC concentrations (Brunsch et al., 2018). Statistical differences between the months were found ($p < 0.05$), but no clear

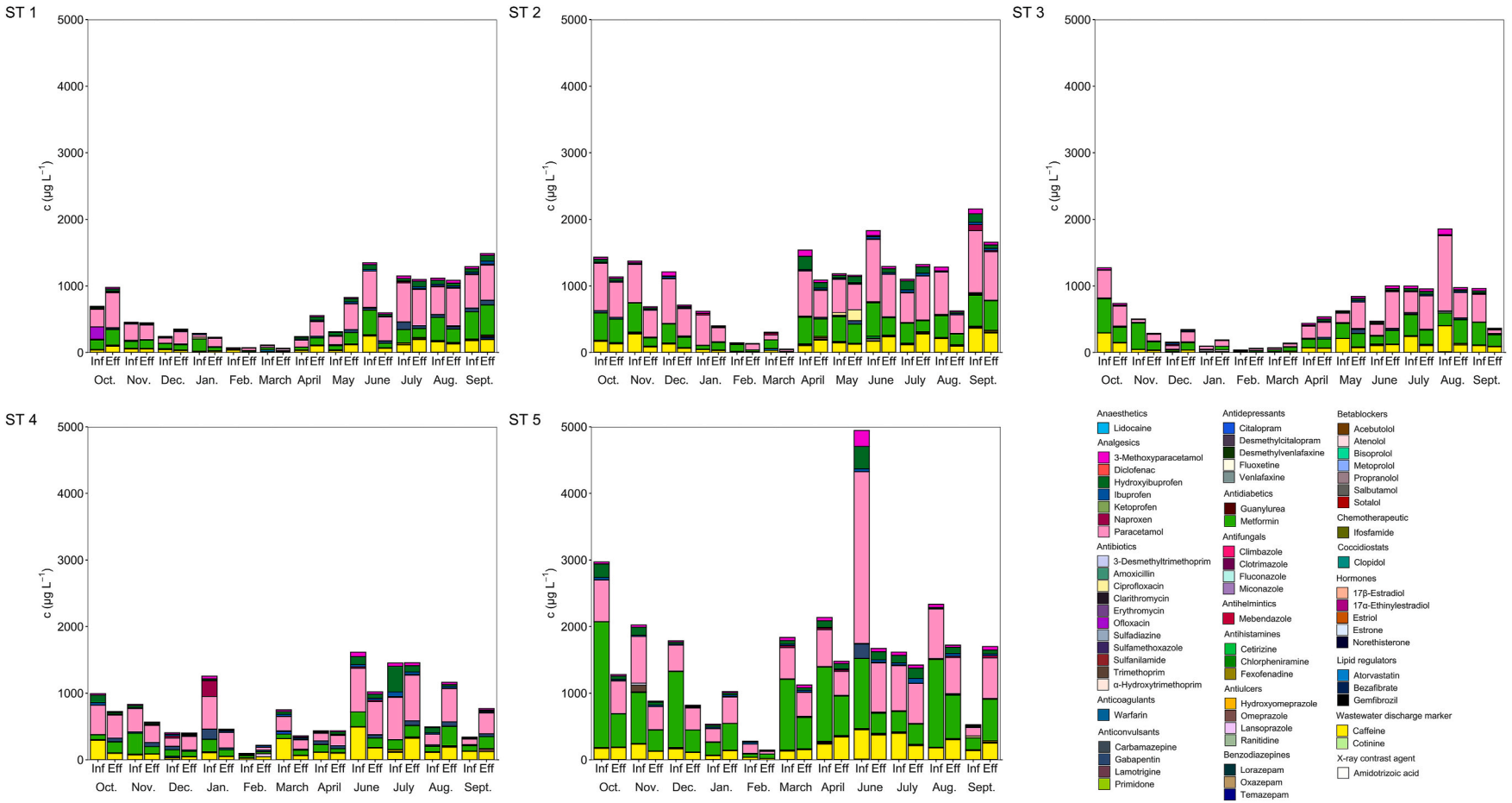

Fig. 1. Sum of detected liquid EC concentrations (c) in individual STs (ST 1–5) in influent (Inf) and effluent (eff), sorted by class.

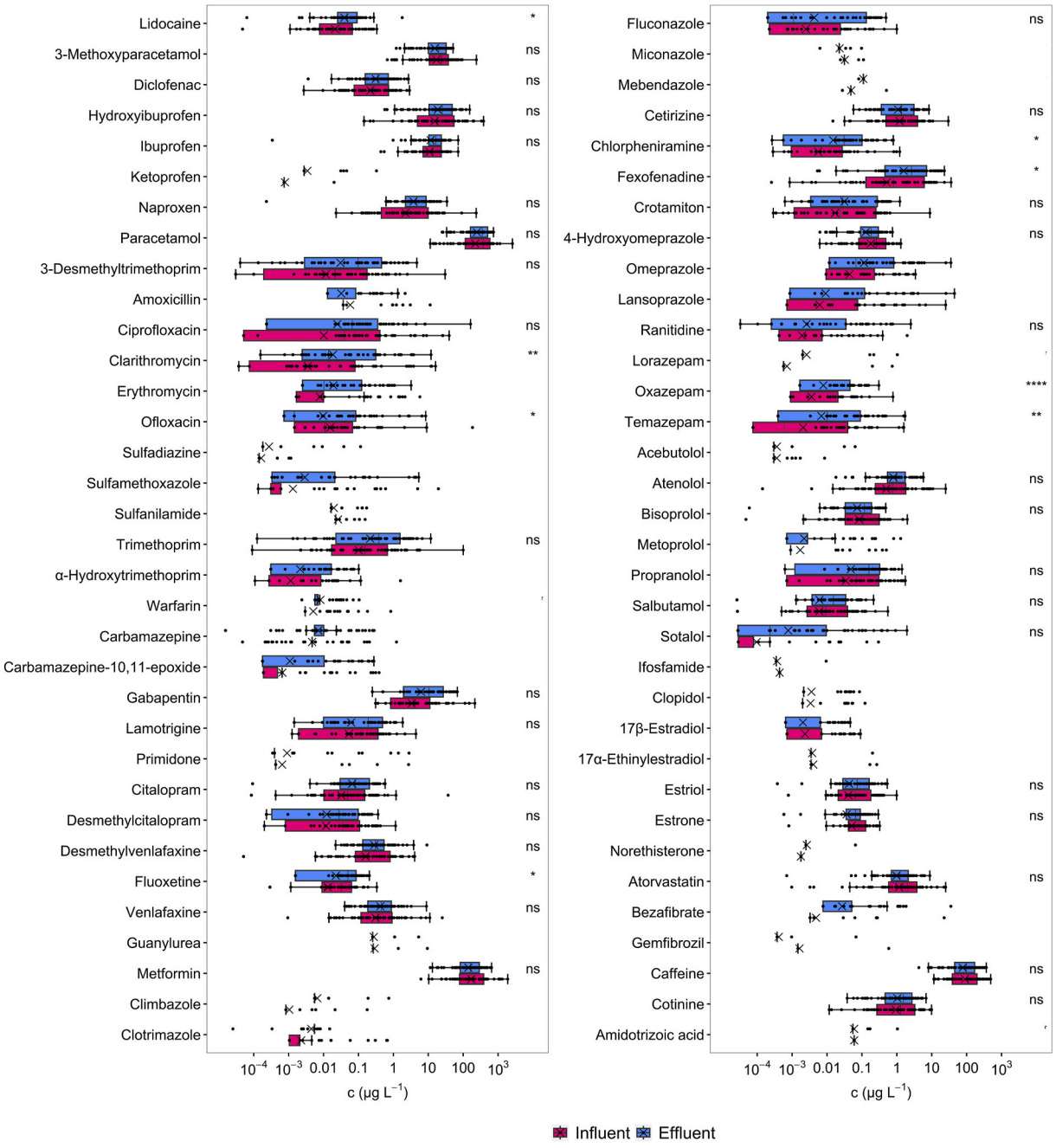

Fig. 2. Liquid influent and effluent concentrations (c, logarithmic scale) for individual EC with results of Wilcoxon test for ECs with detection frequencies >40% (ns = no significant difference between influent and effluent, */** = difference), sorted by class (Fig. 1). Concentrations >500 µg L^{-1}, found for metformin and paracetamol, are above the calibration range and are considered semi-quantitative. Concentrations in individual STs in Fig. S1 and Table S6.

relationship can be identified, and overall, no further seasonal trend was observed, indicating dilution with rainwater is likely more important than seasonal use of ECs. Although seasonal variations are frequently discussed in the literature, a consistent trend in wastewater is hard to identify and can vary for different ECs (Brunsch et al., 2018; Kay et al., 2017; Musolff et al., 2009; Niemi et al., 2020).

Monthly variability is high, especially for pharmaceuticals with acute use, such as antibiotics and antifungals (Fig. 2). Wastewater influent is highly heterogeneous and short-term fluctuations in EC concentrations are reported (Du et al., 2014; Matamoros et al., 2016; Ort et al., 2010). The variability is higher for smaller WWTWs as they receive fewer discrete wastewater inputs (Teerlink et al., 2012a). Shorter transport time could further reduce the mixing observed within sewers.

If detected, EC concentrations, in particular for those with acute use, can exceed those previously found in centralised WWTWs, e.g., maximum effluent concentrations were 12 µg L^{-1} for clarithromycin in June, 40 µg L^{-1} for erythromycin in September, and 163 µg L^{-1} for ciprofloxacin in May (Helwig et al., 2022; Kay et al., 2017; Loos et al., 2013; Niemi et al., 2020). As they are prescribed over short periods of time and used by fewer people at once, a high variability in the data is expected when a small group of people contribute to the wastewater sampled (Schaider et al., 2017).

For the same EC, effluent concentrations were lower, similar to and higher than in the influent depending on the month, highlighting the great variability of ST wastewater. This is for instance, observed for venlafaxine in ST 3 in August, April and September, respectively, where the concentrations were found to be 25 µg L^{-1} and 1.4 µg L^{-1}, 0.39 µg

L^{-1} and 0.53 μg L^{-1}, and 2.3 μg L^{-1} and 8.9 μg L^{-1} in influent and effluent, respectively. Venlafaxine has previously been reported at higher concentrations than other antidepressants (Paíga et al., 2019; Rapp-Wright et al., 2023). Mean influent and effluent concentrations of 1.4 μg L^{-1} and 0.79 μg L^{-1}, were similar to those recently reported in centralised WWTWs in Ireland (Rapp-Wright et al., 2023), but higher than average concentrations in the UK (Baker and Kasprzyk-Hordern, 2013; Petrie et al., 2017) and the EU (Loos et al., 2013).

Generally, the variability in concentrations for pharmaceuticals with chronic use, such as antidepressants and β-blockers, is smaller (Fig. 2). However, less commonly used pharmaceuticals, e.g., metoprolol and sotalol, show a bigger variability in reported concentrations, than highly prescribed pharmaceuticals, such as propranolol and atenolol (Scotland National Statistics, 2022). With mean concentrations of 0.26 μg L^{-1} and 0.24 μg L^{-1}, and maximum concentrations of 1.8 μg L^{-1} and 1.4 μg L^{-1} in the influent and effluent, respectively, propranolol concentrations are similar to previously reported in centralised WWTWs in Scotland (Helwig et al., 2022).

For the majority of compounds, no significant difference was found between influent and effluent concentrations, indicating limited removal (Fig. 2). This is further supported by ST effluent concentrations for a number of high-use ECs, including metformin, ibuprofen, diclofenac and atenolol being similar to concentrations typically observed in influent of centralised WWTWs (Helwig et al., 2022; Kasprzyk-Hordern et al., 2009; Zhang et al., 2008). Removal of the sanitary determinands TSS (33–93%), COD (6–77%), BOD (3–74%) and ammonia (-41–47%; Fig. S2), was not as high as typically reported for centralised WWTWs (Du et al., 2014; Garcia et al., 2013). However, the high variability between different months makes determining exact removal efficiencies difficult (Teerlink et al., 2012b), and removal efficiencies of ECs were not calculated. Considering the high variability of ST influent wastewater, composite sampling may be a more appropriate approach when investigating removal efficiencies. However, this poses a challenge owing to the rural nature of study locations. Limited removal of ECs in STs and other preliminary and primary treatments, has been previously reported (Du et al., 2014; Garcia et al., 2013; Verlicchi et al., 2012).

3.2. Predicting septic tank performance for emerging contaminants through sanitary determinands

Comprehensive monitoring of ECs in all STs is not feasible, given the high costs and the substantial time involved for sampling and analysis. Therefore, if correlations between more routinely measured sanitary determinands and ECs were established, results could be used to predict ST performance. The correlation of ECs with TSS, COD, BOD and ammonia was examined by computing Spearman correlation matrices for influent and effluent (Figs. S3–4). Strong significant correlations were found among the sanitary determinands in influent and effluent ($r \geq 0.73$, $p \leq 5.1 \cdot 10^{-9}$), with sanitary determinands and some ECs (Table 2), and among some ECs. Significant strong correlations between sanitary determinands and ECs were positive and found for high-use ECs with high detection frequencies of 100% in influent and ≥83% in effluent samples, including population markers paracetamol, ibuprofen, metformin, caffeine and cotinine. Strong relationships among ECs were mainly found between those high-use ECs. Furthermore, correlations were found between all except one pharmaceutical with their human metabolites, as they are excreted simultaneously by individuals after drug metabolism, and degradation in STs is limited. Correlations were stronger and observed for more ECs in the effluent than in the influent, potentially due to the lower concentration variability (Fig. S2), and generally, weaker for TSS than for the other sanitary determinands. Previously, no correlations between ECs and sanitary determinands were observed in centralised WWTWs (Comber et al., 2019). Stronger correlations in smaller WWTWs were also found by Harnisz et al. (2020). Due to the high variability in detected EC concentrations and low detection frequencies, sanitary determinands cannot be used to predict ST performance for low-use ECs. Sanitary determinands are not sufficient to determine the quality of wastewater discharges, as low-use ECs, such as antibiotics and hormones, can impact the environment (Bengtsson-Palme and Larsson, 2016; Caldwell et al., 2012). However, they can be used as indicators to identify STs with a higher impact to river water concentrations for high-use ECs. STs with high sanitary determinand concentrations, in particular BOD, COD or ammonia, could be prioritized for further investigation.

3.3. Partitioning of emerging contaminants between bound and liquid phases

In addition to the liquid phase of the wastewater sample, ECs sorbed to TSS in influent and effluent wastewater were analysed. For better comparison with the liquid phase, EC concentrations were converted from μg g^{-1} and reported as μg L^{-1}. In total, 51 ECs were quantified at least once in TSS, at concentrations from $1.4 \cdot 10^{-4}$ μg L^{-1} to 256 μg L^{-1} in influent, and $1.1 \cdot 10^{-4}$ μg L^{-1} to 57 μg L^{-1} in effluent, respectively (Fig. S5). Similar to what has been reported for the liquid phase, a high variation in detection frequencies and concentrations for ECs is observed. High mean concentrations of 0.84 μg L^{-1} and 1.0 μg L^{-1} in influent TSS, and 1.0 μg L^{-1} and 1.3 μg L^{-1} in effluent TSS were, for example, found for ofloxacin and ciprofloxacin, respectively (Fig. 3). Fluoroquinolone antibiotics are known for their adsorption tendency due to electrostatic interactions (Polesel et al., 2015), and are often found at high concentrations in TSS (Lin et al., 2018). Other ECs present at high concentrations in TSS were paracetamol, caffeine and hydroxyibuprofen in line with their high liquid phase concentrations in wastewater (Ledieu et al., 2021).

For the majority of ECs, no significant difference was found between influent and effluent TSS concentrations, indicating limited removal of ECs from the sorbed phase, too. The sorption to TSS nevertheless suggests some removal of ECs due to the sludge formation and reduction of TSS. However, this is limited by the comparatively low reduction of TSS. Increased TSS removal could improve removal for ECs by STs, especially for those with high contribution of TSS to the total concentration.

The percentage of the total EC concentration that was measured on TSS was calculated (Table S9). Overall, a wide range of percentage contribution was found for individual ECs in different samples. For example, the contribution of TSS to the total concentration of trimethoprim when detected in both matrices was 0.77–83% in influent and 0.72–90% in effluent. Sorption is influenced by wastewater properties such as pH, ionic strength, organic matter and temperature, and TSS composition (Lin et al., 2018; Polesel et al., 2015; Xu et al., 2021). Thus, the wide range of percentage contribution is attributed to the dynamic nature of ST wastewaters driven by the low contributing population. For most ECs, the contribution of TSS to the total concentration is low, with mean contributions ≤10% for 33 of the 59 ECs analysed in both phases.

Table 2
Emerging contaminants (ECs) that showed significant ($p < 0.05$) spearman correlations ($r > 0.6$) with sanitary determinands. All correlations were positive (full matrices in Figs. S3–4).

	Influent	Effluent
Correlation (significant)	3-methoxyparacetamol, hydroxyibuprofen, paracetamol, metformin, 4-hydroxyomeprazole, caffeine, cotinine	3-methoxyparacetamol, hydroxyibuprofen, ibuprofen, paracetamol, metformin, cetirizine, fexofenadine, 4-hydroxyomeprazole, atenolol, bisoprolol, salbutamol, estrone, caffeine, cotinine

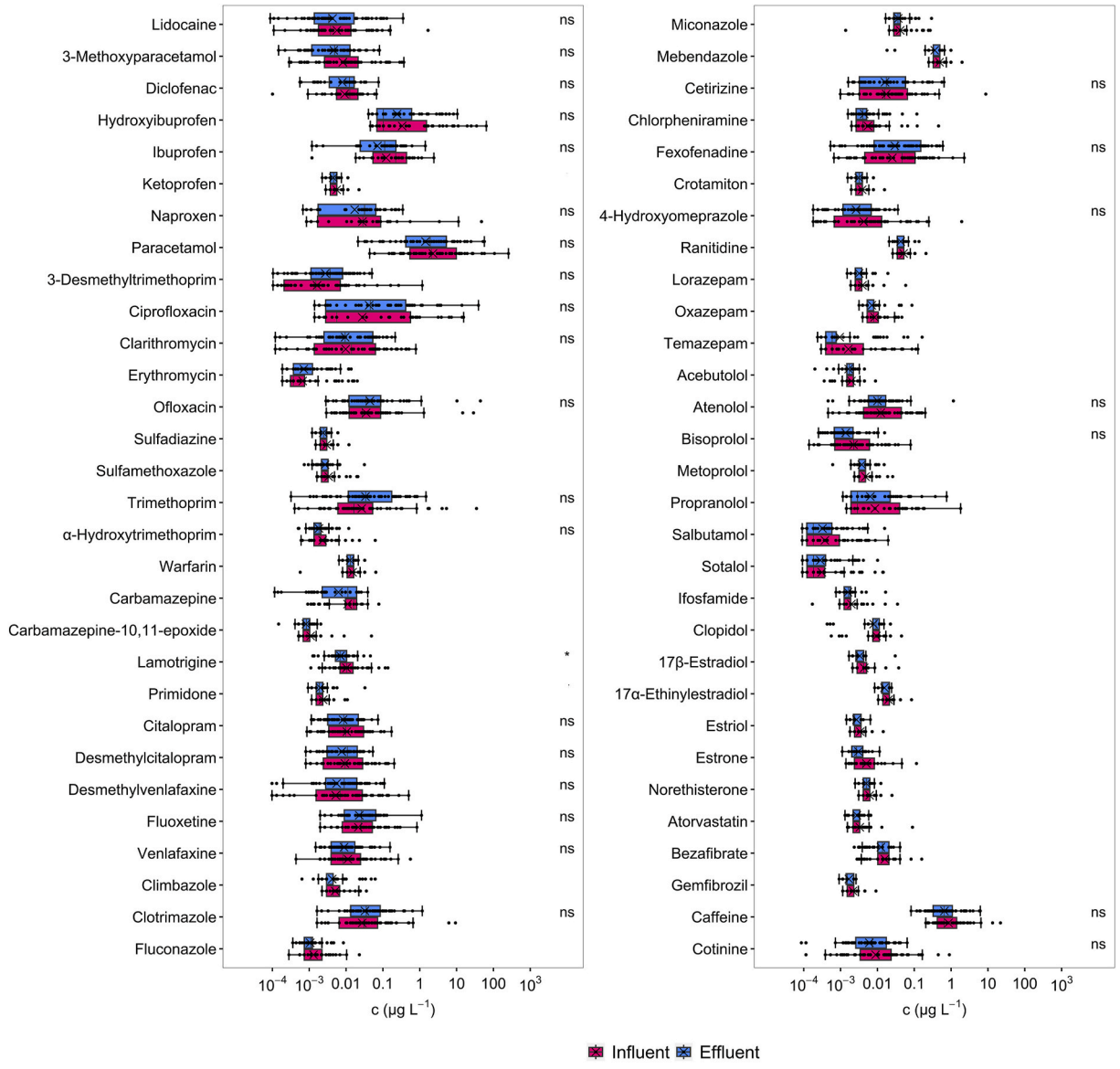

Fig. 3. Total suspended solid concentrations (c) of individual ECs (logarithmic scale) in influent and effluent with results of Wilcoxon test for ECs with detection frequencies >40% (ns = no significant difference between influent and effluent, */** = significant difference), sorted by EC class (Fig. 1). A few concentrations >0.3 µg L^{-1} are above the calibration range and are considered semi-quantitative. This depends on the TSS of individual samples and amount of sample used in the extraction and is mainly observed for caffeine, ciprofloxacin, paracetamol and hydroxyibuprofen. Concentrations in individual STs are in Fig. S6.

