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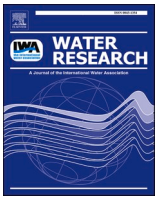

Soil self-cleaning capacity: Removal of organic compounds during sub-surface irrigation with sewage effluent

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ABSTRACT

Globally, the reuse of treated sewage effluent for irrigation purposes is increasingly encouraged as a practical solution against the mismatch between the demand for and availability of freshwater resources. The reuse of sewage effluent for sub-surface irrigation (SSI) in agriculture serves the dual purpose of supplying water to crops and diminishing emissions of contaminants of emerging concern (CoECs) into surface water. To investigate such reuse, in a real scale cropland with SSI using sewage effluent, from September 2017 to March 2019 including the extremely dry year 2018, residues were followed of 133 CoECs as related to their physicochemical properties and quantified by liquid chromatography coupled to high-resolution mass spectrometry. Of the 133 target CoECs, 89 were retrieved in the field, most non-detect CoECs have low persistency. During the growing season with sub-surface irrigation, CoECs spread to the shallow groundwater and rhizosphere. Significantly lower concentrations are found between infiltration pipes as compared to directly next to the pipes in shallow groundwater for all persistency-mobility classes. CoECs belonging to the class pm (low persistency and low mobility) or class PM (high persistency and high mobility) class show no change amongst their removal in the rhizosphere and groundwater in a dry versus normal year. CoECs belonging to the class pM (low persistency and high mobility) show high seasonal dynamics in the rhizosphere and shallow groundwater, indicating that these CoECs break down. CoECs of the class Pm (high persistency and low mobility) only significantly build up in the rhizosphere next to infiltration pipes. Climatic conditions with dry summers and precipitation surplus and drainage in winter strongly affect the fate of CoECs. During the dry summer of 2018 infiltrated effluent is hardly diluted, resulting in significantly higher concentrations for the CoECs belonging to the classes pM and Pm. After the extremely dry year of 2018, cumulative concentrations are still significantly higher, while after a normal year during winter precipitation surplus removes CoECs. For all persistency-mobility classes in the shallow groundwater between the pipes, we find significant removal efficiencies. For the rhizosphere between the pipes, we find the same except for Pm. Next to the pipes however we find no significant removal for all classes in both the rhizosphere and shallow groundwater and even significant accumulation for Pm. For this group of persistent moderately hydrophobic CoECs risk characterization ratio's were calculated for the period of time with the highest normalized concentration. None of the single-chemical RCRs are above one and the ΣRCR is also far below one, implying sufficiently safe ambient exposures. Overall the deeper groundwater (7.0–11.8 m below soil surface) has the lowest response to the sub-surface irrigation for all persistency-mobility. When adopting a SSI STP effluent reuse system care must be taken to monitor the CoECs that are (moderately) hydrophobic as these can build up in the SSI system. For the deeper groundwater and for the discharge to the surface water, we find significant removal for the pM and the PM class but not for other classes. In conclusion, relatively high removal efficiencies are shown benefiting the surface waters that would otherwise receive the STP effluent directly.

Abbreviations: CoEC, contaminants of emerging concern; SE, standard error; SSI, sub-surface irrigation; STP, sewage treatment plant; TPs, transformation products; RCRs, risk characterization ratio's; SSD, species sensitivity distribution.

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1. Introduction

Globally, agricultural irrigation is currently accounting for 69% of freshwater withdrawal (Food and Agriculture Organization of the United Nations, 2021). While significant attention has been paid to the more arid regions of the world (Maceda-Veiga et al., 2018), temperate climates also suffer from seasonal droughts (Hänsel et al., 2019; Narain-Ford et al., 2021; Rey et al., 2017). The pressure on the availability of freshwater resources will continue to increase due to global change, which will enhance prolonged dry periods and thus freshwater demands from several sectors (Bijl et al., 2018; De Vos et al., 2021). Hence, it is crucial that options for the exploitation of alternative freshwater resources such as sewage treatment plant (STP) effluent are explored. Intentional reuse of STP-effluent can compensate for water shortages caused by seasonality or by irregular availability of other water sources for agricultural irrigation throughout the year (Hristov et al., 2021). Such intentional reuse offers better control and management possibilities than currently practiced de facto reuse (Drewes et al., 2017). Additionally, when using sub-surface irrigation (SSI) as a method of supply (De Wit et al., 2022) the quality of STP effluent may improve due to the soil passage and related biodegradation processes, also benefiting the receiving surface waters (Narain-Ford et al., 2020). Nonetheless, the fate of the contaminants of emerging concern (CoECs) present in the effluent - such as pharmaceuticals, biocides, personal care products, and their transformation products - in SSI systems is not yet fully understood. Likewise, direct evidence on the effects of re-using treated effluent for SSI under real farming conditions on the fate of a broad selection of CoECs is currently lacking (Narain-Ford et al., 2020; Revitt et al., 2021).

Of particular concern is the persistent fraction of these contaminants (Reemtsma et al., 2016). Most persistent CoECs capable of bioaccumulation are nonpolar and inherently poorly water-soluble. Therefore, they are readily removed in STPs through sorption processes and preferably sorb to sewage sludge. The remaining persistent hydrophobic fraction that reaches croplands through SSI might lead to soil concentrations building up over time (Christou et al., 2019). Persistent and mobile organic compounds, also known as PMOCs, are a concern for water quality because they are not well removed from water by sorption processes due to their high polarity and thus water solubility (Liu et al., 2021; Reemtsma et al., 2016). These persistent compounds may then result in the exposure of crops and deep groundwater and pose related risks to human health and the environment. Therefore, a better understanding is needed of the environmental fate processes, i.e. degradation, sorption, and horizontal and vertical leaching, of CoECs in these sub-surface irrigation systems and the consequences for exposure to humans and ecosystems.

Only limited quantitative data is available regarding the behavior and fate of many of CoECs in full-scale setups where real STP effluent was applied to croplands, representing actual farming practices (Ben Mordechay et al., 2021; Revitt et al., 2021), as compared to pilot-or lab-scale studies (Christou et al., 2017a; Kesari et al., 2021). These full-scale studies solely focus on aboveground irrigation techniques such as sprinkler, spray, and drip-irrigation. During SSI, water is introduced into shallow groundwater and then capillary rise provides irrigation to the crop. Hence, while aboveground irrigation captures primarily aerobic processes, SSI includes both aerobic and anaerobic processes (Narain-Ford et al., 2020).