Among them are ECs, such as caffeine, paracetamol and hydroxyibuprofen that were found at comparatively high concentrations. However, high contributions >30% were observed for seven ECs in influent and effluent, consistent with other studies (Baker and Kasprzyk-Hordern, 2013; Lin et al., 2018; Subedi and Kannan, 2015). This includes, ECs for which high sorption tendencies have been previously reported, such as antibiotics including ofloxacin and ciprofloxacin (Lin et al., 2018), antidepressants including fluoxetine (Baker and Kasprzyk-Hordern, 2013; Golovko et al., 2020), and the highly lipophilic antifungal clotrimazole (Peng et al., 2012). Since STs can discharge higher TSS concentrations than centralised WWTWs (Du et al., 2014; Garcia et al., 2013), determining the total EC concentration (sum of liquid and TSS phases) becomes increasingly important, to avoid underestimating the possible environmental impact of effluent discharges.

RQs were calculated for all detected ECs in ST effluent using total concentrations to estimate the environmental impact in a worst-case scenario (Fig. 4), as TSS can act as a vector for ECs into the environment (Baker and Kasprzyk-Hordern, 2011; Darwano et al., 2014; Schaider et al., 2017). Most determinations (n = 1633 of 3886) had a RQ ≤ 1. However, a medium or high risk (RQ > 1) was calculated for 35 ECs in at least one effluent sample (743 determinations), more commonly than for effluents from centralised WWTWs (Archer et al., 2017; Paíga et al., 2019; Rapp-Wright et al., 2023). Overall, determined risks are similar for the total and liquid concentration, but can be underestimated for a few ECs and samples when the sorbed concentration is not accounted for (Fig. S6). For clotrimazole the risk would be frequently underestimated when assessed solely based on liquid phase concentrations, as all RQs were <1, whereas RQs >1 were determined for 34 effluent samples using the total concentration (Fig. S6). This is explained with its low detection frequency in the liquid phase and high sorption tendency (Peng et al., 2012). Highest RQs (at least one RQ > 100) were found for caffeine, ciprofloxacin, clarithromycin, 17β-estradiol, 17α-ethinylestradiol and ibuprofen using both total and liquid concentrations. RQs and concentrations demonstrate that ST discharges are reliant on dilution in the environment to mitigate risk. To achieve

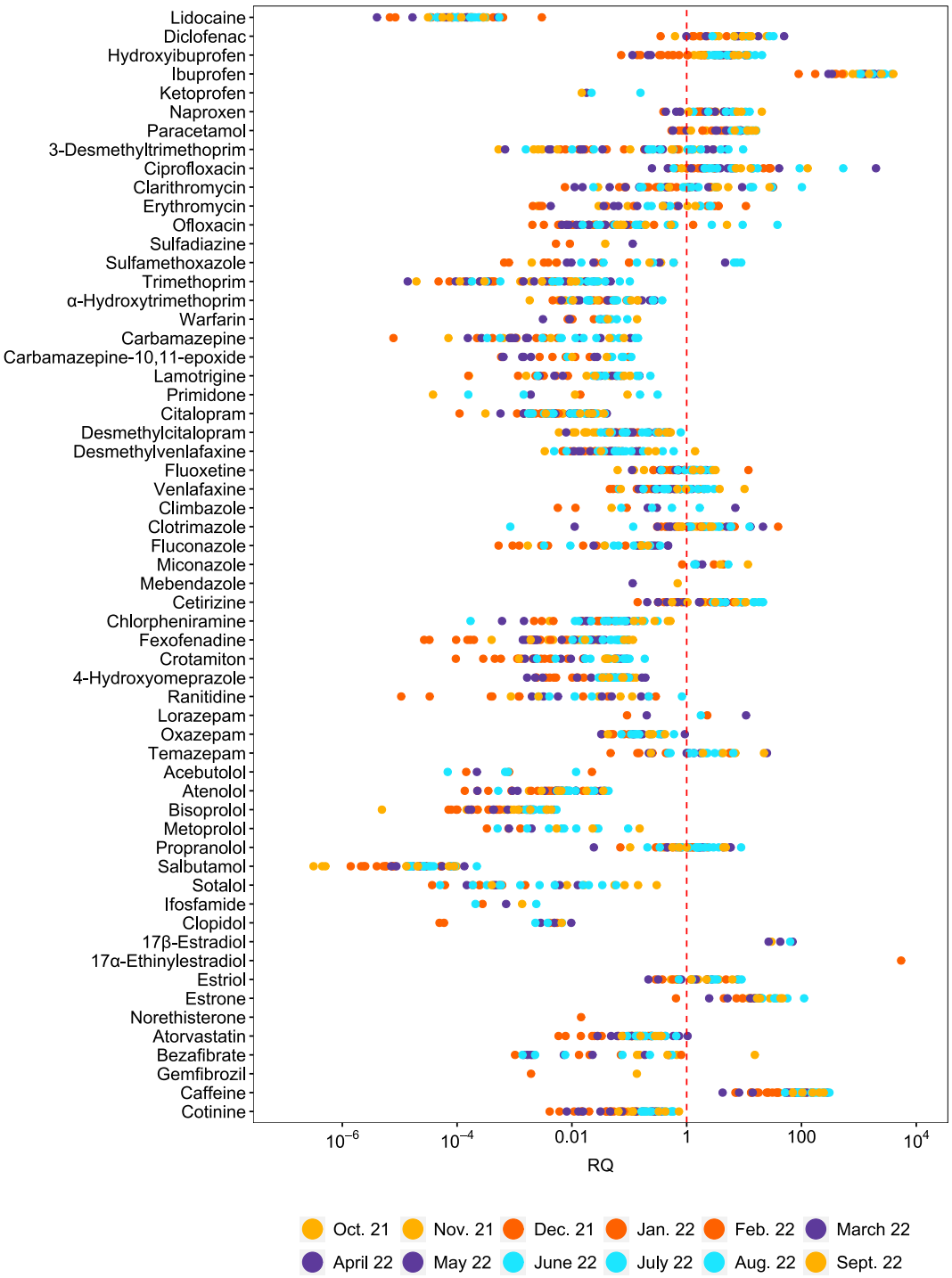

Fig. 4. Risk Quotients (RQ; logarithmic scale) of detected ECs using total concentrations (sum of liquid and TSS concentrations), sorted by class, in septic tank effluents. PNECs in Table S4. Effluent concentrations with RQ $\geq$ 1 (red dotted line) require dilution to mitigate environmental risk. RQs for liquid and TSS concentrations only are in Fig. S2. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

low risks (RQ < 1) for all ECs a minimum dilution of 6600 is required, higher than most dilution factors in this study (Table S3). However, dilution factors were sufficient for the majority of ECs, and only for ibuprofen, ciprofloxacin and caffeine, a medium to high risk to the environment is expected.

3.4. Contribution of septic tanks to receiving surface waters

Surface water was analysed upstream and downstream of the ST discharge points. Due to the low TSS concentrations in river water and low percentage contribution for the majority of ECs in wastewater, only the liquid phase was analysed. In total, 27 ECs were detected at least once (Fig. 5). Highest detection frequencies were observed for the human discharge markers caffeine and cotinine that were detected in 95% of the upstream and downstream samples (Table S10). Furthermore, the frequently consumed over-the-counter drug paracetamol was found in 71% of the upstream samples at a mean concentration of 0.034 µg L^{-1} ($2.7 \cdot 10^{-4}$ – 0.40 µg L^{-1}), and in 95% of the downstream samples

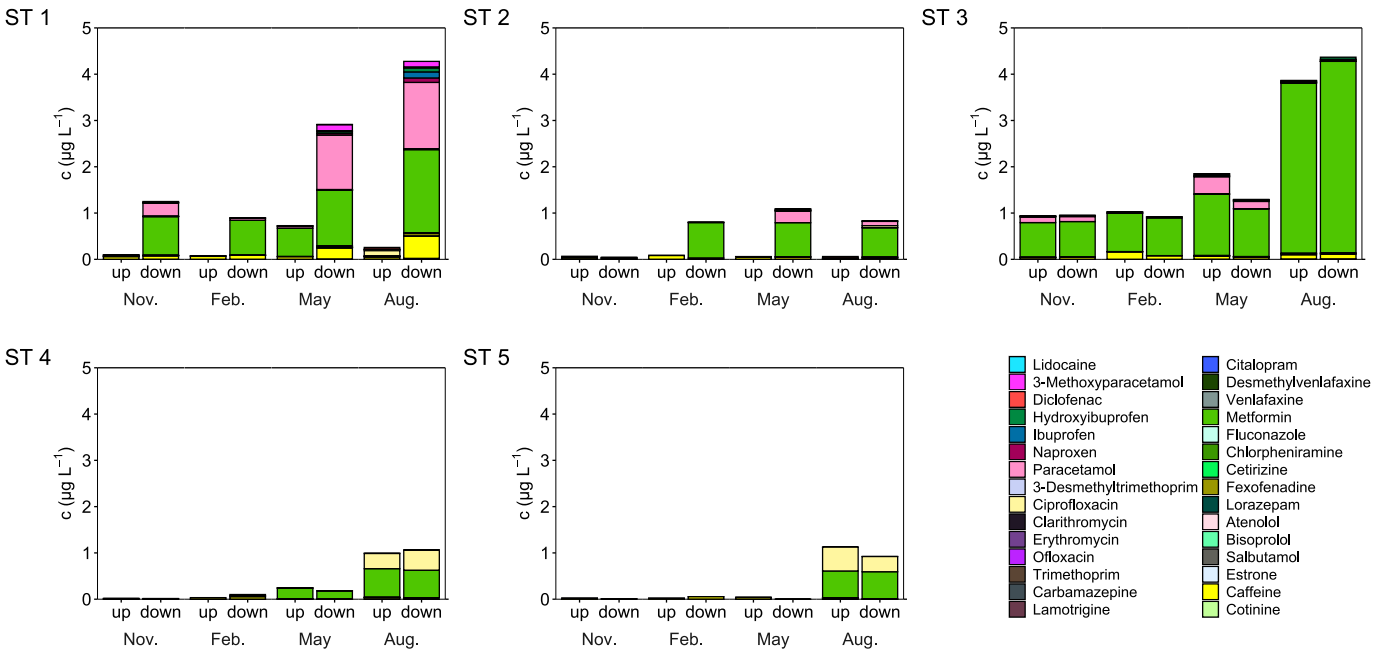

Fig. 5. Sum of detected EC concentrations (c) upstream and downstream of the septic tank discharge points (ST 1–5) in November, February, May and August, sorted by class (Fig. 1). Concentrations of individual ECs in Table S8.

at a mean concentration of 0.18 µg L^{-1} (2.2 · 10^{-4} – 1.5 µg L^{-1}). This is comparable to mean paracetamol concentrations of 0.032–0.13 µg L^{-1} previously reported in Scottish surface waters (Niemi et al., 2022; Ramage et al., 2019; Zhang et al., 2018). The EC found at the highest concentration was metformin at 4.1 µg L^{-1} downstream of ST 3 in August. This is in the same magnitude as mean concentration found in Scottish surface water that were 1.3 µg L^{-1} upstream and 8.8 µg L^{-1} downstream of centralised WWTWs (Helwig et al., 2022). Caffeine, cotinine, metformin and paracetamol are all frequently detected ECs in rivers worldwide, in the ng to µg L^{-1} range (Wilkinson et al., 2022). Other prescription drugs including analgesics, antibiotics, anticonvulsants, antidepressants, antifungals and beta-blockers, and their metabolites were found in smaller concentrations, below 0.4 µg L^{-1}, and in fewer samples (Table S10). For instance, the beta-blocker atenolol was not detected in any upstream samples, but five times downstream of ST 1 and ST 2 at 1.0 · 10^{-4} to 3.4· 10^{-3} µg L^{-1}, similar to concentrations reported in other rivers in the UK (Burns et al., 2018). In line with the wastewater data and findings in Scottish estuaries, bisoprolol was the most detected beta-blocker (Petrie and Moffat, 2022).

ST discharges impact river water quality by increasing EC concentrations (Blum et al., 2018; James et al., 2016; Ramage et al., 2019; Richards et al., 2017). The highest number of ECs (24 in May, and 22 in August) was detected downstream of ST 1 at a sum of EC concentrations up to 4.6 µg L^{-1}. The contribution of the STs to the sum of EC concentrations in the river varies from no difference between upstream and downstream to an increase of 95% (Fig. 5). The similarity in concentrations up- and downstream of ST 3–5 is mainly determined by the presence of metformin. The contribution of ST discharges to river concentrations varies for different ECs (Gago-Ferrero et al., 2017). For instance, there was only a small contribution of ST 1 to detected caffeine concentrations, while there was a significant increase in metformin and cetirizine. Atenolol and carbamazepine were only detected downstream of the STs. Other sources that contribute to ECs concentrations in the rivers upstream are other public and privately owned STs (Spatial, 2023), showing that multiple STs in one area can increase EC concentrations in a river (Gago-Ferrero et al., 2017; Withers et al., 2012).

A seasonal trend in the number of ECs detected and sum of EC concentrations can be observed (Fig. 5) (Burns et al., 2018; James et al., 2016; Niemi et al., 2022). At all locations except for ST 2, the sum of EC concentrations was highest in August, followed by May and lower in November and February. This is consistent with the dilution of the ST discharges into the river, suggesting the seasonal trend is driven by rainfall over seasonal use of ECs (Table S3).

RQs were generally low, indicating minimal risk for the environment, but concentrations exceeded the PNEC for ibuprofen, diclofenac and ciprofloxacin in a few samples in the receiving rivers (Fig. 6). The highest RQ in river water was found for ibuprofen (RQ = 11) in a

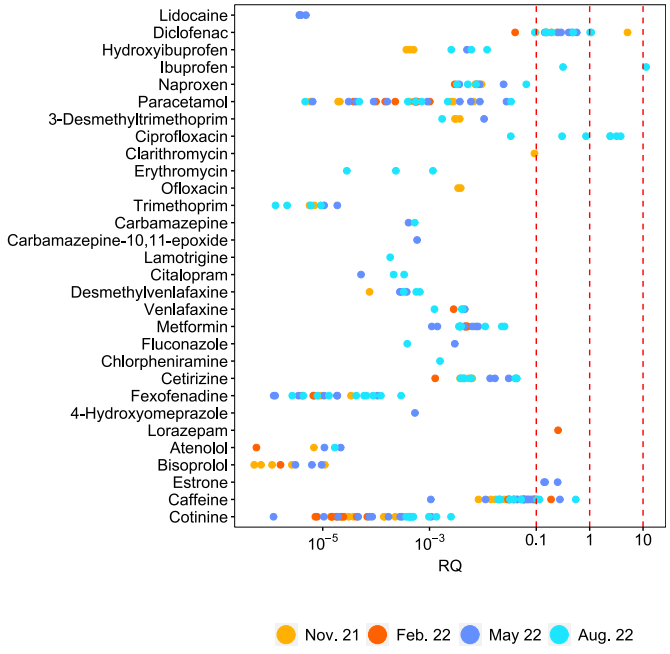

Fig. 6. Risk Quotients (RQ; logarithmic scale) of detected ECs in rivers in November, February, May and August, sorted by class (Fig. 1). The PNECs are in Table S4. Red dotted lines represent risk categories: RQ < 0.1 = insignificant risk, 0.1–1.0 = low risk; 1.0–10 = medium risk; and >10 = high risk. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

downstream sample in August, at 0.13 μg L^{-1}, below maximum concentrations previously found in the UK (Kay et al., 2017; White et al., 2019).

4. Conclusion

All 68 ECs were present in Scottish community STs at concentrations from 0.016 ng L^{-1} – 2605 μg L^{-1}. Overall, the simultaneous analysis of both liquid and suspended phases is recommended to avoid underestimating the total concentration and environmental impact of some ECs, e.g., ofloxacin, ciprofloxacin, fluoxetine, and clotrimazole. There is no or limited removal of ECs in the STs, and dilution of the discharges is required to minimise risk. The ST effluent discharges influence river water quality for some ECs, but RQs in receiving rivers were generally low, indicating small risk for the environment. However, alternative technological or non-technological approaches to reduce EC pollution may be needed at locations where ST discharges have low dilution factors in the environment.

CRediT authorship contribution statement

Maike Wilschnack: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Elise Cartmell:** Writing – review & editing, Resources, Conceptualization. **Kyari Yates:** Writing – review & editing, Supervision, Conceptualization. **Bruce Petrie:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, 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. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2024.124988.

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Electronic Supplementary Material 1

Septic tanks as a pathway for emerging contaminants to the aquatic environment - Need for alternative rural wastewater treatment?

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S1 General and chemical information

Table S1: General and chemical information of target analytes.

Class	Chemical	Cas No.	Mol. Formular	Mol. Weight (g mol^{-1})	Solubility (mg L^{-1})	Log K_{ow}	pKa (most acidic)	pKa (most basic)	Supplier
Anaesthetics	Lidocaine	137-58-6	$C_{14}H_{22}N2O$	234.34	4100 [a]	2.44 [a]	13.78 [e]	7.75 [e]	Sigma Aldrich
Analgesics	3-Methoxyparacetamol	3251-55-6	$C_9H_{11}NO_3$	181.19	-	0.09 [c]	-	-	LGC standards
	Diclofenac	15307-79-6	$C_{14}H_{11}Cl_2NO_2$	296.15	2.37 [a]	4.51 [a]	4 [e]	-2.1 [e]	Sigma Aldrich
	Hydroxyibuprofen	51146-55-5	$C_{13}H_{18}O_3$	222.28	-	2.29 [c]	4.63 [d]	-	Sigma Aldrich
	Ibuprofen	15687-27-1	$C_{13}H_{18}O_2$	206.29	21 [a]	3.97 [a]	4.85 [e]	-	Sigma Aldrich
	Ketoprofen	22071-15-4	$C_{16}H_{14}O_3$	254.29	51 [a]	3.13 [a]	3.88 [e]	-7.5 [e]	Sigma Aldrich
	Naproxen	22204-53-1	$C_{14}H_{14}O_3$	230.27	15.9 [a]	3.18 [a]	4.19 [e]	-4.8 [e]	Sigma Aldrich
	Paracetamol	103-90-2	$C_8H_9NO_2$	151.17	30400 [b]	0.91 [a]	9.46 [e]	-4.4 [e]	Sigma Aldrich
Antibiotics	3-Desmethyltrimethoprim	27653-69-6	$C_{13}H_{16}N_4O_3$	276.29	-	-	-	-	LGC standards
	α-Hydroxytrimethoprim	29606-06-2	$C1_4H_{18}N_4O_4$	306.32	-	-	-	-	LGC standards
	Amoxicillin	26787-78-0	$C_{16}H_{19}N_3O_5S$	365.40	3430 [b]	0.87 [a]	3.23 [e]	7.22 [e]	Sigma Aldrich
	Ciprofloxacin	85721-33-1	$C_{17}H_{18}FN_3O_3$	331.34	11500 [b]	0.28 [a]	5.56 [e]	8.77 [e]	Sigma Aldrich
	Clarithromycin	81103-11-9	$C_{38}H_{69}NO_{13}$	747.97	0.33 [a]	3.16 [a]	12.46 [e]	9 [e]	Sigma Aldrich
	Erythromycin	114-07-8	$C_{37}H_{67}NO_{13}$	733.93	0.52 [b]	2.6 [a]	12.45 [e]	9 [e]	Sigma Aldrich
	Ofloxacin	82419-36-1	$C_{18}H_{20}FN_3O_4$	361.37	28300 [a]	-0.39 [a]	5.35 [e]	6.72 [e]	Sigma Aldrich
	Sulfadiazine	68-35-9	$C_{10}H_{10}N_4O_2S$	250.28	77 [a]	-0.09 [a]	6.99 [e]	2.01 [e]	Sigma Aldrich
	Sulfamethoxazole	723-46-6	$C_{10}H_{11}N_3O_3S$	253.28	610 [a]	0.89 [a]	6.16 [e]	1.97 [e]	Sigma Aldrich
	Sulfanilamide	63-74-1	$C_6H_8N_2O_2S$	172.20	7500 [a]	-0.62 [a]	10.99 [e]	2.27 [e]	Sigma Aldrich
	Trimethoprim	738-70-5	$C_{14}H_{18}N_4O_3$	290.32	400 [a]	0.91 [a]	17.33 [e]	7.16 [e]	Sigma Aldrich
Anticoagulant	Warfarin	81-81-2	$C_{19}H_{16}O_4$	308.33	17 [a]	2.7 [a]	5.56 [e]	-6.9 [e]	Sigma Aldrich
Anticonvulsants	Carbamazepine	298-46-4	$C_{15}H_{12}N_2O$	236.28	17.7 [b]	2.77 [a]	15.96 [e]	-3.8 [e]	Sigma Aldrich
	Carbamazepine-10,11-epoxide	36507-30-9	$C_{15}H_{12}N_2O_2$	252.27	-	0.95 [c]	13.91 [b]	-0.50 [b]	LGC standards
	Gabapentin	60142-96-3	$C_9H_{17}NO_2$	171.24	34000 [c]	1.25 [a]	4.63 [e]	9.91 [e]	Sigma Aldrich
	Lamotrigine	84057-84-1	$C_9H_7Cl_2N_5$	256.09	170 [a]	1.93 [a]	14.98 [e]	5.58 [e]	Sigma Aldrich
	Primidone	125-33-7	$C_{12}H_{14}N_2O_2$	218.25	500 [a]	0.91 [a]	11.5 [e]	-6.2 [e]	Sigma Aldrich
Antidepressants	Citalopram	59729-32-7	$C_{20}H_{21}FN_2O$	324.40	31.1 [b]	3.76 [a]	-	9.78 [a]	Sigma Aldrich
	Desmethylcitalopram	144025-14-9	$C_{19}H_{19}FN_2O$	310.37	-	3.53 [c]	-	10.54 [d]	LGC standards
	Desmethylvenlafaxine	93413-62-8	$C_{16}H_{25}NO_2$	263.38	-	2.69 [d]	10.04 [b]	9.33 [b]	Sigma Aldrich
	Fluoxetine	56296-78-7	$C_{17}H_{18}F_3NO$	309.33	60.3 [b]	4.05 [a]	-	9.8 [e]	LGC standards
	Venlafaxine	99300-78-4	$C_{17}H_{27}N_1O_2$	277.41	267 [b]	3.28 [b]	14.42 [e]	8.91 [e]	Sigma Aldrich
Antidiabetics	Guanylurea	207300-86-5	$C_2H_6N_4O$	102.10	-	-3.57 [c]	-	-	Sigma Aldrich
	Metformin	1115-70-4	$C_4H_{11}N5$	129.17	1000000 [b]	-2.6 [a]	-	12.4 [a]	Sigma Aldrich
Antifungals	Climbazole	38083-17-9	$C_{15}H_{17}ClN_2O_2$	292.76	-	3.76 [c]	18.87 [e]	6.49 [e]	TCI

	Clotrimazole	23593-75-1	$C_{22}H_{17}ClN_2$	344.84	0.49 [a]	6.1 [a]	-	6.26 [e]	Sigma Aldrich
	Fluconazole	86386-73-4	$C_{13}H_{12}F_2N_6O$	306.27	-	0.5 [a]	12.68 [e]	2.3 [e]	TCI
	Miconazole	22916-47-8	$C_{18}H_{14}Cl_4N_2O$	416.13	-	6.25 [c]	-	6.48 [e]	Sigma Aldrich
Antihelmintic	Mebendazole	31431-39-7	$C_{16}H_{13}N_3O_3$	295.29	71.3 [a]	2.83 [a]	8.44 [e]	3.93 [e]	TCI
Antihistamines	Cetirizine	83881-52-1	$C_{21}H_{25}ClN_2O_3$	388.90	101 [a]	2.8 [a]	3.59 [e]	7.42 [b]	Sigma Aldrich
	Chlorpheniramine	113-92-8	$C_{16}H_{19}ClN_2$	274.79	5500 [a]	3.38 [a]	-	9.13 [a]	Sigma Aldrich
	Fexofenadine	153439-40-8	$C_{32}H_{39}NO_4$	501.67	0.02 [b]	2.94 [e]	4.04 [e]	9.01 [e]	Sigma Aldrich
Antipruritic	Crotamiton	483-63-6	$C_{13}H_{17}NO$	203.28	-	2.9 [d]	-	-0.6 [e]	Sigma Aldrich
Antiulcers	4-Hydroxyomeprazole	301669-82-9	$C_{16}H_{17}N_3O_3S$	331.40	-	1.93 [c]	9.68 [d]	3.93 [d]	LGC standards
	Lansoprazole	103577-45-3	$C_{16}H_{14}F3N_3O_2S$	369.36	0.97 [a]	3.68 [c]	9.35 [e]	4.16 [e]	TCI
	Omeprazole	73590-58-6	$C_{17}H_{19}N_3O_3S$	345.52	359 [a]	2.23 [a]	9.29 [e]	4.77 [e]	Sigma Aldrich
	Ranitidine	66357-59-3	$C_{13}H_{22}N_4O_3S$	314.41	24700 [b]	0.2 [a]	-	8.2 [a]	Sigma Aldrich
Benzodiazepines	Lorazepam	846-49-1	$C_{15}H_{10}Cl_2N_2O_2$	321.16	80 [a]	2.39 [a]	10.61 [e]	-2.2 [e]	Sigma Aldrich
	Oxazepam	604-75-1	$C_{15}H_{11}ClN_2O_2$	286.71	179 [b]	2.24 [a]	10.61 [e]	-1.5 [e]	Sigma Aldrich
	Temazepam	846-50-4	$C_{16}H_{13}ClN_2O_2$	300.75	164 [a]	2.19 [a]	10.68 [e]	-1.4 [e]	Sigma Aldrich
Betablockers	Acebutolol	34381-68-5	$C_{18}H_{28}N_2O_4$	336.43	259 [a]	1.71 [a]	13.91 [e]	9.65 [e]	Sigma Aldrich
	Atenolol	29122-68-7	$C_{14}H_{22}N_2O_3$	266.34	13300 [a]	0.16 [a]	14.08 [e]	9.67 [e]	Sigma Aldrich
	Bisoprolol	104344-23-2	$C_{18}H_{31}NO_4$	325.44	2240 [b]	2.2 [a]	14.09 [e]	9.67 [e]	Sigma Aldrich
	Metoprolol	56392-17-7	$C_{15}H_{25}NO_3$	267.37	4770 [b]	2.15 [a]	14.09 [e]	9.67 [e]	Sigma Aldrich
	Propranolol	318-98-9	$C_{16}H_{21}NO_2$	259.35	228 [e]	3.48 [a]	14.09 [e]	9.67 [e]	Sigma Aldrich
	Salbutamol	18559-94-9	$C_{13}H_{21}NO_3$	239.31	14100 [a]	1.4 [a]	10.12 [e]	9.4 [e]	Sigma Aldrich
	Sotalol	959-24-0	$C_{12}H_{20}N_2O_3S$	272.36	-	0.24 [c]	10.07 [e]	9.43 [e]	Sigma Aldrich
Chemotherapeutic	Ifosfamide	3778-73-2	$C_7H_{15}Cl_2N_2O_2P$	261.09	3780 [a]	0.86 [a]	14.64 [e]	-	Sigma Aldrich
Coccidiostat	Clopidol	2971-90-6	$C_7H_7Cl_2NO$	192.04	-	2.1 [c]	10.77 [d]	-	Sigma Aldrich
Hormones	17ß-Estradiol (E2)	50-28-2	$C_{18}H24O_2$	272.39	3.6 [a]	4.01 [a]	10.33 [e]	-0.88 [e]	Sigma Aldrich
	17α-Ethinylestradiol (EE2)	57-63-6	$C_{20}H24O_2$	296.41	11.3 [a]	3.67 [a]	10.33 [e]	-1.7 [e]	Sigma Aldrich
	Estriol (E3)	50-27-1	$C_{18}H_{24}O_3$	288.38	-	2.45 [a]	10.33 [e]	-3.2 [e]	Sigma Aldrich
	Estrone (E1)	53-16-7	$C_{18}H_{22}O_2$	270.37	0.76 [a]	2.6 [a]	10.33 [e]	-5.4 [e]	Sigma Aldrich
	Norethisterone	68-22-4	$C_{20}H_{26}O_2$	298.42	7.04 [c]	2.97 [c]	17.59 [e]	-1.7 [e]	Sigma Aldrich
Lipid regulators	Atorvastatin	344423-98-9	$C_{33}H_{35}FN_2O_5$	558.65	0.00112 [b]	6.36 [a]	4.31 [e]	-2.7 [e]	Sigma Aldrich
	Bezafibrate	41859-67-0	$C_{19}H_{20}ClNO_4$	361.83	1.2 [b]	4.25 [b]	3.83 [e]	-0.84 [e]	Sigma Aldrich
	Gemfibrozil	25812-30-0	$C_{15}H_{22}O_3$	250.33	4.96 [b]	4.39 [a]	4.42 [e]	-4.8 [e]	Sigma Aldrich
Wastewater discharge marker	Caffeine	58-05-02	$C_8H_{10}N_4O_2$	194.19	21700 [a]	0.16 [b]	-	0.52 [b]	Sigma Aldrich
	Cotinine	486-56-6	$C_{10}H_{12}N_2O$	176.22	999000 [b]	1.37 [d]	-	4.79 [d]	Sigma Aldrich
X-ray contrast	Amidotrizoic acid	117-96-4	$C_{11}H_9I_3N_2O_4$	613.91	-	3.3 [a]	2.17 [e]	-4.2 [e]	Sigma Aldrich

[a] Drugbank (Personal Health Analytics, 2022), [b] Proctor et al., 2019 (Proctor et al., 2019), [c] ChemSpider (Royal Society of Chemistry, 2022), [d] ChEMBL ("ChEMBL Database," 2022), [e] Drugbank using ChemAxon (Personal Health Analytics, 2022)

Table S2: CAS Number and supplier for deuterated standards.

Compound	**CAS**	**supplier**
(±)-Acebutolol-d_5 hydrochloride	1189500-68-2	TRC
(±)-Atenolol-d_7	1202864-50-3	Analab
(±)-Bisoprolol-d_5	1189881-87-5	TRC
(±)-Chlorpheniramine-d_6 solution	129806-45-7	Sigma Aldrich
(±)-Citalopram-d_6 solution	1190003-26-9	Sigma Aldrich
(±)-Cotinine-d_3 solution	110952-70-0	Sigma Aldrich
(±)-Fluoxetine-d_6 solution	1173020-43-3	Sigma Aldrich
(±)-Ibuprofen-d_3	121662-14-4	Sigma Aldrich
(±)-Metoprolol-d_7 (+)-tartrate	2378803-75-7	Sigma Aldrich
(±)-Naproxen-d_3	958293-79-3	Sigma Aldrich
(±)-Propranolol-d_7 solution	1613439-56-7	Sigma Aldrich
(±)-Salbutamol-d_3	1219798-60-3	LGC standards
(±)-Sotalol-d_6 hydrochloride	1246820-85-8	LGC standards
(±)-Temazepan-d_5 solution	136765-51-0	Sigma Aldrich
(±)-Venlafaxine-d_6 solution	1062606-12-5	Sigma Aldrich
17β-Estradiol-d_4	66789-03-5	LGC standards
Acetaminophen-d_4	64315-36-2	Sigma Aldrich
Caffeine-^{13}C	202282-98-2	Sigma Aldrich
Carbamazepine-10,11-epoxide-d_{10}	1219804-16-6	LGC standards
Carbamazepine-d_{10} solution	132183-78-9	Sigma Aldrich
Clarithromycin-N-methyl-^{13}C,d_3	78088-19-4	LGC standards
Ciprofloxacin-d_8 Oxalate	1246819-94-2	TRC
Estrone-d_4	53866-34-5	Sigma Aldrich
Metformin-d_6 HCl	1185166-01-1	LGC standards
Ofloxacin-d_3	1173147-91-5	Sigma Aldrich
(±)-Oxazepam-d_5 solution	65854-78-6	Sigma Aldrich
Primidone-d_5	73738-06-4	Supelco

S2 Sampling

The nominal dilution of the septic tank discharge into the river was calculated from the flow of the receiving river per day (f_{river}) and the calculated flow of the septic tank effluent per day (f_{ST}) following equation S1.

$$dilution = \frac{(f_{\mathrm{river}} - f_{\mathrm{ST}})}{f_{\mathrm{ST}}} \quad \text{(S1)}$$

The flow of the river was determined through the SEPA Time series data service (API) (SEPA, 2022) and is included in Table S3. For ST 3 and ST 4 no suitable station with daily or hourly river flow data was available, and the mean flow of the river (f_{mean}) was used instead (Scottish Water, 2015). The flow of the septic tank effluent per day (Table S3) was calculated by multiplying the population equivalents (PE) by the mean daily discharge per person per day (0.7252 m^3 day^{-1}) (equation S2) following industry practice (Scottish Water, 2015).

$$f_{\mathrm{ST}} = \mathrm{PE} \cdot 0.7252\ \mathrm{m}^3\ \mathrm{day}^{-1} \quad \text{(S2)}$$

The hydraulic retention time (HRT) was estimated from (f_{ST}) and ST Volume (V; equation S3).

$$HRT = \frac{f_{\mathrm{ST}}}{V} \quad \text{(S3)}$$

Table S3: Sampling dates of septic tank (ST) 1 – 5 wastewater and receiving surface water with ST outlet temperature (T_{outlet}), mean air temperature (T_{air}), rain, ST flow (f_{ST}), river flows (f_{river} and f_{mean}) and dilution factors. Rain is the mean of the total rain per day from the day of wastewater sampling and the two days prior (SEPA, 2022). The dilution factor is calculated from the mean daily river flow over two hours at sampling time (f_{river}) received from SEPA (SEPA, 2022). The mean dilution factor was calculated from the historic mean daily flow of the river (f_{mean}) available (Scottish Water, 2015).

Month	Septic Tank	Wastewater	River	T_{Outlet} (°C)	T_{air} (°C)	Rain (mm day^{-1})	f_{st} (m^3 day^{-1})	f_{river} (m^3 day^{-1})	Dilution factor	f_{mean} (m^3 day^{-1})	Mean dilution factor
October 2021	ST 1	13/10/2021	-	-	13	0.67	228	$3.5 \cdot 10^5$	1546	9.91	5439
	ST 2	13/10/2021	-	-	13	0.67	223	$3.5 \cdot 10^5$	1579	7.48	2895
	ST 3	13/10/2021	-	-	13	0.13	344	-	-	0.378	96
	ST 4	13/10/2021	-	14	13	3.7	228	-	-	12.7	4808
	ST 5	13/10/2021	-	16	13	3.4	157	$2.7 \cdot 10^6$	17039	29.8	16336
November 2021	ST 1	10/11/2021	10/11/2021	-	7.5	3.1	228	$7.5 \cdot 10^5$	3300	9.91	5439
	ST 2	10/11/2021	10/11/2021	-	7.7	3.1	223	$7.5 \cdot 10^5$	3370	7.48	2895
	ST 3	10/11/2021	10/11/2021	-	7.7	2.0	344	-	-	0.378	96
	ST 4	10/11/2021	11/11/2021	10	7.6	1.1	228	-	-	12.7	4808
	ST 5	10/11/2021	11/11/2021	9.9	7.6	2.1	157	$5.2 \cdot 10^6$	32965	29.8	16336
December 2021	ST 1	14/12/2021	-	-	7.7	2.1	228	$1.1 \cdot 10^6$	4738	9.91	5439
	ST 2	14/12/2021	-	-	7.5	2.1	223	$1.1 \cdot 10^6$	4839	7.48	2895
	ST 3	14/12/2021	-	-	7.5	0.033	344	-	-	0.378	96
	ST 4	14/12/2021	-	8.7	9.0	0.13	228	-	-	12.7	4808
	ST 5	14/12/2021	-	7.7	9.0	2.9	157	$4.3 \cdot 10^6$	27334	29.8	16336
January 2022	ST 1	11/01/2022	-	-	5.2	2.1	228	$1.2 \cdot 10^6$	5102	9.91	5439
	ST 2	11/01/2022	-	-	5.3	2.1	223	$1.2 \cdot 10^6$	5211	7.48	2895
	ST 3	11/01/2022	-	-	5.3	1.2	344	-	-	0.378	96
	ST 4	11/01/2022	-	6.2	5.5	0.80	228	-	-	12.7	4808
	ST 5	11/01/2022	-	5.9	5.5	3.3	157	$2.8 \cdot 10^6$	17773	29.8	16336
February 2022	ST 1	17/02/2022	17/02/2022	-	5.0	10	228	$2.7 \cdot 10^6$	11990	9.91	5439
	ST 2	17/02/2022	17/02/2022	-	4.7	10	223	$2.7 \cdot 10^6$	12244	7.48	2895
	ST 3	17/02/2022	17/02/2022	-	4.7	6.3	344	-	-	0.378	96
	ST 4	17/02/2022	18/02/2022	4.2	2.7	15	228	-	-	12.7	4808
	ST 5	17/02/2022	18/02/2022	3.5	2.7	9.9	157	$5.6 \cdot 10^6$	35476	29.8	16336
March 2022	ST 1	15/03/2022	-	-	6.5	5.3	228	$1.5 \cdot 10^6$	6691	9.91	5439
	ST 2	15/03/2022	-	-	7.0	5.3	223	$1.5 \cdot 10^6$	6833	7.48	2895
	ST 3	15/03/2022	-	-	7.0	2.7	344	-	-	0.378	96
	ST 4	15/03/2022	-	7.0	6.9	0.33	228	-	-	12.7	4808
	ST 5	15/03/2022	-	5.8	6.9	1.3	157	$1.8 \cdot 10^6$	11380	29.8	16336
April 2022	ST 1	19/04/2022	-	-	8.4	2.9	228	$2.7 \cdot 10^5$	1194	9.91	5439
	ST 2	19/04/2022	-	-	8.4	2.9	223	$2.7 \cdot 10^5$	1220	7.48	2895
	ST 3	19/04/2022	-	-	8.4	1.1	344	-	-	0.378	96
	ST 4	19/04/2022	-	9.3	9.5	0.73	228	-	-	12.7	4808
	ST 5	19/04/2022	-	9.6	9.5	0.67	157	$1.9 \cdot 10^6$	11896	29.8	16336
May 2022	ST 1	17/05/2022	17/05/2022	-	13	4.1	228	$2.1 \cdot 10^5$	908	9.91	5439
	ST 2	17/05/2022	17/05/2022	-	13	4.1	223	$2.1 \cdot 10^5$	927	7.48	2895
	ST 3	17/05/2022	17/05/2022	-	13	2.1	344	-	-	0.378	96
	ST 4	-	18/05/2022	-	14	3.7	228	-	-	12.7	4808