Generally, the biodegradation of CoECs in soil is faster and more complete under aerobic conditions (topsoil) as compared to anaerobic conditions (deeper layers of the vadose zone) (Christou et al., 2017a). Aerobic biodegradation may result in the fast initial enzymatic attack and the decomposition of alkyl side-chains and other easily degradable factional groups (e.g. carboxyl groups), whereas anaerobic biodegradation may include various enzymatic processes that biodegrade more complex and stable functional groups and structural moieties, such as aromatic groups, naphthalene rings, and sulfonamides (Greskowiak et al., 2017; Luo et al., 2019). So far, most studies investigating the fate of CoECs in agricultural soils have been under aerobic conditions, while information about their persistence in the absence of oxygen is still scarce, especially in the context of relevant CoECs concentrations (Christou et al., 2017a). The interplay between aerobic and anaerobic processes has been studied before in, e.g. in riverbank filtration (Albergamo et al., 2019; Hamann et al., 2016) and constructed wetlands (He et al., 2021; Hübner et al., 2022). However, these systems were constructed primarily for purification purposes, while SSI primarily serves as an irrigation system with relatively short residence times with regard to crop uptake and longer residence times for groundwater seepage (Narain-Ford et al., 2020).

This study aims to identify and quantify CoECs in a real-scale cropland with direct reuse of STP effluent in a sub-surface irrigation system. We study the fate of CoECs in relation to their physicochemical properties (half-life in soil range of 0.4–1194 days and log *D*ow range of −2.77 to 5.67). Pore-water and groundwater samples were collected at various depths (−0.2 to −11.8 m) and we analyzed 133 CoECs relevant for effluents such as herbicides, industrial chemicals, pharmaceuticals, personal care products, and their transformation products. Such an extensive analysis of a real scale experimental site under real farming conditions is novel and ensures that the environmental fate processes such as (an)aerobic degradation, sorption, drainage, and leaching occur under realistic conditions. This study captured September 2017–March 2019 including the extremely dry year of 2018 to elucidate the maximum influence of the STP effluent reuse on croplands.

2. Material and methods

2.1. Study area

Located in the east of the Netherlands, in Haaksbergen, lies the only Dutch cropland (52°10′42.9"N 6°42′43.8"E) which is intentionally and directly subsurfacely irrigated with municipal effluent during the growing season (Fig. 1). Infiltration of the effluent during the growing season occurs via a series of 6 m parallel pipes at a depth of ± −1.20 m. At the cropland of 58,500 m^2, maize intended for livestock feed is grown. This cropland has SSI with STP effluent since 2015, as part of the initiative on alternative freshwater supply for agriculture in the Dutch higher sandy soils region taken by the water management authority Vechtstromen. Since the start of SSI in 2015, no other direct irrigation has taken place at this site. As reference location, the cropland without SSI on the other side of the surface water with the same farming conditions was selected. An illustration of the monitoring wells installed at different depths in both the saturated and unsaturated zone is presented in SI-1 of the supplementary information.

2.2. Sample collection

Five sampling episodes from September 2017 to April 2019 were carried out. The period of sampling includes the extremely dry year of 2018, water balance components for the full-time period are displayed in Table 1. The irrigated STP effluent volume in the year 2017 was 562.2 mm, whereas 502.8 mm was irrigated in 2018. The drainage volumes for 2017 were not measured, in the year 2018 66.6 mm of water was drained.

Wells that showed elevated chloride/bromide ratio during SSI from the period 2015–2017 (Bartholomeus et al., 2017) were chosen for sampling (Fig. 1). Pore-water and groundwater samples were collected at several depths, ranging from 0.20 m to 11.8 m below the soil surface (Table 2).

To sample pore-water pre-installed rhizon samplers were used, while the groundwater was sampled using pre-installed mini filters. Apart from the sampling episode of May 2018, 24H-effluent was sampled from the STP Haaksbergen. In total, 24 pore-water samples (volume sampled = 250 mL), 104 groundwater samples (volume sampled = two times 250 mL), and five 24H-effluent samples (volume sampled = 500 mL) were

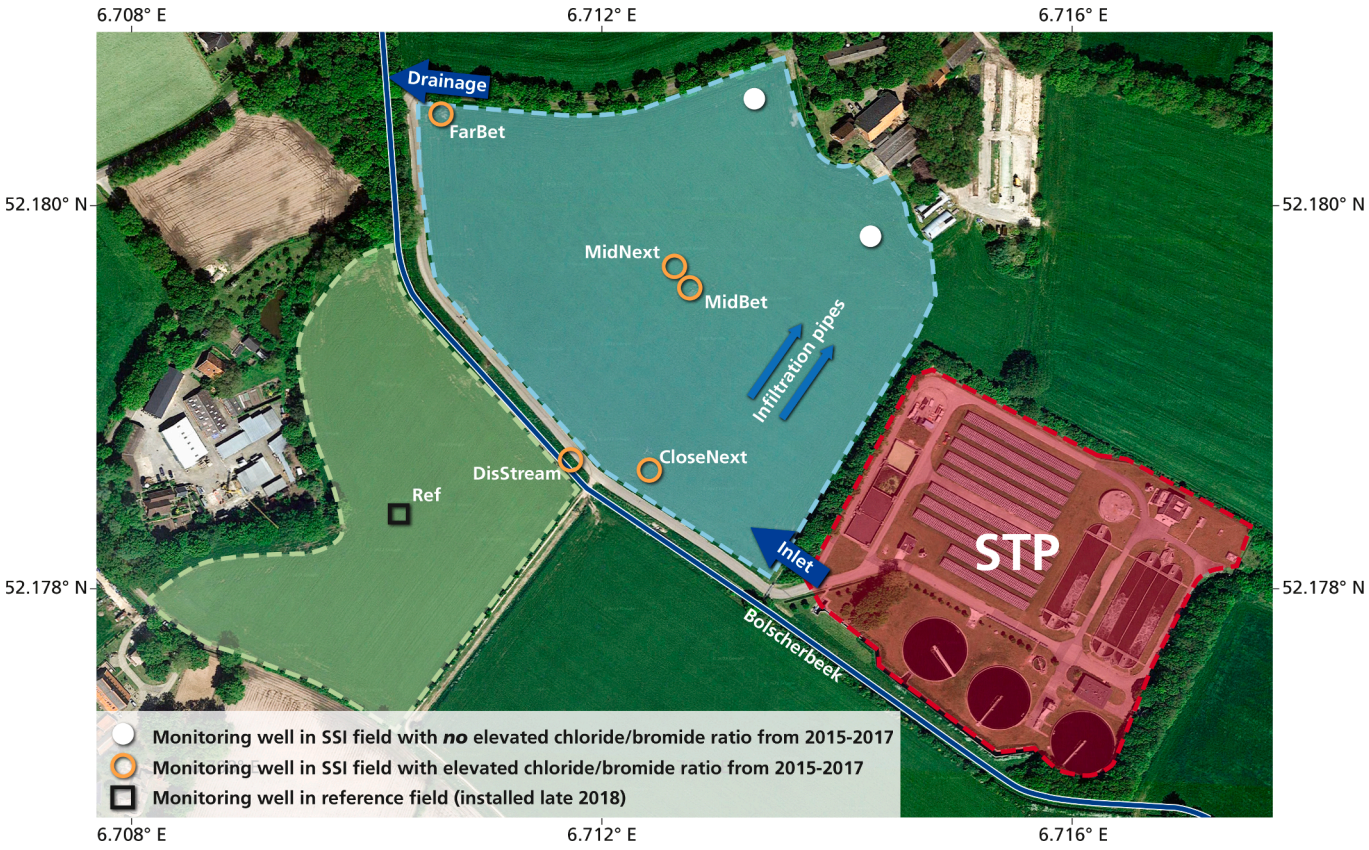

Fig. 1. Study area and locations of the sampling sites.