	ST 5	-	18/05/2022	-	14	2.6	157	$1.8 \cdot 10^6$	11448	29.8	16336
June 2022	ST 1	14/06/2022	-	-	13	1.8	228	$1.5 \cdot 10^5$	650	9.91	5439
	ST 2	14/06/2022	-	-	14	1.8	223	$1.5 \cdot 10^5$	664	7.48	2895
	ST 3	14/06/2022	-	-	14	1.7	344	-	-	0.378	96
	ST 4	14/06/2022	-	13	13	0.13	228	-	-	12.7	4808
	ST 5	14/06/2022	-	13	13	0.067	157	$3.7 \cdot 10^6$	23810	29.8	16336
July 2022	ST 1	19/07/2022	-	-	21	0	228	$1.3 \cdot 10^5$	580	9.91	5439
	ST 2	19/07/2022	-	-	22	0	223	$1.3 \cdot 10^5$	592	7.48	2895
	ST 3	19/07/2022	-	-	22	0.5	344	-	-	0.378	96
	ST 4	19/07/2022	-	16	18	2.2	228	-	-	12.7	4808
	ST 5	19/07/2022	-	16	18	1.7	157	$2.5 \cdot 10^6$	16069	29.8	16336
August 2022	ST 1	23/08/2022	23/08/2022	-	17	4.3	228	$1.6 \cdot 10^5$	685	9.91	5439
	ST 2	23/08/2022	23/08/2022	-	17	4.3	223	$1.6 \cdot 10^5$	700	7.48	2895
	ST 3	23/08/2022	23/08/2022	-	17	5.7	344	-	-	0.378	96
	ST 4	16/08/2022	24/08/2022	16	12	0.13	228	-	-	12.7	4808
	ST 5	16/08/2022	24/08/2022	15	12	0.47	157	$6.7 \cdot 10^5$	4276	29.8	16336
September 2022	ST 1	20/09/2022	-	-	15	1.7	228	$2.0 \cdot 10^5$	882	9.91	5439
	ST 2	20/09/2022	-	-	14	1.7	223	$2.0 \cdot 10^5$	900	7.48	2895
	ST 3	20/09/2022	-	-	14	0.033	344	-	-	0.378	96
	ST 4	27/09/2022	-	-	9.1	0.13	228	-	-	12.7	4808
	ST 5	27/09/2022	-	-	9.1	3.7	157	$1.3 \cdot 10^6$	8306	29.8	16336

S3 Analytical methods

Initially, samples were filtered under vacuum through 0.7 µm GF/F membrane filters within 48 h of sampling, and the filter papers were frozen at -20°C until processing. All samples were prepared in duplicate. 50 mL wastewater, 100 mL river water, or a filter paper were spiked with 10 ng isotopic labelled surrogates to compensate for matrix effects and any potential loss during sample preparation. For direct injection, 450 µL of a water samples, filtered through a PVDF-HL syringe filter, was spiked. Solid samples were left overnight, and liquid samples were mixed and left for at least 30 min.

Briefly, water samples for SPE were loaded onto pre-conditioned Oasis HLB cartridges, dried, and eluted under gravity with 4 mL methanol. The solvent was evaporated at 40°C under nitrogen and the dried residue was then redissolved in 500 µL water/methanol (95/5, v/v), and filtered through a PVDF-HL syringe filter prior to UHPLC-MS/MS injection.

Ultrasonic extraction of the suspended solids was performed at 50°C using three extraction cycles with 2 mL of 2% NH_4OH in methanol, 2 mL of 2% formic acid in methanol and 2 mL of methanol. In each cycle, the mixture was vortexed, ultra-sonicated for 15 min at 50°C, and centrifuged at 2260 g for 15 min. The combined supernatants were filtered through a wet GF/F disc, diluted with water to 100 mL and processed as described for the water samples. 500 µL water/methanol (50/50, v/v) were used to redissolve the residue for UHPLC-MS/MS analysis.

Samples were analysed using a fully validated UHPLC-MS/MS methodology using an ACQUITY UPLC system from Waters (Waters Corporation, Milford, MA) with a Xevo TQ-XS Triple Quadrupole Mass Spectrometer. Two separate methods were applied to achieve maximum sensitivity of both acidic and basic ECs using methanol-water-gradients along with 5 mM ammonium formate and 0.1 % formic acid in positive ionisation, and 0.5 mM NH_4F in negative ionisation (Table S4). ECs were quantified using multiple reaction monitoring (MRM) transitions (Table S5). The fragment with the highest response was used for quantification, and for all ECs except for ibuprofen, gemfibrozil and lidocaine, a second fragment was analysed for confirmation. Ion ratios, retention times and signal-to-noise ratios (S/N) were monitored (European Commission, 2002). In addition to the spiked samples, one unspiked Milli-Q sample were processed with the environmental samples for direct injection and SPE. Milli-Q blanks were injected before and after every batch of samples, and quality control standards (1, 10, and 50 µg L^{-1}) were analysed at least every 24 environmental injections. In general, ion ratios were acceptable for all ECs, except for guanylurea detections with low S/N that were considered < LOQ. Retention time

shifts > 0.02 min were generally an indication for instrumental issues and injections were repeated, however following EU guidelines (European Commission, 2002) retention time changes up 5 % were accepted in few SPE samples, when relative retention times of isotopically labelled compounds changed in the same manner. A full description of the method is available in Wilschnack et al. (Wilschnack et al., 2024).

Table S4: LC solvent gradient program, mobile phase A: Water with additives, mobile phase B: methanol with additives. Additives were 5 mM ammonium formate and 0.1% formic acid in the positive method, and 0.1 mM ammonium fluoride in the negative method. The total run time was 14 min for the positive, and 12 min for the negative method (Wilschnack et al., 2024).

Time /min	**% A**	
	positive	**negative**
0	95	95
0.5	95	95
8		20
9	20	20
9.1		95
11	20	95
11.1	95	95
12	95	95
14	95	

Table S5: MS/MS detection parameters for studied compounds (precursor ion, cone voltage (CV), quantifier and qualifier ions with collision energies (CE)), LC method used, retention time (RT), and assigned deuterated surrogate (Wilschnack et al., 2024).

Class	Chemical	Precursor Ion /m/z	CV /V	Quantifier Ion	CE /eV	Qualifier Ion	CE /eV	method	RT /min	calibration
Anaesthetics	Lidocaine	235.2	29	86.1	17	-	-	positive	4.0	Carbamazepine-d_{10}
Analgesics	3-Methoxyparacetamol	182.2	22	108.1	16	80.1	29	positive	2.9	Cotinine-d_3
	Diclofenac	294.1	21	250.0	10	178.1	29	negative	7.0	Ibuprofen-d_3
	Hydroxyibuprofen	240.2	25	205.2	12	163.2	16	positive	6.8	Paracetamol-d_4
	Ibuprofen	205.1	12	161.3	12	-	-	negative	7.6	Ibuprofen-d_3
	Ibuprofen-d_3	208.1	13	164.2	8	-	-	negative	7.6	-
	Ketoprofen	255.2	50	209.2	15	105.1	22	positive	7.8	Temazepam-d_5
	Naproxen	229.0	9	170.1	14	185.1	5	negative	6.0	Ibuprofen-d_3
	Paracetamol	151.9	26	110.0	16	92.9	24	positive	2.4	Paracetamol-d_4
	Paracetamol-d_4	156.1	23	114.1	16	-	-	positive	2.3	-
Antibiotics	3-Desmethyltrimethoprim	277.2	30	261.2	25	123.2	35	positive	3.0	Caffeine-^{13}C
	α-Hydroxytrimethoprim	307.2	22	289.2	14	274.2	20	positive	3.1	Caffeine-^{13}C
	Amoxicillin	366.1	29	114.1	19	208.2	12	positive	2.2	Paracetamol-d_4
	Ciprofloxacin	332.1	17	314.2	21	288.2	17	positive	3.9	Ofloxacin-d_8
	Clarithromycin	748.5	29	158.2	32	558.4	24	positive	8.1	Clarithromycin-^{13}C-d_3
	Clarithromycin-^{13}C-d_3	752.6	25	162.2	29	-	-	positive	8.1	-
	Erythromycin	734.5	37	158.2	30	576.4	19	positive	7.4	Clarithromycin-^{13}C-d_3
	Ofloxacin	362.2	30	318.2	18	261.2	25	positive	3.7	Ofloxacin-d_8
	Ofloxacin-d_8	365.1	30	261.2	27	-	-	positive	3.7	-
	Sulfadiazine	251.1	18	156.1	15	92.1	26	positive	2.6	Caffeine-^{13}C
	Sulfamethoxazole	254.1	32	156.1	16	92.2	28	positive	4.1	Caffeine-^{13}C
	Sulfanilamide	173.1	27	92.1	16	108.1	14	positive	1.2	Primidone-d_5
	Trimethoprim	291.2	23	230.1	15	261.2	23	positive	3.6	Paracetamol-d_4
Anticoagulant	Warfarin	309.1	32	163.1	14	251.2	19	positive	8.2	Carbamazepine-d_{10}
Anticonvulsants	Carbamazepine	237.2	33	194.2	18	179.2	32	positive	6.9	Carbamazepine-d_{10}
	Carbamazepine-d_{10}	247.1	33	204.2	20	-	-	positive	6.9	-
	Carbamazepine-10,11-epoxide	253.1	20	180.1	20	210.2	14	positive	5.9	Carbamazepine-d_{10}
	Gabapentin	172.2	23	154.2	12	137.2	15	positive	3.3	Caffeine-^{13}C
	Lamotrigine	256.1	24	211.1	25	187.1	27	positive	4.7	Carbamazepine-d_{10}
	Primidone	219.1	28	162.1	12	91.1	25	positive	4.8	Primidone-d_5
	Primidone-d_5	227.1	14	164.2	12	-	-	positive	4.8	-
Antidepressants	Citalopram	325.2	24	262.2	20	116.1	25	positive	6.2	Citalopram-d_6
	Citalopram-d_6	331.2	24	109.1	31	-	-	positive	6.2	-

	Desmethylcitalopram	311.2	22	109.1	20	262.2	17	positive	6.2	Citalopram-d_6
	Desmethylvenlafaxine	264.3	29	246.3	12	107.1	30	positive	4.5	Venlafaxine-d_6
	Fluoxetine	310.2	34	44.1	10	148.1	10	positive	7.7	Fluoxetine-d_6
	Fluoxetine-d_6	316.1	19	154.2	9	-	-	positive	7.7	-
	Venlafaxine	278.3	36	260.3	10	215.2	16	positive	5.9	Venlafaxine-d_6
	Venlaflaxine-d_6	284.3	34	266.3	12	-	-	positive	5.8	-
Antidiabetics	Guanylurea	103.1	16	60.1	10	86.1	8	positive	0.7	Salbutamol-d_3
	Metformin	130.2	27	60.1	12	71.2	17	positive	0.8	Metformin-d_6
	Metformin-d_6	136.3	28	60.1	13	-	-	positive	0.8	-
Antifungals	Climbazole	293.1	23	69.2	21	41.2	26	positive	7.7	Clarithromycin-^{13}C-d_3
	Clotrimazole	277.1	27	165.2	20	242.2	20	positive	8.1	Clarithromycin-^{13}C-d_3
	Fluconazole	307.1	29	238.2	15	220.1	18	positive	4.8	Caffeine-^{13}C
	Miconazole	417.0	18	159.1	30	161.1	28	positive	9.3	external
Antihelmintic	Mebendazole	296.1	19	264.2	23	105.1	33	positive	7.1	Carbamazepine-d_{10}
Antihistamines	Cetirizine	389.2	30	201.2	22	166.1	40	positive	7.8	Metoprolol-d_7
	Chlorpheniramine	275.2	30	230.1	18	167.1	43	positive	5.8	Chlorpheniramine-d_6
	Chlorpheniramine-d_6	281.1	26	230.1	16	-	-	positive	5.8	-
	Fexofenadine	502.4	37	466.5	25	171.2	35	positive	7.3	Venlafaxine-d_6
Antipruritic	Crotamiton	204.2	27	69.1	22	136.2	17	positive	8.2	Carbamazepine-d_{10}
Antiulcers	4-Hydroxyomeprazole	316.2	22	168.1	24	149.2	24	positive	5.5	Carbamazepine-d_{10}
	Lansoprazole	370.1	29	252.1	11	119.2	20	positive	7.3	Venlafaxine-d_6
	Omeprazole	346.2	21	198.1	11	180.1	23	positive	6.4	Caffeine-^{13}C
	Ranitidine	315.1	31	176.1	16	130.1	25	positive	2.5	Paracetamol-d_4
Benzodiazepines	Lorazepam	321.1	25	275.1	22	303.1	16	positive	7.6	Temazepam-d_5
	Oxazepam	287.1	26	241.1	25	269.1	17	positive	7.5	Oxazepam-d_5
	Oxazepam-d_5	292.1	26	246.2	25	-	-	positive	7.5	-
	Temazepam	301.1	24	255.2	21	283.2	14	positive	7.8	Temazepam-d_5
	Temazepam-d_5	306.1	24	260.2	21	-	-	positive	7.8	-
Betablockers	Acebutolol	337.3	20	116.2	18	319.3	16	positive	4.7	Acebutolol-d_5
	Acebutolol-d_5	342.3	19	121.2	23	-	-	positive	4.7	-
	Atenolol	267.3	38	145.1	30	190.1	16	positive	2.5	Atenolol-d_7
	Atenolol-d_7	274.2	23	145.1	24	-	-	positive	2.5	-
	Bisoprolol	326.3	20	116.2	16	222.2	10	positive	5.9	Bisoprolol-d_5
	Bisoprolol-d_5	331.2	23	121.2	17	-	-	positive	5.9	-
	Metoprolol	268.2	30	159.1	22	191.2	17	positive	4.8	Metoprolol-d_7
	Metoprolol-d_7	275.3	29	123.2	18	-	-	positive	4.8	-
	Propranolol	260.2	50	116.1	16	183.1	18	positive	6.1	Propranolol-d_7
	Propranolol-d_7	267.1	22	189.2	18	-	-	positive	6.0	-
	Salbutamol	240.2	27	148.1	20	166.1	12	positive	2.5	Salbutamol-d_3
	Salbutamol-d_3	243.0	21	151.2	21	-	-	positive	2.5	-

	Sotalol	273.2	25	133.2	28	213.2	17	positive	2.3	Sotalol-d_6
	Sotalol-d_6	279.2	24	214.1	17	-	-	positive	2.2	-
Chemotherapeutic	Ifosfamide	261.1	15	92.1	23	154.0	18	positive	5.4	Venlafaxine-d_6
Coccidiostat	Clopidol	192.1	27	101.1	24	87.1	28	positive	3.3	Caffeine-^{13}C
Hormones	17ß-Estradiol (E2)	271.2	25	145.1	40	183.2	40	negative	7.4	17β-Estradiol-d_4
	17β-Estradiol-d_4	275.2	35	147.3	37	160.2	30	negative	7.4	-
	17α-Ethinylestradiol (EE2)	295.1	20	159.1	36	145.1	38	negative	7.5	17β-Estradiol-d_4
	Estriol (E3)	287.1	36	171.1	37	145.1	39	negative	5.7	Estrone-d_4
	Estrone (E1)	269.1	35	145.1	38	159.2	34	negative	7.5	Estrone-d_4
	Estrone-d_4	273.2	39	147.1	36	160.1	36	negative	7.5	-
	Norethisterone	299.2	16	231.2	18	109.2	26	positive	8.1	Carbamazepine-d_{10}
Lipid regulators	Atorvastatin	559.2	28	440.3	23	250.2	43	positive	9.0	external
	Bezafibrate	362.1	25	139.1	25	316.2	14	positive	8.1	Carbamazepine-d_{10}
	Gemfibrozil	249.0	13	121.1	20	-	-	negative	8.7	Ibuprofen-d_3
Wastewater discharge marker	Caffeine	195.1	16	138.1	17	110.1	23	positive	3.6	Caffeine-^{13}C
	Caffeine-^{13}C	198.1	31	140.1	19	-	-	positive	3.6	-
	Cotinine	177.1	34	80.1	19	98.1	21	positive	1.7	Cotinine-d_3
	Cotinine-d_3	180.2	13	80.1	22	-	-	positive	1.7	-
X-ray contrast	Amidotrizoic acid	631.9	29	361.2	26	233.2	46	positive	2.0	Salbutamol-d_3

Table S6: Method detection (w) and quantitation limits (MQL) (Wilschnack et al., 2024), and predicted no effect concentrations (PNEC) in freshwater (NORMAN Ecotoxicology Database, 2023).