Table 1
Water balance components (mm) of the cropland in Haaksbergen directly irrigated with STP effluent.

Year		Precipitation	Reference evapotranspiration (ETref) (KNMI., 2022)[1]	Surplus/ Deficit	Sampling episodes
2017		853.5	575.2	278.3	
	1jan - 31 mar	196.1	64.8	131.3	
	1april-30sep	411.1	467.3	-56.2	
	1oct-31dec	246.3	43.1	203.2	26-Sept 2017
2018		610.2	689.3	-79.1	
	1jan-31mar	194.6	59	135.6	14-May 2018
	1 apr-30sep	267.3	574.6	-307.3	09-Aug-2018
	1oct-31dec	148.3	55.7	92.6	23-Oct-2018
2019		774.4	640.2	134.2	
	1jan-31mar	236.4	61.7	174.7	30-April 2019

[1] determined by the Royal Netherlands Meteorological Institute (KNMI) according to Makkink (1957) with the weather stations Twente (290) and Hupsel (283).

collected in 250 mL polypropylene pre-cleaned bottles from sampling faucets built on each well and immediately transported to the laboratory where they were kept at −20 °C until chemical analysis. Further details about sampling are provided in Bartholomeus et al., (2017).

2.3. CoECs selection criteria

Scientific literature data were reviewed to select 133 model chemical organic CoECs (123 parent compounds and 10 transformation products) based on their wide detection in STPs (Mourid et al., 2021; Münze et al., 2017; Serna-Galvis et al., 2019), surface water (Golovko et al., 2021; Ruff et al., 2015), groundwater (K'oreje et al., 2022; McCance et al., 2020), and/or croplands (Ben Mordechay et al., 2021; Christou et al., 2017c). All selected compounds are amenable for analysis by liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS). The selection covers a broad range of physicochemical properties and represents a variety of chemical uses. The pH-dependent octanol-water distribution coefficient expressed as log *D*ow (pH = 7.4, which matches the effluent and field samples) is used as a measure of mobility, to account for ionizable CoECs and ranges from −2.77 (acesulfame) to 5.69 (flufenoxuron). The pH was measured on-site with a portable WTW meter. The half-life (DT_{50}) of CoECs is used to embody persistency. The persistency diverges from 0.4 days (Propanil) to 1194 days (2,6-Dichlorobenzamide/ BAM). For parametrization of log *D* and half-life data, we followed preferences as explained in Table 3. Available data from the highest priority were used.

The CoECs are assigned to four persistency-mobility classes, i.e. high persistency and high mobility (PM), high persistency and low mobility (Pm), low persistency and high mobility (pM), and low persistency and low mobility (pm), as based on frequencies in the set of CoECs of half-lives and log *D* of all selected compounds (Fig. 2). The empirical distribution function plots are presented in SI-2.

Our 50th percentile cut-off value of 57-day half-life in soil is comparable with Annex XIII of REACH(ECHA, 2017), which considers a chemical to be persistent in soil or water-sediment if its DT_{50} is more than 120 days and very persistent if it is more than 180 days. Note that this half-life ideally refers to 12°C, considered as the mean temperature in European surface waters. Half-lives at this temperature were not available, data and models for 20–25 °C were used and not corrected further. There is no formal mobility criterion in REACH, the 50th percentile in our set of chemicals is a log *D* of 1.49.

Table 2
Depths available at the selected locations.

Compartment	Measuring point	Specifics	Depth[2](soil surface-m)	Volume of sample (mL) 26-Sept 2017	14-May 2018	09-Aug 2018	23-Oct 2018	30-April 2019	Nr of samples
24-H STP effluent	24-H effl	Standardized program at STP		250	*SSI inactive*	250	250	*SSI inactive*	4
SSI field-Rhizosphere	CloseNext	Close to STP, next to pipe	0.2	0[3]	0[3]	25	0[3]	0[3]	24
			0.6	50	50	140	100	25	
			1	50	100	115	125	100	
	MidNext	Middle of field, next to pipe	0.2	0[3]	0[3]	0[3]	0[3]	0[3]	
			0.6	50	0[3]	0[3]	0[3]	0[3]	
			1	75	100	0[3]	200	150	
	MidBet	Middle of field, in between pipes	0.2	0[3]	0[3]	0[3]	0[3]	0[3]	
			0.6	100	100	0[3]	75	100	
			1	75	50	0[3]	75	75	
SSI field-Shallow groundwater	CloseNext	Close to STP, next to pipe	1.25	150	200	250	100	250	55
			1.80	150	200	250	100	100	
			2.30	200	250	0[3]	125	250	
	MidNext	Middle of field, next to pipe	1.29	250	250	0[3]	200	250	
			1.84	200	200	150	150	250	
			2.34	200	200	250	150	250	
	MidBet	Middle of field, in between pipes	1.30	200	250	250	125	250	
			1.85	200	225	250	200	250	
			2.35	125	250	250	125	250	
	FarBet	Farthest from STP, in between pipes	1.04	*N/A*[1]	250	150	150	250	
			1.59	*N/A*[1]	200	150	125	250	
			2.09	*N/A*[1]	250	200	150	250	
SSI field-Deeper groundwater	MidBet	Middle of field, in between pipes	5	0[3]	0[3]	0[3]	0[3]	0[3]	21
			7.5	150	200	250	200	250	
			11.8	175	200	225	200	250	
	FarBet	Farthest from STP, in between pipes	5	*N/A*[1]	200	125	150	250	
			7	*N/A*[1]	150	0[3]	150	250	
			9	*N/A*[1]	225	225	100	250	
SSI discharge to stream	DisStream	Outside the SSI field, next to the surface water	1.5	200	250	250	125	250	21
			2.5	0[3]	0[3]	0[3]	50	100	
			5	200	250	0[3]	160	250	
			7.5	200	250	200	150	250	
			10	100	200	250	150	250	
Reference field - Shallow groundwater	Ref		grab sample from phreatic groundwater	*N/A*[1]	*N/A*[1]	*N/A*[1]	*N/A*[1]	250	1

[1] N/A stands for sample not taken.
[2] Soil surface (m + mean sea level): 20.322 - 20.995.
[3] A sampling value of 0 means that there was no water available.

Table 3
Preferred data sources for persistency and mobility parametrization.

Priority	Source	
1st	Predicted ACD labs, pH =7.4 https://www.chemspider.com/ (Royal Society of Chemistry, 2022)	
2nd	ECHA Reach https://echa.europa.eu/nl/home (European Chemicals Agency, 2022)	1.In soil (20–25 °C) 2.In water and sediment simulation 3.In water (screening test)
3rd	PPDB database http://sitem.herts.ac.uk/aeru/ppdb/en/search.htm (Agriculture & Environment Research Unit (AERU) at the University of Hertfordshire., 2022)	1.In soil (lab at 20 °C) 2.Field data 3.Typical data
4th	EPI Suite Level III Fugacity Model Half-life in soil https://www.chemspider.com/ (Royal Society of Chemistry, 2022)	

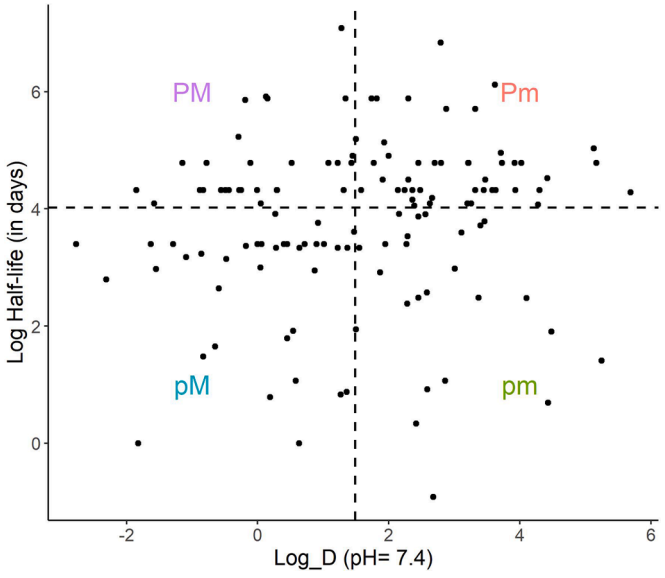

Fig. 2. The four classes that 133 CoECs (black points) are assigned to, based on their half-life in soil (persistency) and log *D* (mobility). 50th percentile cut-off values are indicated with dashed black lines.

2.4. Organic chemical analysis

2.4.1. Standards and reagents

All chemicals used were of analytical grade. More details are provided in section SI-3.

2.4.2. Sample preparation

A sample preparation method validated previously (Albergamo

et al., 2018) was adapted to our chemical analysis. In short, pore-water and groundwater samples (V=50 mL, in triplo) were spiked to 100 ng/L of isotope-labeled standards and concentrated by solid-phase extraction (SPE) with OasisHLB (150 mg) from Waters (Etten-Leur, The Netherlands). The cartridges were conditioned with 5 mL of methanol and equilibrated with 5 mL of ultrapure water. The samples were loaded onto the cartridges, and subsequently washed with 2.5 mL of ultrapure water and dried under vacuum for 20 min. The cartridges were eluted 4 times with 2.5 mL of methanol. The 10 mL extracts were filtered with 0.22mm PPfilters (Nantong FilterBio Membrane Co., Ltd, Nantong, China), and evaporated to 0.5 mL. Then, extracts were transferred to 1.5 mL PP LC vials and stored in the dark at −20 °C. Prior to analysis the extracts were vortexed and diluted five times in ultrapure water to be more compatible with the aqueous mobile phase used for chromatography separation. The procedure resulted in an enrichment factor of 20 and a concentration of isotope-labeled standards equal to 2 μg/L to match that of the standards used for the calibration series.

2.4.3. LC-HRMS analysis

The UHPLC-q-ToF-MS/MS analysis was performed on a Nexera UHPLC system (Shimadzu, Den Bosch, the Netherlands) coupled to a maXis 4G high-resolution q-TOF-MS/MS upgraded with a HD collision cell and equipped with an ESI source (Bruker Daltonics, Wormer, the Netherlands). The instrumental methods were adapted from Albergamo et al. (2018). In brief, before starting an analysis batch the MS detector was calibrated with a 2 mM sodium acetate solution in H_2O and MeOH (1:1, v:v) in both positive and negative ESI mode. MS detection separation of a 20 μL sample in both positive and negative ESI mode was achieved with a core-shell Kinetex biphenyl column (100×2.1 mm, 2.6 μm particle size, and 100 Å pore size, Phenomenex, Utrecht, the Netherlands). The mobile phase consisted of two solutions, i.e. a) ultrapure water with acetic acid (0.05%) and b) methanol. With a flow rate of 0.3 mL/min, the LC-gradient was 0% methanol from 0 to 2 min, increased linearly to 100% at 17 min, and kept equal until 25 min. The system was allowed to re-equilibrate for 7 min before the next injection. Prior to each injection, a 50 μM sodium acetate solution in H_2O:MeOH (1:1, v:v) was introduced automatically for m/z recalibration of the system during data processing. The column oven was kept at 40 °C. MS and data-independent MS/MS data were acquired with positive and negative ESI in separate runs with a resolving power typically of 30, 000–60,000 FWHM.

2.4.4. Target screening and quantification method

Blind target screening of the CoECs was carried out with TASQ version 2021.0316 (Bruker Daltonics, Wormer, the Netherlands). This analysis was based on the mass accuracy of full-scan HRMS spectra and MS/MS qualifiers, acquired in data-independent MS/MS mode (DIA), the retention time, and isotopic fit. In sections SI-4 and SI-5, the screening parameters for the target analytes are provided, as well as recoveries and limit of detection and quantification. Recoveries vary between 75% and 125% with residual standard deviation lower than 20% and 10% for intraday and interday repeatability was considered satisfactory. Limits of detection and limits of quantification, recoveries, and precision were investigated in 24H-effluent and groundwater from our pilot site ($n = 6$) at concentrations matching the 5 lowest points of the calibration series. Calibration curves for quantification were calculated by analyzing ultrapure water spiked with 25 μg/L of CoECs and serially diluted to obtain 7 concentration levels, with 390.63 ng/L being the lowest concentration of the calibration series. The SPE method was suitable to further lower the detection limits by a factor of 20.

2.5. Statistical analysis

Statistical analysis for all measurements was performed with the R statistical environment (R Core Team, 2021) version 4.1.2 (1 November 2021). All data used are based on means ± standard error (SE) of three replicates, except when stated differently, and were first tested for normality by Shapiro-Wilk tests. If the significance value of the Shapiro-Wilk test was below 0.05, the data was considered significantly deviated from a normal distribution. As outlined by Helsel et al. (2020) when dealing with non-normal data nonparametric tests can be many times more powerful than parametric tests. A non-parametric Kruskal-Wallis (KW) test was used to compare the transport of CoECs through time, space and depth.