Class	**EC**	**Influent / µg L^{-1}**		**Effluent / µg L^{-1}**		**River / µg L^{-1}**		**Solids / µg kg^{-1}**		**PNEC / µg L^{-1}**
		MDL	MQL	MDL	MQL	MDL	MQL	MDL	MQL	
Anaesthetics	Lidocaine	$9.6 \cdot 10^{-5}$	$3.2 \cdot 10^{-4}$	$1.3 \cdot 10^{-4}$	$4.2 \cdot 10^{-4}$	$3.6 \cdot 10^{-5}$	$1.2 \cdot 10^{-4}$	0.054	0.18	600
Analgesics	3-Methoxyparacetamol	$3.7 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	$3.4 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	$1.7 \cdot 10^{-4}$	$5.7 \cdot 10^{-4}$	0.19	0.63	-
	Diclofenac	[b]	$7.2 \cdot 10^{-3}$	[b]	$5.4 \cdot 10^{-3}$	[b]	$2.9 \cdot 10^{-3}$	[b]	5.1	0.05
	Hydroxyibuprofen	0.011	0.021	$8.2 \cdot 10^{-3}$	0.016	$5.0 \cdot 10^{-3}$	0.010	7.4	15	7.9
	Ibuprofen	$5.2 \cdot 10^{-4}$	$1.7 \cdot 10^{-3}$	$6.8 \cdot 10^{-4}$	$2.3 \cdot 10^{-3}$	$4.3 \cdot 10^{-4}$	$1.4 \cdot 10^{-3}$	0.47	1.6	0.011
	Ketoprofen	$1.5 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$	$5.6 \cdot 10^{-3}$	0.019	$8.2 \cdot 10^{-4}$	$2.7 \cdot 10^{-3}$	0.65	2.2	2.1
	Naproxen	$6.2 \cdot 10^{-4}$	0.012	$4.6 \cdot 10^{-4}$	$9.2 \cdot 10^{-3}$	$2.4 \cdot 10^{-4}$	$4.8 \cdot 10^{-3}$	0.25	4.9	1.7
	Paracetamol	$1.1 \cdot 10^{-3}$	$3.8 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$5.6 \cdot 10^{-3}$	$6.5 \cdot 10^{-4}$	$2.2 \cdot 10^{-3}$	1.0	3.1	46
Antibiotics	3-Desmethyltrimethoprim	$6.1 \cdot 10^{-5}$	$2.0 \cdot 10^{-4}$	$8.2 \cdot 10^{-5}$	$2.7 \cdot 10^{-4}$	$3.3 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$	0.041	0.14	0.49
	α-Hydroxytrimethoprim	$5.5 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	$6.2 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	$2.9 \cdot 10^{-4}$	$5.8 \cdot 10^{-4}$	0.57	1.1	0.27
	Amoxicillin	0.073	0.091	0.026	0.032	0.40	0.50	[a]	[a]	0.078
	Ciprofloxacin	$1.0 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$4.7 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	$1.1 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$	0.56	1.4	0.089
	Clarithromycin	$7.5 \cdot 10^{-5}$	$1.5 \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$	$6.3 \cdot 10^{-4}$	$9.3 \cdot 10^{-5}$	$1.9 \cdot 10^{-4}$	0.11	0.22	0.12
	Erythromycin	$3.3 \cdot 10^{-3}$	0.017	$5.0 \cdot 10^{-3}$	0.025	$2.4 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	0.15	0.76	0.30
	Ofloxacin	$2.9 \cdot 10^{-3}$	$5.9 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$2.9 \cdot 10^{-3}$	$6.3 \cdot 10^{-3}$	0.013	1.6	3.2	1.4
	Sulfadiazine	$2.9 \cdot 10^{-4}$	$9.5 \cdot 10^{-4}$	$3.6 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	$1.3 \cdot 10^{-4}$	$4.4 \cdot 10^{-4}$	0.49	1.6	1.0
	Sulfamethoxazole	$6.2 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	$6.7 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	$2.8 \cdot 10^{-4}$	$5.7 \cdot 10^{-4}$	0.54	1.1	0.60
	Sulfanilamide	0.045	0.091	0.033	0.067	0.016	0.031	[a]	[a]	17
	Trimethoprim	$1.8 \cdot 10^{-4}$	$6.0 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	$8.3 \cdot 10^{-4}$	$8.3 \cdot 10^{-5}$	$2.8 \cdot 10^{-4}$	0.12	0.39	120
Anticoagulant	Warfarin	$6.0 \cdot 10^{-3}$	0.016	0.011	0.030	$2.3 \cdot 10^{-3}$	$6.0 \cdot 10^{-3}$	2.3	5.8	0.76
Anticonvulsants	Carbamazepine	[b]	$9.4 \cdot 10^{-3}$	[b]	0.011	[b]	$3.5 \cdot 10^{-3}$	[b]	3.9	2.0
	Carbamazepine-10,11-epoxide	$3.8 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	$3.6 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	$1.8 \cdot 10^{-4}$	$6.0 \cdot 10^{-4}$	0.16	0.54	2.6
	Gabapentin	0.62	1.2	0.50	0.99	0.60	1.2	[a]	[a]	1000
	Lamotrigine	$3.8 \cdot 10^{-3}$	0.013	$2.9 \cdot 10^{-3}$	$9.6 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	$4.1 \cdot 10^{-3}$	3.1	10	8.0
	Primidone	$8.5 \cdot 10^{-4}$	$2.8 \cdot 10^{-3}$	$7.8 \cdot 10^{-4}$	$2.6 \cdot 10^{-3}$	$3.3 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	0.36	1.2	9.1
Antidepressants	Citalopram	$1.7 \cdot 10^{-4}$	$8.5 \cdot 10^{-4}$	$1.9 \cdot 10^{-4}$	$9.3 \cdot 10^{-4}$	$8.3 \cdot 10^{-4}$	$4.2 \cdot 10^{-3}$	0.14	0.68	16
	Desmethylcitalopram	$4.0 \cdot 10^{-4}$	$1.6 \cdot 10^{-3}$	$4.6 \cdot 10^{-4}$	$1.9 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$	$7.1 \cdot 10^{-3}$	1.7	6.6	0.05
	Desmethylvenlafaxine	$1.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$	$7.8 \cdot 10^{-5}$	$1.6 \cdot 10^{-4}$	$3.3 \cdot 10^{-5}$	$6.6 \cdot 10^{-5}$	0.046	0.093	6.6
	Fluoxetine	$5.8 \cdot 10^{-4}$	$2.3 \cdot 10^{-3}$	$3.1 \cdot 10^{-3}$	0.013	0.013	0.050	2.5	10	0.1
	Venlafaxine	$1.9 \cdot 10^{-3}$	$4.7 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$	$4.1 \cdot 10^{-3}$	$9.1 \cdot 10^{-4}$	$2.3 \cdot 10^{-3}$	1.0	2.5	0.88
Antidiabetics	Guanylurea	0.53	1.1	0.51	1.0	0.15	0.30	[a]	[a]	100
	Metformin	0.035	0.069	0.029	0.058	0.030	0.060	[a]	[a]	160
Antifungals	Climbazole	$1.7 \cdot 10^{-3}$	$4.2 \cdot 10^{-3}$	0.011	0.028	$2.8 \cdot 10^{-3}$	$6.9 \cdot 10^{-3}$	1.4	3.5	0.11

	Clotrimazole	$2.1 \cdot 10^{-3}$	$4.2 \cdot 10^{-3}$	$2.6 \cdot 10^{-3}$	$5.3 \cdot 10^{-3}$	0.025	0.050	0.98	2.0	0.03
	Fluconazole	$4.5 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$	$4.0 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	$1.8 \cdot 10^{-4}$	$6.0 \cdot 10^{-4}$	0.17	0.55	1.0
	Miconazole	[b]	0.063	[b]	0.045	[b]	0.25	[b]	8.3	0.025
Antihelmintic	Mebendazole	[b]	0.096	[b]	0.22	[b]	0.076	[b]	49	0.16
Antihistamines	Cetirizine	$1.6 \cdot 10^{-3}$	$5.3 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$	$3.4 \cdot 10^{-3}$	$6.5 \cdot 10^{-4}$	$2.2 \cdot 10^{-3}$	0.67	2.2	0.41
	Chlorpheniramine	$5.7 \cdot 10^{-4}$	$1.9 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$	$3.7 \cdot 10^{-3}$	$2.7 \cdot 10^{-3}$	$8.9 \cdot 10^{-3}$	0.79	2.6	1.6
	Fexofenadine	$5.1 \cdot 10^{-4}$	$1.7 \cdot 10^{-3}$	$4.7 \cdot 10^{-4}$	$1.6 \cdot 10^{-3}$	$2.3 \cdot 10^{-4}$	$7.8 \cdot 10^{-4}$	0.15	0.49	200
Antipruritic	Crotamiton	$6.9 \cdot 10^{-4}$	$2.3 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$	$6.6 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	$8.4 \cdot 10^{-4}$	0.38	1.3	6.6
Antiulcer	4-Hydroxyomeprazole	$1.8 \cdot 10^{-4}$	$1.8 \cdot 10^{-3}$	$1.8 \cdot 10^{-4}$	$1.8 \cdot 10^{-3}$	$7.2 \cdot 10^{-5}$	$7.2 \cdot 10^{-4}$	0.058	0.58	4.0
	Lansoprazole	$1.4 \cdot 10^{-3}$	0.028	$1.7 \cdot 10^{-3}$	0.034	$1.3 \cdot 10^{-3}$	0.026	[a]	[a]	0.47
	Omeprazole	0.019	0.027	0.023	0.033	$6.5 \cdot 10^{-3}$	$9.3 \cdot 10^{-3}$	[a]	[a]	18
	Ranitidine	$8.5 \cdot 10^{-4}$	$1.7 \cdot 10^{-3}$	$5.1 \cdot 10^{-4}$	$1.0 \cdot 10^{-3}$	$2.9 \cdot 10^{-4}$	$5.9 \cdot 10^{-4}$	[a]	[a]	3.1
Benzodiazepines	Lorazepam	$1.1 \cdot 10^{-3}$	$5.7 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$	0.020	$6.7 \cdot 10^{-4}$	$3.3 \cdot 10^{-3}$	0.60	3.0	0.10
	Oxazepam	$1.8 \cdot 10^{-3}$	$4.5 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$	$8.3 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$3.7 \cdot 10^{-3}$	1.3	3.1	0.37
	Temazepam	$1.5 \cdot 10^{-4}$	$5.1 \cdot 10^{-4}$	$7.9 \cdot 10^{-4}$	$2.6 \cdot 10^{-3}$	$1.0 \cdot 10^{-4}$	$3.5 \cdot 10^{-4}$	0.095	0.32	0.071
Betablockers	Acebutolol	$6.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-3}$	$6.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-3}$	$3.2 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	1.1	3.7	2.9
	Atenolol	$2.8 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	$3.0 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	$1.4 \cdot 10^{-4}$	$5.4 \cdot 10^{-4}$	0.33	1.3	150
	Bisoprolol	$9.5 \cdot 10^{-5}$	$2.9 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$	$3.6 \cdot 10^{-4}$	$5.9 \cdot 10^{-5}$	$1.8 \cdot 10^{-4}$	0.21	0.62	92
	Metoprolol	$1.8 \cdot 10^{-3}$	$9.1 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	$7.0 \cdot 10^{-3}$	$6.5 \cdot 10^{-4}$	$3.2 \cdot 10^{-3}$	2.3	12	8.6
	Propranolol	[b]	$1.3 \cdot 10^{-3}$	[b]	$1.4 \cdot 10^{-3}$	[b]	$2.0 \cdot 10^{-3}$	[b]	1.6	0.2
	Salbutamol	$5.4 \cdot 10^{-5}$	$4.3 \cdot 10^{-4}$	$5.3 \cdot 10^{-5}$	$4.2 \cdot 10^{-4}$	$3.2 \cdot 10^{-5}$	$2.5 \cdot 10^{-4}$	0.19	1.6	1000
	Sotalol	$5.8 \cdot 10^{-5}$	$4.6 \cdot 10^{-4}$	$5.6 \cdot 10^{-5}$	$4.5 \cdot 10^{-4}$	$2.9 \cdot 10^{-5}$	$2.3 \cdot 10^{-4}$	0.090	0.72	6.5
Chemotherapeutic	Ifosfamide	$8.8 \cdot 10^{-4}$	$4.4 \cdot 10^{-3}$	$7.0 \cdot 10^{-4}$	$3.5 \cdot 10^{-3}$	$2.9 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$	0.32	1.6	7.0
Coccidiostat	Clopidol	$4.0 \cdot 10^{-3}$	0.013	$4.3 \cdot 10^{-3}$	0.014	$2.3 \cdot 10^{-3}$	$7.5 \cdot 10^{-3}$	2.1	6.9	8.8
Hormones	17ß-Estradiol (E2)	$1.4 \cdot 10^{-3}$	0.014	$1.3 \cdot 10^{-3}$	0.013	$1.2 \cdot 10^{-3}$	0.012	1.4	14	$4.0 \cdot 10^{-4}$
	17α-Ethinylestradiol (EE2)	$7.0 \cdot 10^{-3}$	0.014	$7.0 \cdot 10^{-3}$	0.014	0.013	0.026	7.2	14	$3.7 \cdot 10^{-5}$
	Estriol (E3)	$1.6 \cdot 10^{-3}$	$7.8 \cdot 10^{-3}$	$7.6 \cdot 10^{-4}$	$3.8 \cdot 10^{-3}$	$5.9 \cdot 10^{-4}$	$2.9 \cdot 10^{-3}$	0.68	3.4	0.06
	Estrone (E1)	$1.6 \cdot 10^{-3}$	$4.8 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	$3.5 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	$3.7 \cdot 10^{-3}$	1.4	4.2	$3.6 \cdot 10^{-3}$
	Norethisterone	$3.6 \cdot 10^{-3}$	0.012	$5.0 \cdot 10^{-3}$	0.017	$1.4 \cdot 10^{-3}$	$4.5 \cdot 10^{-3}$	1.6	5.2	4.5
Lipid regulators	Atorvastatin	$1.9 \cdot 10^{-3}$	$6.5 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	$4.7 \cdot 10^{-3}$	$8.5 \cdot 10^{-4}$	$2.8 \cdot 10^{-3}$	0.66	2.2	8.5
	Bezafibrate	$6.5 \cdot 10^{-3}$	0.022	0.015	0.051	$3.2 \cdot 10^{-3}$	0.011	2.4	7.9	2.3
	Gemfibrozil	$2.9 \cdot 10^{-3}$	$5.9 \cdot 10^{-3}$	$7.5 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$	$3.3 \cdot 10^{-4}$	$6.7 \cdot 10^{-4}$	0.70	1.4	0.5
Wastewater discharge marker	Caffeine	$9.3 \cdot 10^{-4}$	$3.3 \cdot 10^{-3}$	$9.8 \cdot 10^{-3}$	$3.4 \cdot 10^{-3}$	$4.3 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$	0.40	1.4	1.2
	Cotinine	$6.3 \cdot 10^{-5}$	$2.0 \cdot 10^{-4}$	$6.1 \cdot 10^{-5}$	$2.0 \cdot 10^{-4}$	$2.9 \cdot 10^{-5}$	$8.9 \cdot 10^{-5}$	0.025	0.080	9.4
X-ray contrast	Amidotrizoic acid	0.12	0.35	0.11	0.34	0.10	0.36	[a]	[a]	0.073

[a] method not suitable, [b] blank that could be corrected for

Table S7: Mean accuracy and standard deviation (both in %) for standards (1, 10, and 50 µg L^{-1}), and spiked samples analysed by direct injection (10 µg L^{-1}) and SPE (0.1 µg L^{-1} in influent and effluent, and 0.05 µg L^{-1} in river water). Each data point represents mean of quality control data from individual months (n = 1 - 12). When accuracies were outside the acceptable range of 75 – 125%, concentrations were corrected and considered semi-quantitative.

Class	**EC**	**Standard**			**Direct injection**		**SPE**		
		1	10	50	Influent	Effluent	Influent	Effluent	River
Anaesthetics	Lidocaine	75 ± 32	75 ± 18	86 ± 21	96 ± 15	89 ± 11	95 ± 26	82 ± 26	85 ± 29
Analgesics	3-Methoxyparacetamol	129 ± 32	126 ± 33	144 ± 33	121 ± 35	130 ± 39	[a]	[a]	197 ± 31
	Diclofenac	118 ± 43	71 ± 19	91 ± 15	86 ± 30	85 ± 26	93 ± 40	99 ± 27	132 ± 53
	Hydroxyibuprofen	112 ± 43	78 ± 24	92 ± 20	88 ± 39	91 ± 30	80 ± 3	[a]	55 ± 35
	Ibuprofen	[b]	109 ± 21	92 ± 10	[a]	63[a]	[a]	104[a]	366 ± 98
	Ketoprofen	114 ± 44	91 ± 18	105 ± 23	132 ± 34	124 ± 44	160 ± 54	143 ± 37	82 ± 5
	Naproxen	91 ± 39	93 ± 21	93 ± 27	90 ± 30	99 ± 31	[a]	77 ± 15	128 ± 38
	Paracetamol	78 ± 19	92 ± 17	102 ± 17	53[a]	75 ± 34	[a]	[a]	100 ± 24
Antibiotics	3-Desmethyltrimethoprim	98 ± 35	113 ± 45	125 ± 32	139 ± 17	144 ± 23	101 ± 25	123 ± 41	184 ± 37
	α-Hydroxytrimethoprim	106 ± 39	110 ± 24	115 ± 27	126 ± 15	108 ± 16	92 ± 25	95 ± 27	119 ± 12
	Amoxicillin	50 ± 37	56 ± 25	63 ± 30	88 ± 30	85 ± 24	210 ± 159	292 ± 267	[b]
	Ciprofloxacin	146 ± 29	202 ± 146	238 ± 123	416 ± 612	303 ± 190	207 ± 177	172 ± 110	301 ± 282
	Clarithromycin	79 ± 19	98 ± 31	98 ± 15	119 ± 50	110 ± 41	106 ± 35	97 ± 32	87 ± 13
	Erythromycin	88 ± 24	60 ± 39	[c]	19 ± 12[f]	17 ± 12[f]	73 ± 25	98 ± 64	13 ± 5
	Ofloxacin	102 ± 53	160 ± 81	262 ± 214	256 ± 362	268 ± 190	253 ± 212	280 ± 149	156 ± 146
	Sulfadiazine	80 ± 24	86 ± 14	86 ± 14	108 ± 26	92 ± 25	124 ± 44	83 ± 29	86 ± 24
	Sulfamethoxazole	87 ± 17	97 ± 16	99 ± 17	119 ± 34	113 ± 35	104 ± 30	102 ± 29	87 ± 41
	Sulfanilamide	110 ± 46	99 ± 26	108 ± 26	158 ± 49	131 ± 43	226 ± 156	197 ± 120	247 ± 74
	Trimethoprim	78 ± 29	82 ± 22	93 ± 20	112 ± 24	97 ± 21	102 ± 40	116 ± 61	64 ± 8
Anticoagulants	Warfarin	116 ± 30	102 ± 26	106 ± 27	133 ± 58	120 ± 48	180 ± 102	110 ± 49	92 ± 15
Anticonvulsants	Carbamazepine	93 ± 19	95 ± 14	101 ± 14	131 ± 31	127 ± 30	111 ± 45	104 ± 38	126 ± 34
	Carbamazepine-10,11-epoxide	92 ± 53	96 ± 31	103 ± 32	119 ± 14	112 ± 11	88 ± 43	92 ± 45	147 ± 43
	Gabapentin	71 ± 36	85 ± 13	93 ± 13	93 ± 25	82 ± 16	[d]	[d]	[d]
	Lamotrigine	82 ± 41	88 ± 19	97 ± 19	109 ± 19	106 ± 15	67 ± 15	104 ± 36	98 ± 18
	Primidone	73 ± 23	97 ± 11	110 ± 13	122 ± 35	112 ± 27	123 ± 29	111 ± 22	114 ± 17
Antidepressants	Citalopram	67 ± 33	91 ± 15	103 ± 16	96 ± 22	107 ± 22	62 ± 17	61 ± 20	90 ± 36
	Desmethylcitalopram	72 ± 38	105 ± 20	113 ± 27	107 ± 24	105 ± 23	63 ± 23	97 ± 63	109 ± 73
	Desmethylvenlafaxine	93 ± 30	102 ± 22	105 ± 18	106 ± 19	111 ± 23	106 ± 24	132 ± 36	134 ± 41
	Fluoxetine	103 ± 14	125 ± 28	111 ± 31	119 ± 50	112 ± 29	93 ± 30	100 ± 44	[a]
	Venlafaxine	85 ± 42	104 ± 22	112 ± 21	108 ± 18	124 ± 24	125 ± 25	125 ± 19	154 ± 46
Antidiabetics	Guanylurea	53 ± 34	63 ± 28	67 ± 28	82 ± 36	72 ± 36	[d]	[d]	[d]
	Metformin	87 ± 19	72 ± 18	88 ± 18	60[a]	91[a]	[d]	[d]	81 ± 21[d]