To account for dilution by precipitation, groundwater and pore water CoECs concentrations were normalized using the dilution factor of the artificial sweetener saccharin, which is used as a tracer for effluent (Richards et al., 2017; Van Stempvoort et al., 2020) according to:

$$DF = \left(\frac{\text{sach\_sample}}{\text{sach\_effluent}}\right)$$

Where DF is the dilution factor, sach_sample is the saccharin concentration of the sample, and sach_effluent is the saccharin concentration in the corresponding 24H-effluent. At our reference location saccharin was not detected, thus it was excluded when normalizing. For dates where the SSI was still inactive (May 2018 and April 2019) we took the corresponding effluent before the stop of the growing season (Table 4), and further tested the robustness of our approach (see SI-6). The normalized CoEC concentration is then the measured CoEC concentration divided by DF. Normalized concentrations were only used to calculate CoEC removal efficiencies expressed as related to the effluent, for each chemical and each sampling location, time, and depth. These removal efficiencies were then averaged per persistency-mobility class, for the rhizosphere next to and in between infiltration pipes, for shallow groundwater next to and in between infiltration pipes, and for deep groundwater.

The one-sample Wilcoxon signed-rank test was used to determine whether the removal efficiencies over the full sampling period differentiated from 0. Comparisons between the removal efficiencies for the four persistency-mobility classes were conducted with a non-parametric Kruskal-Wallis (KW) test. The Dunn test resulted in an adjusted p-value based on the Benjamin-Hochberg method.

2.6. Risk characterization

Risk characterizations were made by coupling normalized concentrations with hazard information from Posthuma et al. (2019). As policy-adopted predicted no-effect concentrations (PNECs) are lacking for many chemicals, we used chronic NOECs and acute EC50s distributions derived from ecotoxicity data (Posthuma et al., 2019). Risk characterization ratio's (RCRs) were obtained by dividing the normalized concentrations by the species sensitivity distributions (SSD) midpoint concentration. The most acknowledged 'default' mixture toxicity approach to yield ΣRCRs assumes that concentration addition is applicable for all components in the mixture (Martin et al., 2021). In this approach, environmental 'non-toxic' or acceptable risk conditions are defined by RCR < 1 in the hypothetical case of single substance environments, and ΣRCR < 1 in case of co-exposures. RCR ≥ 1 and ΣRCR ≥ 1 define insufficient protection, also referred to as unacceptable environmental risk in chemical safety assessment.

Table 4
Saccharin concentration [ng/L] in 24H-Effluent for each sampling episode.

Year	Date sampling episode	Saccharin concentration [ng/L] in 24H-effluent
2017	26-Sept 2017	105.0
2018	14-May-2018	*SSI inactive*
	08-Aug 2018	133.3
	23-Oct 2018	61.7
2019	30-April 2019	*SSI inactive*

3. Results and discussion

3.1. Occurrence of CoECs

When STP effluent enters the shallow groundwater via SSI, the CoECs present in the effluent can migrate from shallow groundwater to the rhizosphere and/or to deeper groundwater (Narain-Ford et al., 2020). From the 133 CoECs in our target list, 89 are retrieved in our samples. 39 out of the 44 CoECs not detected belong to a class of low persistency and/or mobility (16 pm, 10 pM, and 13 Pm), the remaining 5 non-detected CoECs are three transformation products (TPs) and two biocides belonging to the PM class. 57 out of the 89 detected CoECs can be directly traced back to the STP effluent (Fig. 3). The shallow groundwater (1–2.35 m below soil surface) of the SSI system, where the STP effluent enters, shows the highest number of CoECs (83/89). The deeper groundwater (5–11.8 m below surface) has the lowest number of CoECs. CoECs of the class pm (low persistency and low mobility) are underrepresented in all compartments. From the 89 CoECs detected, seven -out of 10 present in the target list- are transformation products (TPs) and are present variably across compartments (SI-7 of the supplementary information). In the reference field (shallow groundwater, one sampling episode), only two CoECs from our target list are retrieved.

Fig. 4 shows the intersections of the compartments, specified per persistency-mobility class, over the full sampling period. Columns 1–7 (57/89) display the intersections that STP effluent has with the other five compartments. Only 2/57 CoECs can be found in all six compartments of this study, while 24/57 CoECs can be found in all compartments except for the reference field, and two CoECs are exclusive to the STP effluent (column 7). Consequently, 32/89 (sum of columns 8–17) detected CoECs not found in the compartments "24-H STP effluent" nor in "Reference field" can be found in other compartments inside of the SSI system and also in the "SSI discharge to stream" compartment. Of these 32 CoECs only one is a transformation product. Only two of these parent compounds are of the class pm, while the other 29 parent compounds are either highly persistent, highly mobile, or both. When looking at the uses of the CoECs not detected in the STP effluent compartment, 11 are below the limit of quantification (LoQ) and the remaining 21 CoECs can be classified as biocide (52%), industrial chemical (10%) and as pharmaceuticals/personal care product (38%). It is therefore likely that most of these CoECs not detected in the STP effluent do occur in the effluent but are below the limit of detection also because of effluent matrix effects. It is well known that STPs are not optimized for the removal of highly persistent and/or mobile CoECs, and STPs are major contributors to CoECs in the environment (Blum et al., 2018; Golovko et al., 2021; Serna-Galvis et al., 2019). Hence, for further analysis of the transport of CoECs and their subsequent removal we assumed that all 89 CoECs (82 parent CoECs and 7 TPs) originate from STP effluent.

3.2. Transport of CoECs in time, space, and depth

For the detected CoECs, overall detection frequencies ranged from 1% to 95% (Fig. 5A). 4,6 dinitro-o-cresol, carbamazepine, PFBA, gemfibrozil, PFOA, 1H-benzotriazole, bentazon, saccharin, MCPP-p, diclofenac, acesulfame, and pentachlorophenol were detected at over 50% across all sampling points over the full sampling period. For all CoECs their respective quantities are displayed in Fig. 5B, with mean maximal concentrations of 1024 ng/L. In SI-8 the detection frequency and non-normalized concentration are presented separately for the rhizosphere, shallow groundwater, deeper groundwater, and SSI discharge to the stream. Aside from the pm group having fewer CoECs retrieved, no clear differences in mean concentrations are observed between individual CoECs among the four classes. Cumulative CoECs concentrations of the four persistency and mobility classes are visualized in Fig. 6 for five time periods from sept-2017 to April-2019 in the SSI system; see https://doi.org/10.17632/4x77nynfnx.1 for further data specified for the rhizosphere, shallow groundwater, and deep groundwater.