Antifungals	Climbazole	[b]	104 ± 31	94 ± 13	69 ± 31	73 ± 36	67 ± 36	37 ± 19	91 ± 60
	Clotrimazole	103 ± 69	98 ± 39	58 ± 22	107 ± 34	95 ± 25	21 ± 15	86 ± 37	[b]
	Fluconazole	74 ± 25	84 ± 30	95 ± 33	106 ± 23	101 ± 23	96 ± 32	121 ± 40	75 ± 28
	Miconazole	140 ± 107	129 ± 81	120 ± 102	183 ± 99	119 ± 85	355 ± 160	206 ± 273	[b]
Antihelmintic	Mebendazole	61 ± 35	105 ± 66	86 ± 34	155 ± 103	174 ± 118	120 ± 96	42 ± 68	193 ± 89
Antihistamines	Cetirizine	272 ± 180	286 ± 189	177 ± 65	170 ± 75	230 ± 109	132 ± 51	75 ± 14	130 ± 60
	Chlorpheniramine	76 ± 16	73 ± 42	99 ± 12	56 ± 30	107 ± 69	77 ± 30	47 ± 16	110 ± 102
	Fexofenadine	117 ± 38	125 ± 33	141 ± 39	113 ± 24	113 ± 28	89[a]	110 ± 31	139 ± 67
Antipruritic	Crotamiton	65 ± 25	70 ± 28	75 ± 14	92 ± 31	84 ± 26	74 ± 28	72 ± 24	76 ± 21
Antiulcers	4-Hydroxyomeprazole	73 ± 34	85 ± 26	93 ± 14	101 ± 19	93 ± 14	67 ± 14	109 ± 35	92 ± 9
	Lansoprazole	100 ± 51	92 ± 50	55 ± 37	71 ± 21	65 ± 11	247	142 ± 107	33 ± 4
	Omeprazole	126	175 ± 155	82 ± 69	80 ± 10	64 ± 10	54	271 ± 270	[b]
	Ranitidine	57 ± 12	78 ± 32	101 ± 36	143 ± 63	151 ± 63	106 ± 47	189 ± 104	44 ± 20
Benzodiazepines	Lorazepam	128 ± 44	100 ± 55	114 ± 52	136 ± 56	118 ± 54	137 ± 60	131 ± 58	156 ± 105
	Oxazepam	147 ± 71	113 ± 31	128 ± 52	162 ± 46	151 ± 36	114 ± 68	100 ± 62	145 ± 41
	Temazepam	117 ± 42	113 ± 35	124 ± 35	148 ± 40	136 ± 47	124 ± 49	131 ± 61	116 ± 2
Betablockers	Acebutolol	85 ± 23	98 ± 12	109 ± 16	114 ± 32	112 ± 28	98 ± 33	98 ± 31	121 ± 16
	Atenolol	72 ± 32	85 ± 19	97 ± 22	108 ± 18	102 ± 22	101 ± 2	160 ± 32	83 ± 30
	Bisoprolol	84 ± 21	81 ± 22	89 ± 24	86 ± 16	92 ± 17	84 ± 13	86 ± 18	107 ± 11
	Metoprolol	81 ± 35	94 ± 14	105 ± 12	109 ± 26	113 ± 27	113 ± 24	127 ± 36	94 ± 21
	Propranolol	100 ± 72	86 ± 16	97 ± 14	100 ± 22	120 ± 27	129 ± 56	129 ± 36	151 ± 33
	Salbutamol	88 ± 27	96 ± 19	108 ± 25	104 ± 20	104 ± 25	104 ± 23	99 ± 22	106 ± 18
	Sotalol	76 ± 25	84 ± 18	93 ± 17	111 ± 18	101 ± 17	107 ± 34	112 ± 30	84 ± 17
Chemotherapeutic	Ifosfamide	102 ± 26	112 ± 24	118 ± 30	102 ± 29	117 ± 37	125 ± 40	149 ± 54	191 ± 58
Coccidiostat	Clopidol	109 ± 57	99 ± 17	109 ± 19	130 ± 34	121 ± 31	105 ± 31	107 ± 38	146 ± 59
Hormones	17ß-Estradiol (E2)	86 ± 27	74 ± 16	82 ± 18	90 ± 21	89 ± 16	102 ± 28	93 ± 17	103 ± 15
	17α-Ethinylestradiol (EE2)	101 ± 24	85 ± 15	93 ± 19	103 ± 32	100 ± 19	94 ± 31	94 ± 31	119 ± 38
	Estriol (E3)	61 ± 26	66 ± 27	65 ± 21	75 ± 20	79 ± 30	90 ± 17	94 ± 32	68 ± 12
	Estrone (E1)	77 ± 20	71 ± 18	74 ± 17	83 ± 15	85 ± 16	86 ± 17	84 ± 17	95 ± 8
	Norethisterone	141 ± 50	100 ± 27	109 ± 31	150 ± 73[f]	144 ± 63[f]	193 ± 103	135 ± 77	109 ± 27
Lipid regulators	Atorvastatin	111 ± 36	113 ± 50	95 ± 48	96 ± 34	114 ± 32	124 ± 50	148 ± 68	102 ± 35
	Bezafibrate	79 ± 23	70 ± 17	75 ± 17	81 ± 13	75 ± 13	154 ± 25	61 ± 33	90 ± 37
	Gemfibrozil	56 ± 24	66 ± 16	72 ± 17	79 ± 29	79 ± 23	106 ± 34	109 ± 37	113 ± 53
Wastewater discharge marker	Caffeine	118 ± 54	105 ± 23	105 ± 19	100 ± 13	94 ± 19	[a]	[a]	108 ± 32
	Cotinine	94 ± 21	92 ± 9	105 ± 10	109 ± 24	113 ± 26	88 ± 12	94 ± 18	118 ± 18
X-ray contrast	Amidotrizoic acid	88 ± 28	81 ± 20	90 ± 19	91 ± 18	89 ± 14	[d]	[d]	[d]

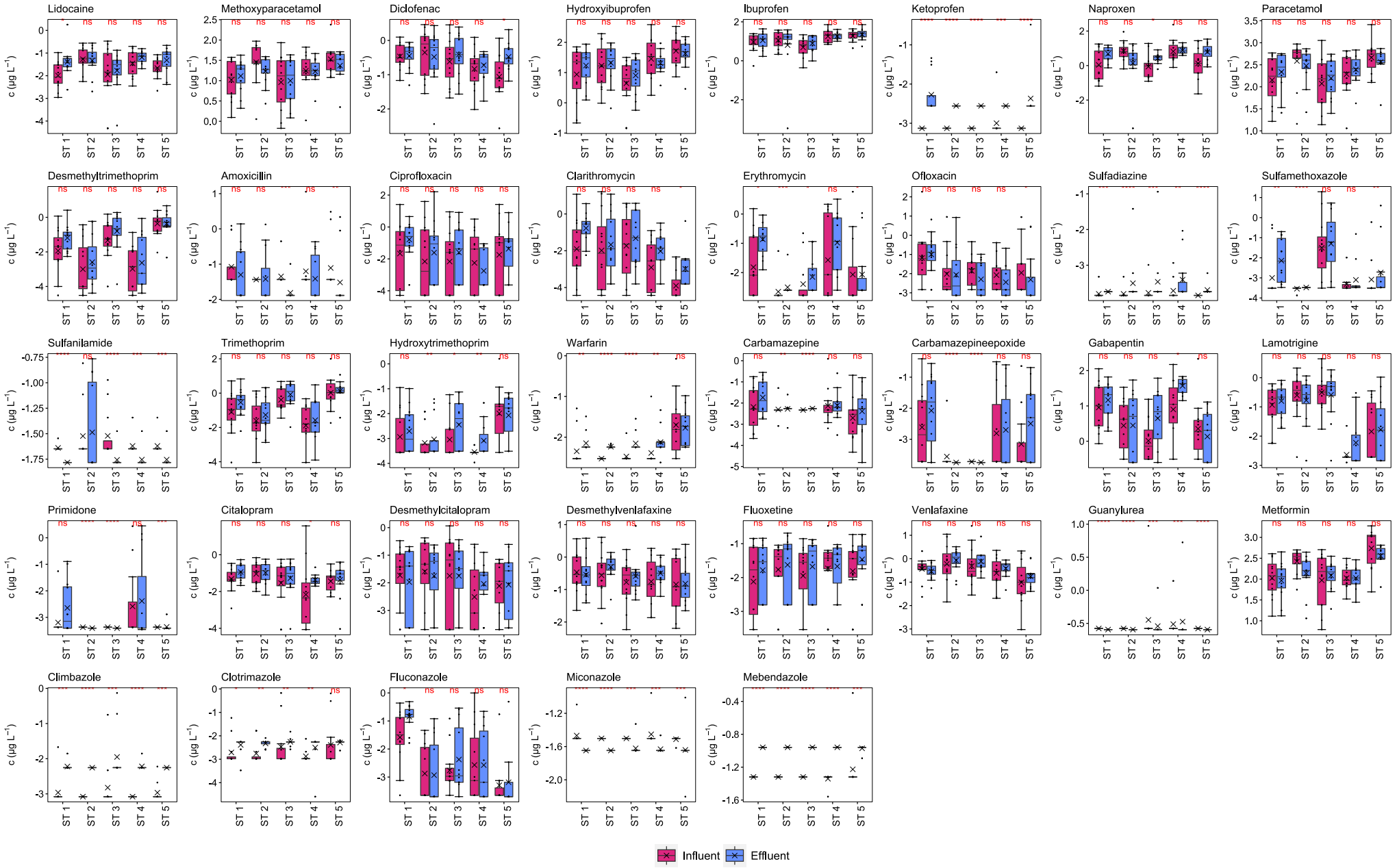
[a] concentration in all (all except one) samples too high to calculate accuracy, [b] < LOQ (in river), [c] outside calibration range, [d] only analysed by direct injection

S4 Results

Table S8: Influent and effluent concentrations (25th percentile, mean, 75th percentile, maximum) in µg L^{-1} and number of samples (n) with concentrations > MQL, n_{total} = 116. Concentrations < MQL and < MDL were substituted with half of the value. Statistical results < MDL were reported as such (European Commission, 2009).

Class	**EC**	**Influent**					**Effluent**				
		25th	Mean	75th	Max	n	25th	Mean	75th	Max	n
Anaesthetics	Lidocaine	$7.8 \cdot 10^{-3}$	0.058	0.067	0.34	56	0.025	0.094	0.091	1.8	57
Analgesics	3-Methoxyparacetamol	11	31	38	240	58	10	21	32	51	58
	Diclofenac	0.076	0.52	0.73	2.9	54	0.16	0.55	0.71	2.7	53
	Hydroxyibuprofen	4.9	49	55	380	58	11	35	48	150	58
	Ibuprofen	7.1	17	24	72	58	10	18	24	72	57
	Ketoprofen	< MDL	< MDL	< MDL	0.020	1	< MDL	0.010	< MDL	0.33	4
	Naproxen	0.46	12	9.9	240	56	2.2	6.7	8.7	34	55
	Paracetamol	120	400	580	2600	58	160	340	500	740	58
Antibiotics	3-Desmethyltrimethoprim	$4.3 \cdot 10^{-4}$	0.73	0.18	30	43	$3.0 \cdot 10^{-3}$	0.41	0.46	4.7	49
	α-Hydroxytrimethoprim	< MDL	0.036	$8.5 \cdot 10^{-3}$	1.6	20	< MDL	0.014	0.017	0.10	28
	Amoxicillin	< MDL	0.37	< MDL	11	8	< MDL	0.16	0.088	2.2	16
	Ciprofloxacin	< MDL	2.2	0.41	40	30	< MDL	3.4	0.37	160	34
	Clarithromycin	$7.5 \cdot 10^{-5}$	0.95	0.080	16	39	$2.5 \cdot 10^{-3}$	0.63	0.31	12	41
	Erythromycin	< MDL	0.26	0.010	5.8	19	< MDL	0.20	0.12	3.2	27
	Ofloxacin	< MDL	3.6	0.069	190	29	< MDL	0.43	0.084	8.4	28
	Sulfadiazine	< MDL	< MDL	< MDL	$1.2 \cdot 10^{-3}$	2	< MDL	$3.1 \cdot 10^{-3}$	< MDL	0.11	4
	Sulfamethoxazole	< MDL	0.46	< MDL	20	15	< MDL	0.32	0.021	5.3	23
	Sulfanilamide	< MDL	< MDL	< MDL	0.16	6	< MDL	< MDL	< MDL	0.17	4
	Trimethoprim	0.017	2.5	0.68	100	54	0.023	1.2	1.6	12	57
Anticoagulants	Warfarin	< MDL	0.026	< MDL	0.84	12	< MDL	0.012	< MDL	0.10	17
Anticonvulsants	Carbamazepine	< MDL	0.038	< MDL	1.2	26	< MDL	0.028	0.010	0.28	31
	Carbamazepine-10,11-epoxide	< MDL	0.025	$5.3 \cdot 10^{-4}$	0.39	14	< MDL	0.027	0.011	0.28	20
	Gabapentin	0.84	16	11	220	45	2.0	19	27	68	46
	Lamotrigine	$1.9 \cdot 10^{-3}$	0.35	0.36	4.4	42	0.010	0.30	0.49	1.8	46
	Primidone	< MDL	0.055	< MDL	2.7	4	< MDL	0.092	< MDL	2.8	9
Antidepressants	Citalopram	0.010	0.76	0.15	37	52	0.030	0.14	0.21	0.58	56
	Desmethylcitalopram	$8.0 \cdot 10^{-4}$	0.100	0.11	1.2	39	< MDL	0.064	0.099	0.36	42
	Desmethylvenlafaxine	0.082	0.59	0.81	4.1	56	0.13	0.64	0.54	9.1	58
	Fluoxetine	$9.1 \cdot 10^{-3}$	0.046	0.063	0.34	45	$1.6 \cdot 10^{-3}$	0.058	0.085	0.21	41
	Venlafaxine	0.12	1.4	0.91	25	57	0.19	0.79	0.87	8.9	58
Antidiabetics	Guanylurea	< MDL	< MDL	< MDL	9.4	2	< MDL	< MDL	< MDL	5.3	2

	Metformin	79	320	390	1900	58	83	200	290	650	58
Antifungals	Climbazole	< MDL	$4.4 \cdot 10^{-3}$	< MDL	0.18	4	< MDL	0.022	< MDL	0.74	2
	Clotrimazole	$1.1 \cdot 10^{-3}$	0.034	$2.1 \cdot 10^{-3}$	0.67	12	$5.5 \cdot 10^{-3}$	$5.2 \cdot 10^{-3}$	$5.5 \cdot 10^{-3}$	0.015	9
	Fluconazole	< MDL [4]	0.050	0.024	1.0	29	< MDL	0.075	0.13	0.49	31
	Miconazole	< MDL	< MDL	< MDL	0.11	4	< MDL	< MDL	< MDL	0.098	4
Antihelmintic	Mebendazole	< MDL	< MDL	< MDL	0.50	2	< MDL	< MDL	< MDL	0.081	1
Antihistamines	Cetirizine	0.49	3.0	3.9	30	58	0.36	2.0	3.1	8.3	58
	Chlorpheniramine	$9.5 \cdot 10^{-4}$	0.073	0.027	1.2	37	$5.6 \cdot 10^{-4}$	0.093	0.10	0.79	41
	Fexofenadine	0.13	3.9	6.1	36	55	0.46	5.2	7.1	23	58
Antipruritic	Crotamiton	$1.2 \cdot 10^{-3}$	0.27	0.25	8.9	45	$3.4 \cdot 10^{-3}$	0.16	0.28	1.2	46
Antiulcers	4-Hydroxyomeprazole	0.081	0.33	0.48	1.3	58	0.093	0.21	0.30	0.75	58
	Lansoprazole	$7.1 \cdot 10^{-4}$	0.75	0.075	25	16	$8.6 \cdot 10^{-4}$	1.5	0.12	45	15
	Omeprazole	< MDL	0.40	0.23	3.4	18	0.012	1.8	0.82	35	26
	Ranitidine	< MDL	0.060	$7.2 \cdot 10^{-3}$	2.0	19	< MDL	0.11	0.035	2.5	29
Benzodiazepines	Lorazepam	< MDL	0.017	< MDL	0.74	2	< MDL	0.026	< MDL	1.0	3
	Oxazepam	< MDL	0.029	0.021	0.78	24	< MDL	0.033	0.045	0.31	26
	Temazepam	< MDL	0.13	0.039	1.6	29	< MDL	0.13	0.090	1.7	32
Betablockers	Acebutolol	< MDL	< MDL	< MDL	$8.5 \cdot 10^{-3}$	4	< MDL	$1.9 \cdot 10^{-3}$	< MDL	0.064	2
	Atenolol	0.24	2.2	1.8	25	56	0.54	1.5	1.7	5.8	58
	Bisoprolol	0.033	0.23	0.31	2.0	57	0.033	0.14	0.19	0.48	57
	Metoprolol	< MDL	0.025	< MDL	0.50	9	< MDL	0.054	$3.4 \cdot 10^{-3}$	1.3	15
	Propranolol	$7.0 \cdot 10^{-4}$	0.26	0.31	1.8	42	$2.6 \cdot 10^{-3}$	0.24	0.32	1.4	43
	Salbutamol	$2.7 \cdot 10^{-3}$	0.038	0.039	0.55	50	$3.7 \cdot 10^{-3}$	0.029	0.034	0.22	48
	Sotalol	< MDL	$9.3 \cdot 10^{-3}$	$8.9 \cdot 10^{-5}$	0.30	11	< MDL	0.086	$9.6 \cdot 10^{-3}$	2.0	29
Chemotherapeutic	Ifosfamide	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	$9.4 \cdot 10^{-3}$	1
Coccidiostat	Clopidol	< MDL	$9.5 \cdot 10^{-3}$	< MDL	0.12	10	< MDL	$9.5 \cdot 10^{-3}$	< MDL	0.085	10
Hormones	17ß-Estradiol (E2)	< MDL	0.012	$7.0 \cdot 10^{-3}$	0.091	14	< MDL	$7.5 \cdot 10^{-3}$	$6.5 \cdot 10^{-3}$	0.046	14
	17α-Ethinylestradiol (EE2)	< MDL	0.011	< MDL	0.27	2	< MDL	< MDL	< MDL	0.20	1
	Estriol (E3)	0.021	0.12	0.18	0.99	49	0.028	0.12	0.16	0.53	50
	Estrone (E1)	0.041	0.095	0.13	0.32	52	0.036	0.073	0.090	0.29	51
	Norethisterone	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	0.065	1
Lipid regulators	Atorvastatin	0.59	3.4	3.8	25	57	0.70	1.7	2.1	8.8	57
	Bezafibrate	< MDL	0.41	< MDL	23	6	< MDL	0.81	0.051	35	19
	Gemfibrozil	< MDL	0.012	< MDL	0.59	1	< MDL	$1.5 \cdot 10^{-3}$	< MDL	0.068	2
Wastewater discharge marker	Caffeine	39	140	200	490	58	46	120	170	370	58
	Cotinine	0.27	2.2	3.3	9.9	58	0.46	1.8	2.7	6.9	58
X-ray contrast	Amidotrizoic acid	< MDL	< MDL	< MDL	0.060	1	< MDL	< MDL	< MDL	1.0	3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Amoxicillin
Ciprofloxacin
Clarithromycin
Erythromycin
Ofloxacin
Sulfadiazine
Sulfamethoxazole
Sulfanilamide
Trimethoprim
Hydroxytrimethoprim
Warfarin
Carbamazepine
Carbamazepineepoxide
Gabapentin
Lamotrigine
Primidone
Citalopram
Desmethylcitalopram
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Fluoxetine
Venlafaxine
Guanylurea
Metformin
Climbazole
Clotrimazole
Fluconazole
Miconazole
Mebendazole
c (µg L⁻¹)
ST 1
ST 2
ST 3
ST 4
ST 5
ns
Influent
Effluent

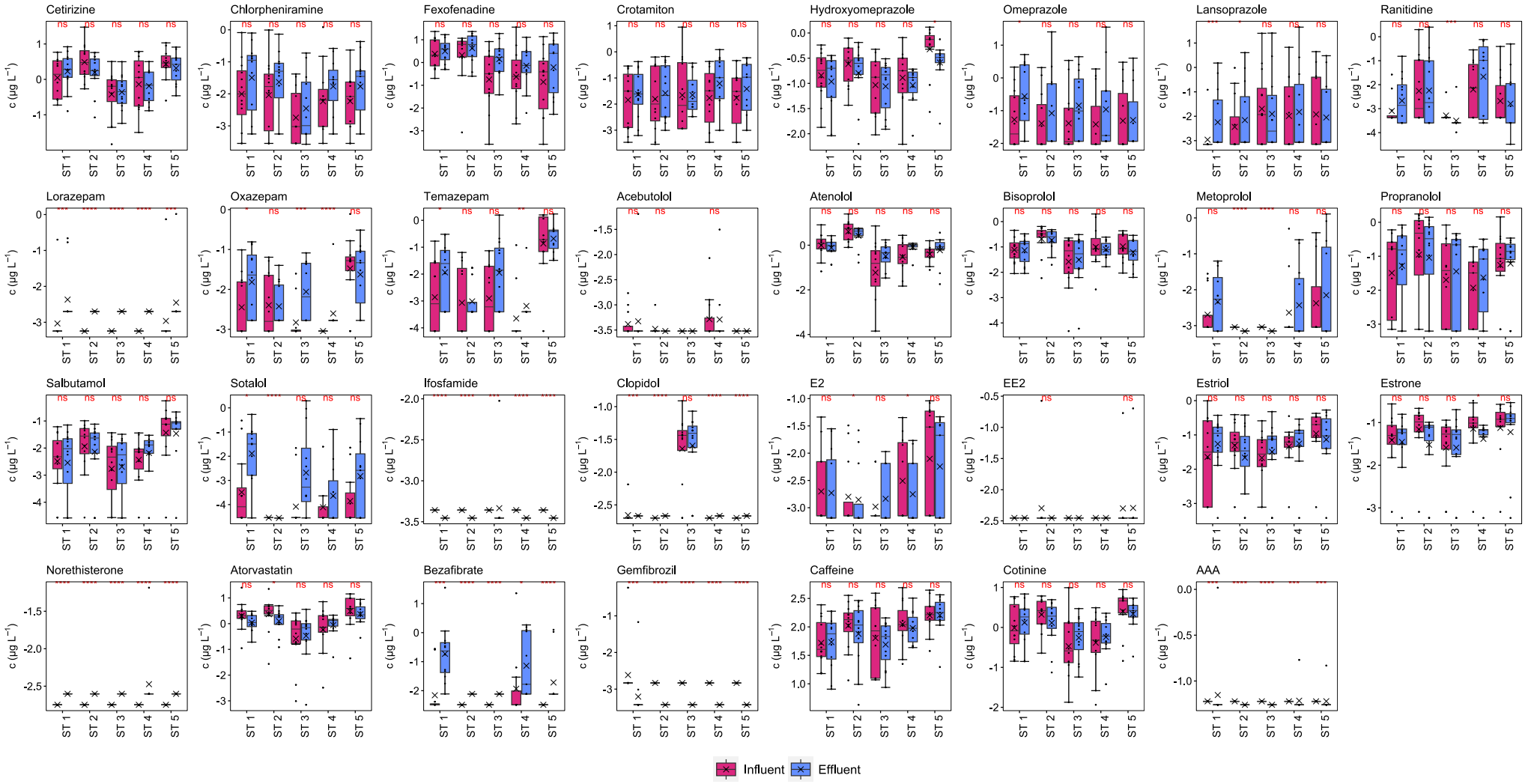


Figure S1: Emerging contaminant concentrations (logarithmic scale) of individual septic tanks (ST) in influent and effluent wastewater with wilcoxon test results (ns = no significant difference, */** = significant difference).