3.2.1. Seasonal dynamics

During the dry summer of 2018 (Brakkee et al., 2022; Wolff and van Vliet, 2021; Zscheischler and Fischer, 2020) infiltrated effluent is hardly diluted by precipitation, resulting in significantly higher values for the CoECs belonging to the classes pM and Pm for Aug and Oct 2018 (Table 5 and Fig. 6). After the extremely dry year of 2018 and the subsequent winter, the cumulative concentrations in April-2019 are still significantly higher as compared to May-2018 (Fig. 6). This increase in concentrations is not seen after a normal year of infiltration; during the winter 2017–2018 when SSI is inactive, precipitation surplus and drainage remove CoECs from the SSI system. However, it should be noted that even after a normal year CoECs belonging to the Pm class are present in higher concentrations in the rhizosphere of the SSI field compared to the effluent taken during that sampling episode (Sept 2017, Fig. 6). Mordechay et al. (2022) examined the fate of CoECs in the irrigation water-soil-plant continuum and also found that the soil acts as a reservoir/sink for persistent (moderately) hydrophobic CoECs. These CoECs can be released into the soil solution between irrigations and during the rainy season allowing their uptake into irrigated as well as rain-fed crops. Moreover, this implies that mitigation strategies for soils irrigated with reclaimed wastewater should also consider soil treatment.

For CoECs from the PM and pm classes, no significant differences were observed over the study period, except shortly for the deep groundwater for PM. When distinguishing between sampling locations CloseNext also shows significant differences in time for PM. Fig. 6 shows

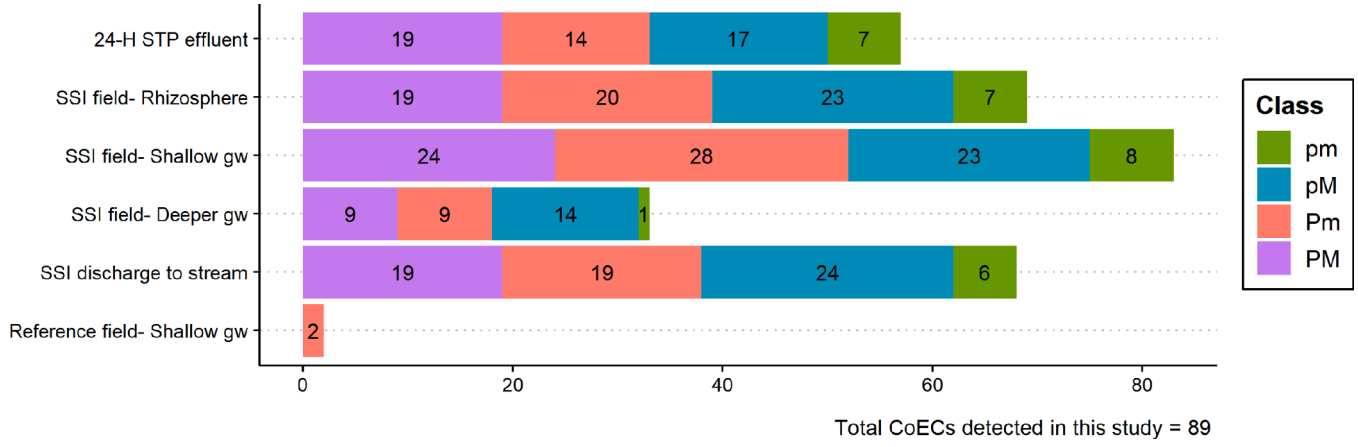

Fig. 3. Numbers of CoECs specified per persistency-mobility class (pM = low persistency and high mobility), detected in the compartments over the full sampling period.

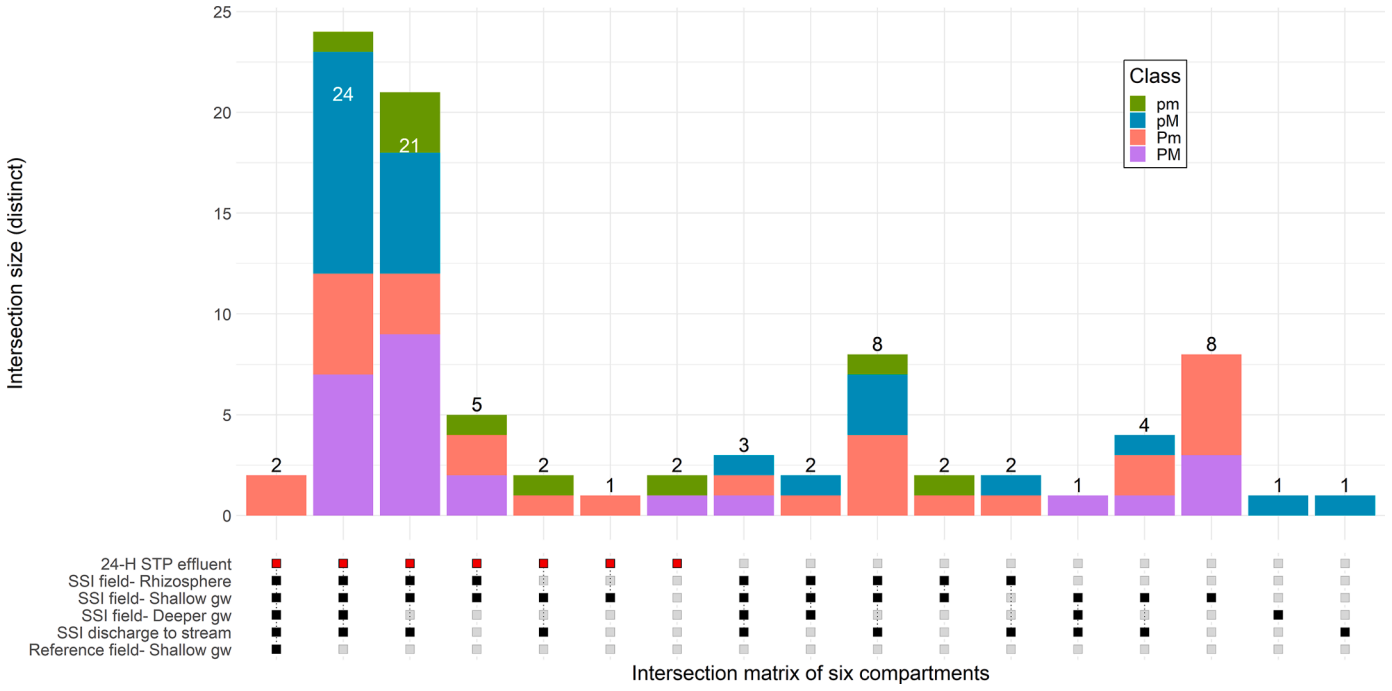

Fig. 4. Intersections of the compartments specified per persistency-mobility class (pM = low persistency and high mobility), over the full sampling period.