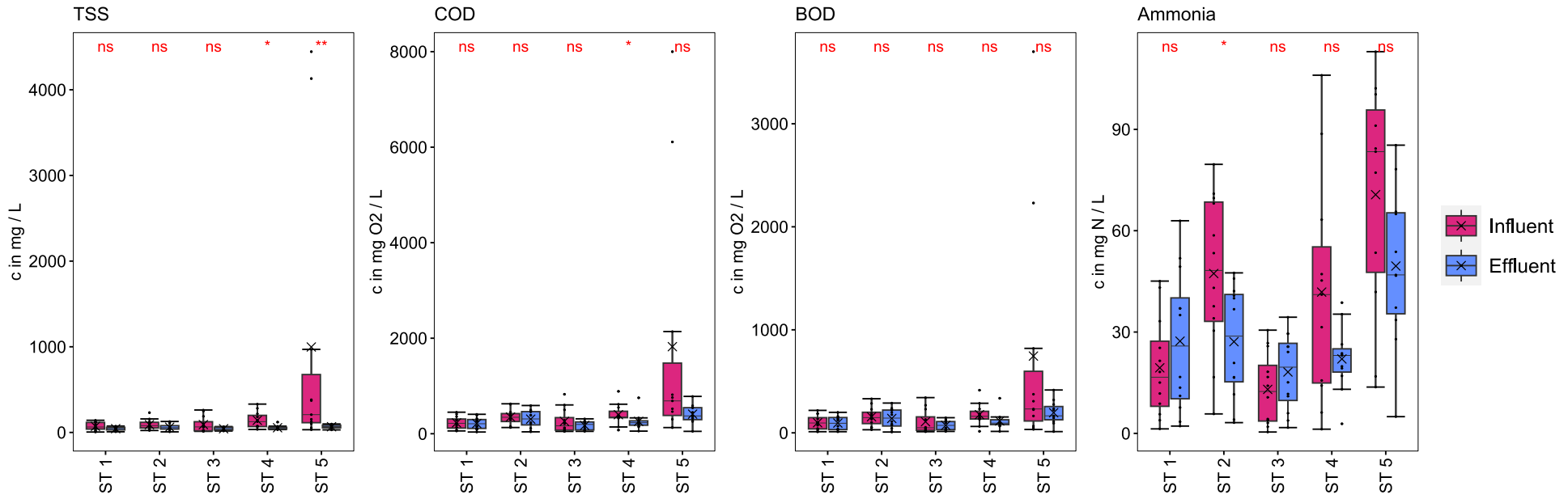


Figure S2: Sanitary determinands TSS, COD, BOD, and Ammonia in septic tank effluent and influent with Wilcoxon results (NS = no significant difference, */** = significant difference).

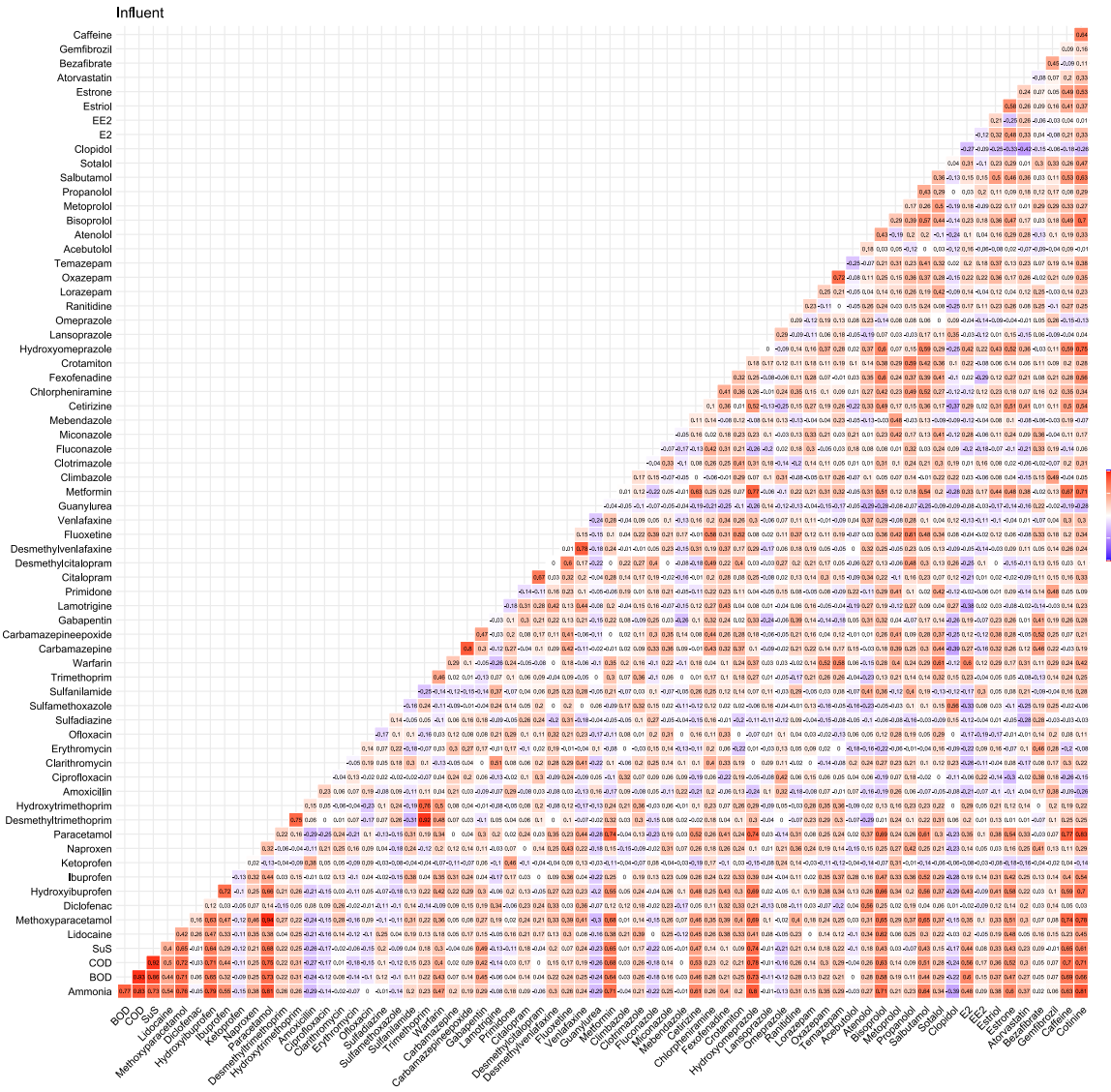


Figure S3: Spearman correlation matrix for sanitary determinands and ECs in septic tank influent.

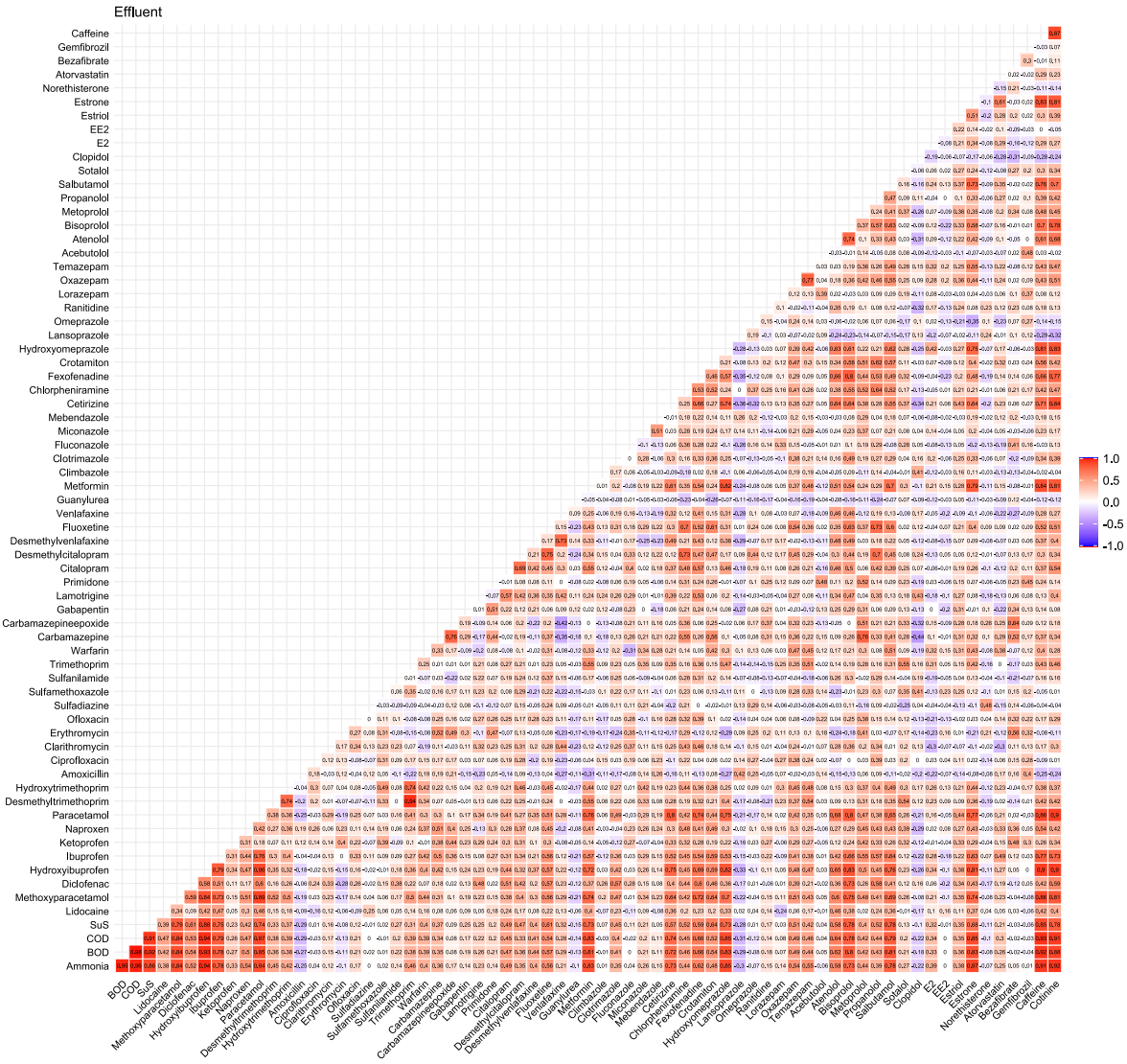
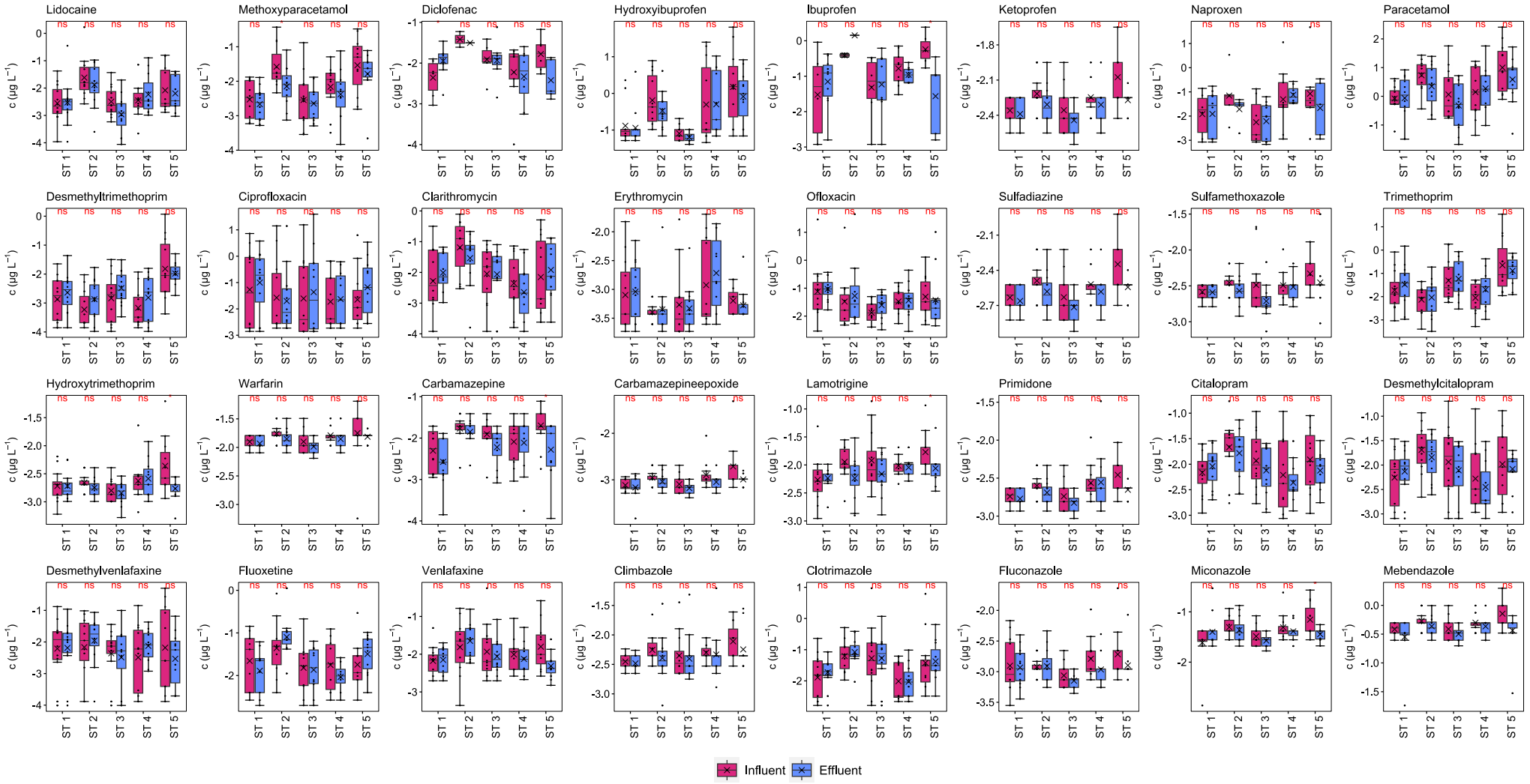


Figure S4: Spearman correlation matrix for sanitary determinands and ECs in septic tank effluent.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Methoxyparacetamol
Diclofenac
Hydroxyibuprofen
Ibuprofen
Ketoprofen
Naproxen
Paracetamol
Desmethyltrimethoprim
Ciprofloxacin
Clarithromycin
Erythromycin
Ofloxacin
Sulfadiazine
Sulfamethoxazole
Trimethoprim
Hydroxytrimethoprim
Warfarin
Carbamazepine
Carbamazepineepoxide
Lamotrigine
Primidone
Citalopram
Desmethylcitalopram
Desmethylvenlafaxine
Fluoxetine
Venlafaxine
Climbazole
Clotrimazole
Fluconazole
Miconazole
Mebendazole
c (µg L⁻¹)
ST 1
ST 2
ST 3
ST 4
ST 5
ns
Influent
Effluent

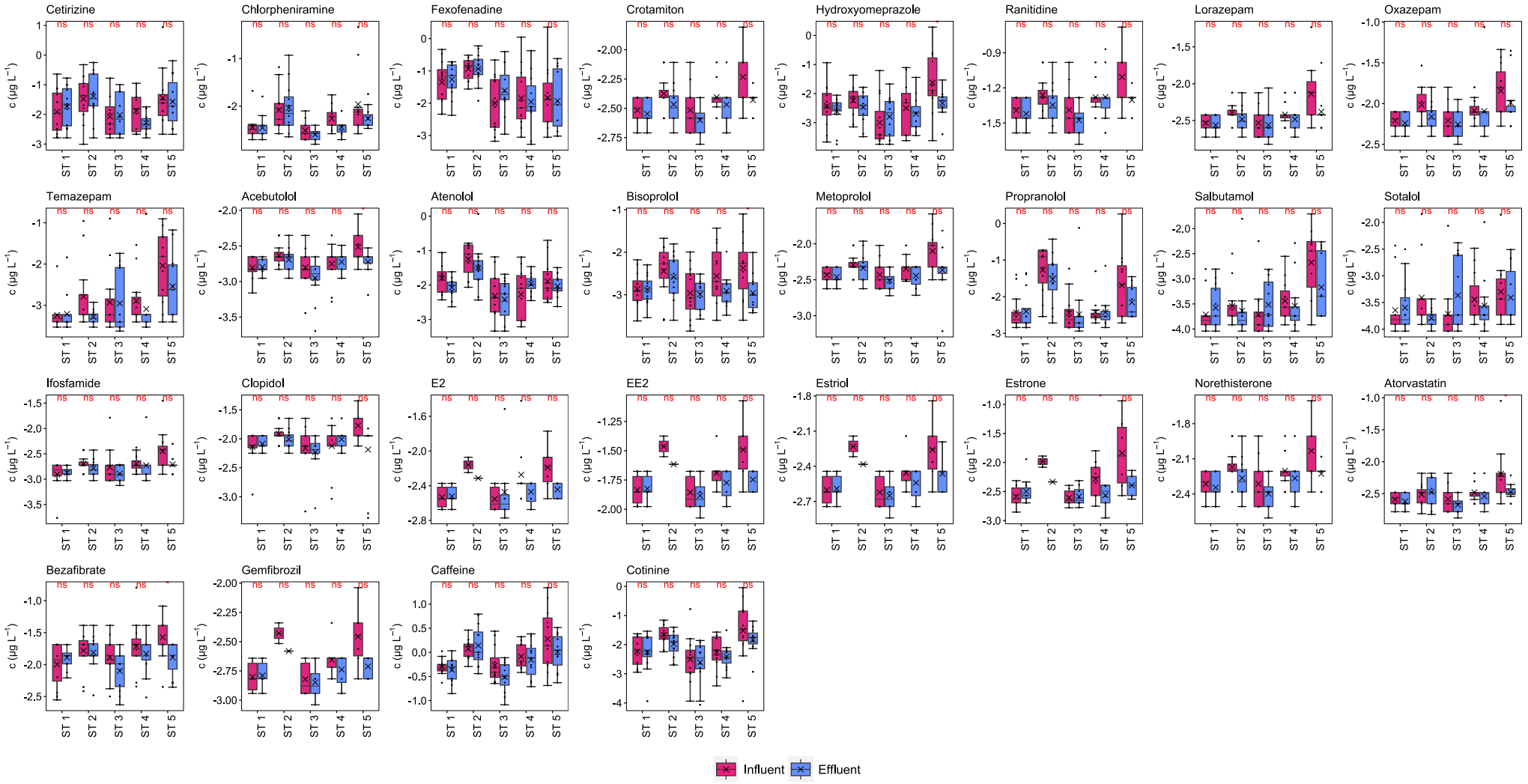

Figure S5: Emerging contaminant concentrations (logarithmic scale) of individual septic tanks (ST) in influent and effluent TSS with wilcoxon test results (ns = no significant difference, */** = significant difference).