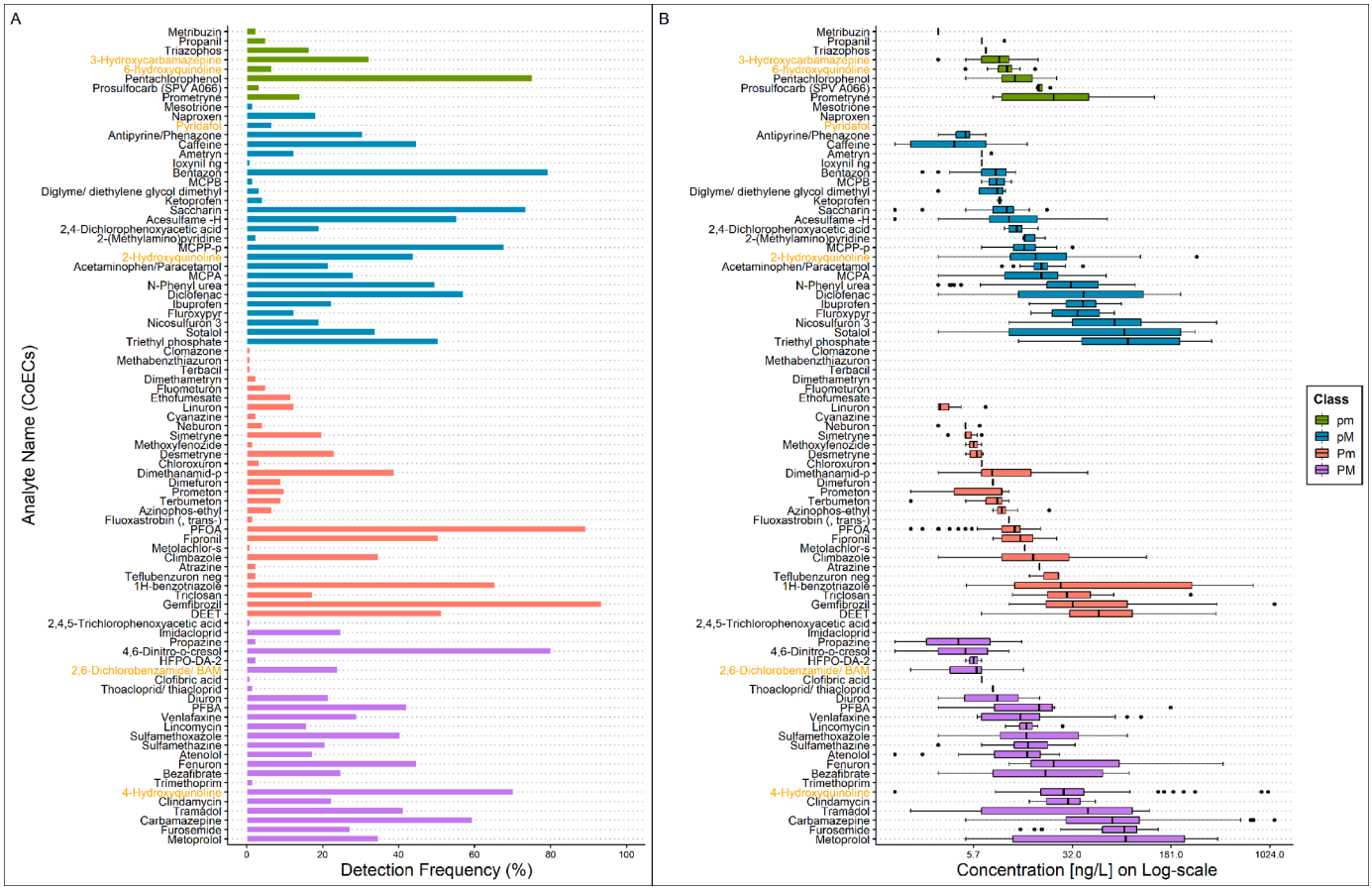

Fig. 5. (A) Detection frequencies (nr. of samples = 121) and (B) measured (non-normalized) concentrations [ng/L] of individual CoECs sorted by the median in the SSI system and SSI discharge to surface water. The six-orange colored CoECs names are transformation products. The CoECs are grouped based on their persistency-mobility class (pM = low persistency and high mobility).

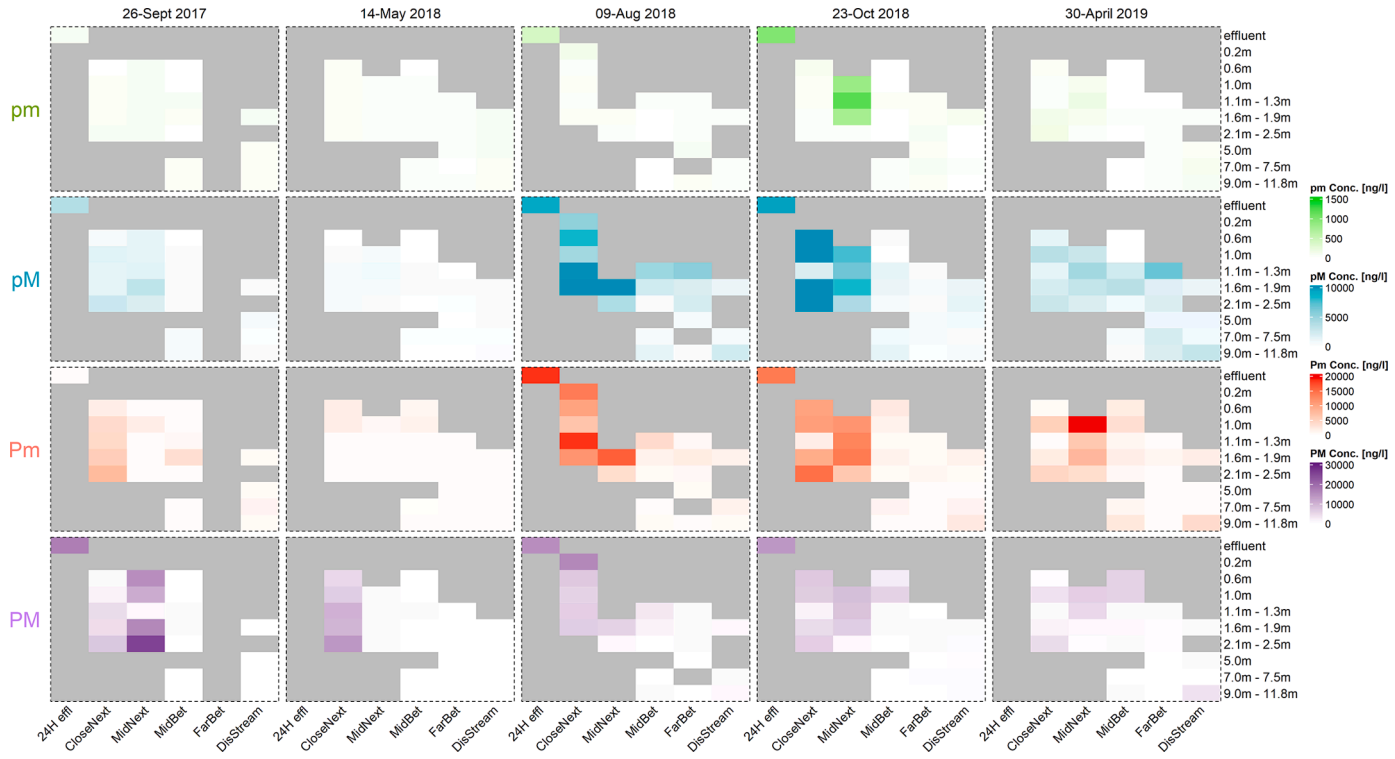

Fig. 6. Heatmap of the cumulative non-normalized concentrations for the 82 parent CoECs in **time** (26-Sept 2017 until the 30-April 2019), **space** (24Heffl → CloseNext → MidNext → MidBet → FarBet → DisStream), and **depth** (*rhizosphere*: 0.2–1.0m below the soil surface, *shallow groundwater* from 1.1m to 2.5m below the soil surface and *deep groundwater*: 7.0–11.8m below soil surface), specified per persistency mobility class (pM = low persistency and high mobility). The 24H effluent is infiltrated at a depth of ± 1.20m below soil surface. NA values are indicated with grey, meaning no sample was available (e.g. due to too dry soil conditions) during that sampling episode.