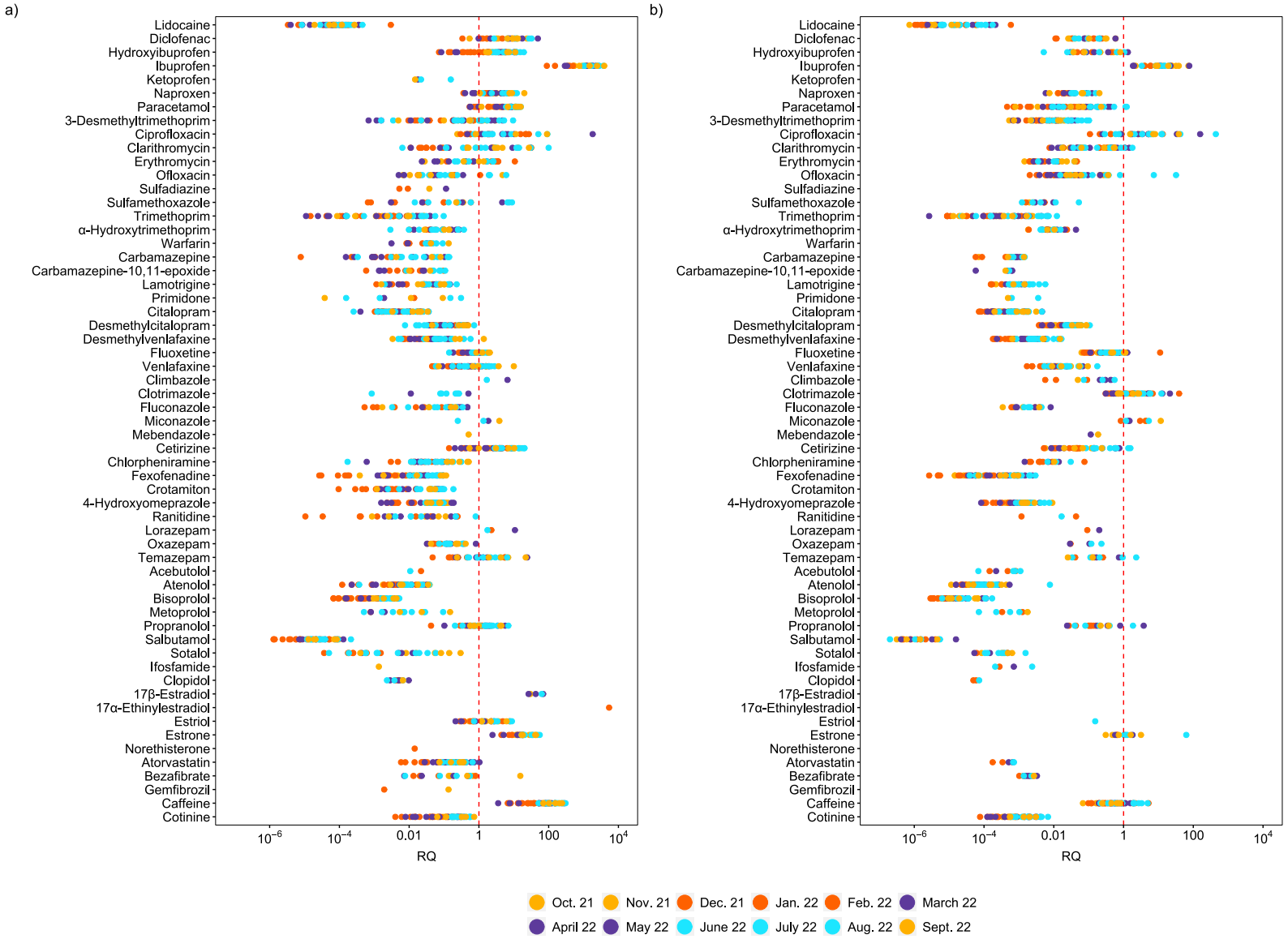

Figure S6: Risk Quotients (RQ; logarithmic scale) of detected ECs using a) liquid and b) TSS concentration, sorted by class, in septic tank effluents. PNECs in Table S4. Effluent concentrations with RQ ≥ 1 (red dotted line) require dilution to mitigate environmental risk.

Table S9: TSS contribution to total concentrations (25th percentile, mean, 75th percentile, maximum) in influent and effluent in % including samples with liquid and TSS concentration > MQL, and number of samples (n) with concentrations > MQL in TSS, n_{total} = 116.

Class	**EC**	**Influent**					**Effluent**				
		25th	Mean	75th	Max	n	25th	Mean	75th	Max	n
Anaesthetics	Lidocaine	6.0	26	36	98	55	4.3	19	30	94	57
Analgesics	3-Methoxyparacetamol	0.021	0.086	0.10	0.69	56	0.015	0.049	0.062	0.22	54
	Diclofenac	2.2	13	18	60	25	1.4	5.1	5.4	21	26
	Hydroxyibuprofen	2.9	9.6	8.6	58	24	1.3	8.2	10	42	25
	Ibuprofen	1.2	4.2	4.0	33	26	0.58	2.6	3.1	12	28
	Ketoprofen	< MQL	< MQL	< MQL	< MQL	0	< MQL	< MQL	< MQL	< MQL	0
	Naproxen	0.92	7.9	6.3	70	24	0.70	2.8	1.9	49	28
	Paracetamol	0.31	2.7	2.4	35	57	0.21	1.3	1.6	8.0	58
Antibiotics	3-Desmethyltrimethoprim	1.4	6.2	6.0	44	42	1.3	8.8	4.8	92	51
	α-Hydroxytrimethoprim	3.7	19	28	47	19	2.3	16	15	84	25
	Ciprofloxacin	15	47	74	100	26	20	43	67	90	36
	Clarithromycin	4.9	32	59	99	48	2.1	23	29	99	51
	Erythromycin	0.81	8.0	6.9	37	13	0.20	4.1	2.8	35	23
	Ofloxacin	19	40	55	90	44	38	50	69	85	52
	Sulfadiazine	< MQL	< MQL	< MQL	< MQL	0	< MQL	< MQL	< MQL	< MQL	0
	Sulfamethoxazole	0.25	5.0	7.4	14	7	0.13	8.2	0.91	63	13
	Trimethoprim	6.7	20	25	83	57	4.6	20	25	90	58
Anticoagulant	Warfarin	1.2	1.2	1.2	1.2	1	< MQL	< MQL	< MQL	< MQL	0
Anticonvulsants	Carbamazepine	2.3	11	7.0	77	14	1.6	10.0	8.0	49	21
	Carbamazepine-10,11-epoxide	0.62	1.3	1.9	2.8	4	0.42	0.87	1.2	1.7	6
	Lamotrigine	1.3	4.7	2.3	31	23	0.87	3.0	4.0	20	25
	Primidone	0.49	0.58	0.67	0.77	2	0.46	0.69	0.84	1.1	3
Antidepressants	Citalopram	2.3	11	7.0	77	55	1.6	10.0	8.0	49	58
	Desmethylcitalopram	7.7	21	19	87	43	4.8	13	13	88	48
	Desmethylvenlafaxine	1.7	6.3	6.9	46	43	1.7	4.0	3.8	27	49
	Fluoxetine	40	50	57	90	34	27	38	51	94	40
	Venlafaxine	1.5	4.8	4.5	35	41	1.2	3.2	2.8	39	48
Antifungal	Climbazole	14	24	33	44	9	6.1	6.1	6.1	6.1	10
	Clotrimazole	65	73	91	97	40	94	96	97	99	48
	Fluconazole	1.0	2.8	2.8	12	9	0.41	1.1	1.6	3.7	15
	Miconazole	< MQL	< MQL	< MQL	< MQL	6	83	83	83	83	9
Antihelmintic	Mebendazole	40	40	40	40	1	27	27	27	27	2
Antihistamines	Cetirizine	0.99	4.2	3.7	49	38	1.2	3.9	4.1	18	43
	Chlorpheniramine	22	45	66	95	16	9.0	24	29	87	15
	Fexofenadine	1.7	3.9	4.1	34	50	1.3	2.5	3.2	10	56

Antipruritic	Crotamiton	< MQL	< MQL	< MQL	< MQL	0	< MQL	< MQL	< MQL	< MQL	0
Antiulcers	4-Hydroxyomeprazole	1.5	7.4	6.5	72	46	1.4	3.4	3.9	16	50
	Ranitidine	2.0	2.0	2.0	2.0	1	5.3	8.5	12	15	3
Benzodiazepines	Lorazepam	< MQL	< MQL	< MQL	< MQL	1	< MQL	< MQL	< MQL	< MQL	2
	Oxazepam	22	28	33	39	5	17	29	39	49	5
	Temazepam	2.9	14	17	69	17	0.70	13	17	59	13
Betablockers	Acebutolol	12	19	25	32	7	3.9	5.7	7.5	9.3	8
	Atenolol	1.1	3.1	3.6	24	51	0.82	2.2	1.4	29	55
	Bisoprolol	1.2	3.8	3.9	30	51	1.0	2.4	3.2	14	55
	Metoprolol	2.8	5.0	7.3	9.5	5	0.78	3.5	1.2	14	7
	Propranolol	10	24	39	84	21	8.1	19	18	77	22
	Salbutamol	2.7	12	13	76	18	2.7	13	19	48	21
	Sotalol	1.5	13	15	43	11	0.47	11	2.1	67	16
Chemotherapeutic	Ifosfamide	< MQL	< MQL	< MQL	< MQL	6	< MQL	< MQL	< MQL	< MQL	4
Coccidiostat	Clopidol	1.7	1.7	1.7	1.7	4	1.1	1.1	1.1	1.1	3
Hormones	17ß-Estradiol (E2)	< MQL	< MQL	< MQL	< MQL	0	< MQL	< MQL	< MQL	< MQL	0
	17α-Ethinylestradiol (EE2)	< MQL	< MQL	< MQL	< MQL	0	< MQL	< MQL	< MQL	< MQL	0
	Estriol (E3)	2.1	2.1	2.1	2.1	1	1.2	1.2	1.2	1.2	1
	Estrone (E1)	3.5	14	13	58	18	3.4	6.1	6.3	37	14
	Norethisterone	< MQL	< MQL	< MQL	< MQL	0	< MQL	< MQL	< MQL	< MQL	0
Lipid regulators	Atorvastatin	0.049	0.17	0.20	0.63	8	0.13	0.21	0.24	0.52	7
	Bezafibrate	1.1	1.5	2.0	2.4	12	0.25	0.72	0.96	1.9	12
	Gemfibrozil	< MQL	< MQL	< MQL	< MQL	0	< MQL	< MQL	< MQL	< MQL	0
Wastewater discharge marker	Caffeine	0.51	1.4	1.8	9.7	57	0.45	2.0	1.2	39	58
	Cotinine	0.53	1.7	1.4	18	55	0.43	0.75	0.93	2.6	55

Table S10: River concentrations (25th percentile, mean, 75th percentile, maximum) upstream and downstream in µg L^{-1} and number of samples (n) with concentrations > MQL, n_{total} = 20.

Class	**EC**	**Upstream**					**Downstream**				
		25th	Mean	75th	Max	n	25th	Mean	75th	Max	n
Anaesthetics	Lidocaine	< MDL	$1.8 \cdot 10^{-4}$	< MDL	$3.2 \cdot 10^{-3}$	1	< MDL	$3.9 \cdot 10^{-4}$	< MDL	$2.6 \cdot 10^{-3}$	3
Analgesics	3-Methoxyparacetamol	< MDL	$2.2 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$	0.032	6	< MDL	0.016	$7.3 \cdot 10^{-3}$	0.13	10
	Diclofenac	< MDL	$7.5 \cdot 10^{-3}$	$5.7 \cdot 10^{-3}$	0.040	9	< MDL	$5.4 \cdot 10^{-3}$	$7.6 \cdot 10^{-3}$	0.021	9
	Hydroxyibuprofen	< MDL	$3.3 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$	0.019	2	< MDL	0.011	$2.7 \cdot 10^{-3}$	0.090	5
	Ibuprofen	< MDL	$3.8 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$	$3.5 \cdot 10^{-3}$	1	< MDL	$6.5 \cdot 10^{-3}$	$2.2 \cdot 10^{-4}$	0.13	1
	Ketoprofen	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Naproxen	< MDL	$2.0 \cdot 10^{-3}$	$1.2 \cdot 10^{-4}$	0.014	4	$1.2 \cdot 10^{-4}$	$9.4 \cdot 10^{-3}$	0.011	0.096	8
	Paracetamol	$3.3 \cdot 10^{-4}$	0.034	0.023	0.37	15	$1.2 \cdot 10^{-3}$	0.18	0.12	1.4	19
Antibiotics	3-Desmethyltrimethoprim	< MDL	$2.0 \cdot 10^{-4}$	< MDL	$2.0 \cdot 10^{-3}$	2	< MDL	$4.4 \cdot 10^{-4}$	< MDL	$5.8 \cdot 10^{-3}$	3
	α-Hydroxytrimethoprim	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Amoxicillin	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Ciprofloxacin	< MDL	0.048	< MDL	0.51	3	< MDL	0.040	< MDL	0.43	4
	Clarithromycin	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Erythromycin	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	$2.4 \cdot 10^{-4}$	2
	Ofloxacin	< MDL	< MDL	< MDL	$4.7 \cdot 10^{-3}$	1	< MDL	< MDL	< MDL	< MDL	0
	Sulfadiazine	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Sulfamethoxazole	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Sulfanilamide	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Trimethoprim	< MDL	$1.3 \cdot 10^{-4}$	< MDL	$6.8 \cdot 10^{-4}$	2	< MDL	$2.3 \cdot 10^{-4}$	< MDL	$1.8 \cdot 10^{-3}$	5
Anticoagulant	Warfarin	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
Anticonvulsants	Carbamazepine	< MDL	< MDL	< MDL	< MDL	0	< MDL	$1.0 \cdot 10^{-4}$	< MDL	$1.0 \cdot 10^{-3}$	2
	Carbamazepine-10,11-epoxide	< MDL	< MDL	< MDL	< MDL	0	< MDL	$1.6 \cdot 10^{-4}$	< MDL	$1.4 \cdot 10^{-3}$	1
	Gabapentin	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Lamotrigine	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	$1.5 \cdot 10^{-3}$	1
	Primidone	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
Antidepressants	Citalopram	< MDL	< MDL	< MDL	$5.2 \cdot 10^{-3}$	2	< MDL	< MDL	< MDL	$3.3 \cdot 10^{-3}$	1
	Desmethylcitalopram	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Desmethylvenlafaxine	< MDL	$2.8 \cdot 10^{-4}$	< MDL	$3.5 \cdot 10^{-3}$	2	< MDL	$5.5 \cdot 10^{-4}$	$1.3 \cdot 10^{-4}$	$4.1 \cdot 10^{-3}$	5
	Fluoxetine	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Venlafaxine	< MDL	< MDL	< MDL	$3.4 \cdot 10^{-3}$	2	< MDL	< MDL	< MDL	$3.7 \cdot 10^{-3}$	3
Antidiabetics	Guanylurea	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Metformin	0.032	0.45	0.61	3.7	8	0.032	0.75	0.82	4.1	14
Antifungals	Climbazole	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Clotrimazole	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0

	Fluconazole	< MDL	< MDL	< MDL	< MDL	0	< MDL	$2.6 \cdot 10^{-4}$	< MDL	$3.2 \cdot 10^{-3}$	2
	Miconazole	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
Antihelmintic	Mebendazole	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
Antihistamines	Cetirizine	< MDL	$1.2 \cdot 10^{-3}$	$9.8 \cdot 10^{-4}$	0.010	7	< MDL	$2.1 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	0.011	9
	Chlorpheniramine	< MDL	< MDL	< MDL	$2.4 \cdot 10^{-3}$	1	< MDL	< MDL	< MDL	< MDL	0
	Fexofenadine	< MDL	$2.7 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$	0.024	11	< MDL	$6.4 \cdot 10^{-3}$	$4.4 \cdot 10^{-3}$	0.057	12
Antipruritic	Crotamiton	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
Antiulcer	4-Hydroxyomeprazole	< MDL	< MDL	< MDL	< MDL	0	< MDL	$1.4 \cdot 10^{-4}$	< MDL	$2.2 \cdot 10^{-3}$	1
	Lansoprazole	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Omeprazole	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Ranitidine	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
Benzodiazepines	Lorazepam	< MDL	< MDL	< MDL	< MDL	0	< MDL	$1.5 \cdot 10^{-3}$	< MDL	0.023	1
	Oxazepam	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Temazepam	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
Betablockers	Acebutolol	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Atenolol	< MDL	< MDL	< MDL	< MDL	0	< MDL	$4.9 \cdot 10^{-4}$	< MDL	$3.3 \cdot 10^{-3}$	5
	Bisoprolol	< MDL	$1.3 \cdot 10^{-4}$	< MDL	$9.9 \cdot 10^{-4}$	4	< MDL	$8.2 \cdot 10^{-5}$	< MDL	$5.7 \cdot 10^{-4}$	5
	Metoprolol	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Propranolol	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Salbutamol	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Sotalol	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
Chemotherapeutic	Ifosfamide	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
Coccidiostat	Clopidol	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
Hormones	17ß-Estradiol (E2)	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	17α-Ethinylestradiol (EE2)	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Estriol (E3)	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Estrone (E1)	< MDL	< MDL	< MDL	$8.8 \cdot 10^{-4}$	1	< MDL	< MDL	< MDL	$5.1 \cdot 10^{-4}$	2
	Norethisterone	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
Lipid regulators	Atorvastatin	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Bezafibrate	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
	Gemfibrozil	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0
Wastewater discharge marker	Caffeine	0.028	0.049	0.061	0.17	20	0.017	0.071	0.077	0.48	18
	Cotinine	$1.8 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$	$2.7 \cdot 10^{-3}$	$8.3 \cdot 10^{-3}$	20	$1.3 \cdot 10^{-4}$	$3.1 \cdot 10^{-3}$	$3.3 \cdot 10^{-3}$	0.021	18
X-ray contrast	Amidotrizoic acid	< MDL	< MDL	< MDL	< MDL	0	< MDL	< MDL	< MDL	< MDL	0

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