that apart from CloseNext, PM CoECs seem to follow the flow of the water (Reemtsma et al., 2016), i.e. independent of seasonal dynamics their decrease in concentration from their point of entry in SSI systems (shallow groundwater ± 1.20m below soil surface) seems to be mainly due to dilution. The CoECs belonging to the pm class break down easily, especially under warmer temperatures (Kahl et al., 2017).

Accompanied by the removal of the CoECs during the drought of 2018 is the increase in the formation of transformation products (SI-7 of the supplementary information), which may be due to higher aerobic transformation (Serna-Galvis et al., 2019) in the subsoil as a consequence of lower groundwater levels, the relatively high temperatures during summer 2018 (Philip et al., 2020) and/or due to the more concentrated effluent which according to Poursat et al. (2019) can lead to higher biodegradation rates. Indeed, also the effluent itself was more concentrated during and after the drought period (https://doi.org/10.17632/4x77nynfnx.1). The highest non-normalized concentration for the transformation products (TPs) was measured for 4-Hydroxyquinoline in the shallow groundwater (21 µg/L) and in the deeper groundwater (18 µg/L). The TPs formed during SSI can sometimes represent a higher toxicity concern than parent substances. In addition, they are often more mobile than the parent compounds (Alygizakis et al., 2020; Christou et al., 2017b). The potential uptake of TPs present in croplands as a result of biotic and abiotic transformation by plants warrants further investigation.

3.2.2. Location and depth dependence

Significantly lower non-normalized concentrations between infiltration pipes (MidBet and FarBet) versus directly next to an infiltration pipe (CloseNext and MidNext) (Table 6) are visible in the shallow groundwater for all persistency-mobility classes and in the rhizosphere for all classes except for Pm. Both the deeper groundwater and the discharge to the surface water have significantly lower concentrations as compared to the effluent being irrigated in the shallow groundwater (sampling points next to infiltration pipe) for all classes. Indeed, the SSI uses the cleaning capacity of the soil and thus leads to a lower emission to surface water. However in the rhizosphere, 0.2 to 1 m below soil surface (above the infiltration pipes), concentrations do not significantly differ from concentrations in the shallow groundwater measured next to the pipe. This confirms that the division between the rhizosphere and shallow groundwater is not so sharp and that in certain periods the shallow groundwater may reach 1 m below soil surface. CoECs with low persistency (pm and pM) do show much lower concentrations in the rhizosphere between the pipes. The pM class shows a higher concentration in the deeper groundwater as compared to the other classes. The CoECs with the highest concentration in this class (pM) are nicosulfuron (1448 ng/L), ibuprofen (475 ng/L), N-phenyl urea (437 ng/L), acesulfame (363 ng/L) and triethyl phosphate (346 ng/L). According to Kahl et al. (2017), CoECs with low persistency (<two months) under aerobic conditions can persist under anoxic conditions.

Overall for the 82 parent CoECs retrieved, the deeper groundwater has the lowest response to the sub-surface irrigation (Table 6). In this field, under the SSI system is a loamy clay layer hindering the transport of CoECs (Gil et al., 2021). Additionally, Bartholomeus et al., (2017b) shows that the lateral groundwater flow towards the stream is large, compared to downward seepage.

3.3. Removal efficiency

The overall removal efficiency by the soil system as related to the effluent was calculated with normalized concentrations over our two-year study period including both an extremely dry year and a normal year (Fig. 7).

For all persistency-mobility classes in shallow groundwater between the pipes, we find significantly positive removal efficiencies, with an

Table 5
Mean±SE of the cumulative CoEC concentration [ng/L] per time and depth, specified for sampling points located in between versus directly next to an infiltration pipe. Time points found to differ significantly ($p<0.05$ based on the Benjamin- Hochberg method of the Dunn test) from other time points for the same sampling points and persistency-mobility class are indicated with different letters.

		Next versus in between infiltration pipes	KW-χ^2 p-value	26-Sept 2017	14-May 2018	09-Aug 2018	23-Oct 2018	30-April 2019
pm	Rhizosphere	Next [1]	ns*	43 ± 14	42 ± 5.9	67 ± 25	319 ± 256	58 ± 21
	(0.2–1.0m)	Between [2]	ns*	0.0 ± 0.0	14 ± 14	N/A	0.0 ± 0.0	0.0 ± 0.0
	Shallow gw (1.1–2.5m)	Next [1]	ns*	64 ± 2.9	40 ± 4.4	34 ± 8.2	350 ± 207	102 ± 25
		Between [3]	ns*	38 ± 19	28 ± 1.8	16 ± 6	37 ± 12	5.0 ± 2.2
	Deeper gw	Next (N/A)	N/A	N/A	N/A	N/A	N/A	N/A
	(7.0–11.8m)	Between [3]	ns*	50 ± 0	22 ± 5.5	30 ± 17	42 ± 13	7.9 ± 3.3
	Disstream	N/A	ns*	55 ± 2.9	60 ± 3.8	29 ± 4.8	19 ± 17	60 ± 14
pM	Rhizosphere (0.2–1.0m)	Next [1]	0.008	1148 ± 284 **ab**	140 ± 89 **a**	6037 ± 1095 **b**	9425 ± 943.83 **b**	2488 ± 637 **ab**
		Between [2]	ns*	80 ± 80	0.0 ± 0.0	N/A	106 ± 86	13 ± 13
	Shallow gw (1.1–2.5m)	Next [1]	0.000	1946 ± 307 **ab**	451 ± 97 **a**	8683 ± 1550 **b**	7012 ± 1455 **b**	2608 ± 447 **ab**
		Between [3]	0.000	179 ± 39 **ab**	98 ± 44 **a**	2863 ± 820 **bc**	574 ± 190 **ac**	2789 ± 869 **bc**
	Deeper gw (7.0–11.8m)	Next (N/A)	N/A	N/A	N/A	N/A	N/A	N/A
		Between [3]	0.014	350 ± 7.9 **ab**	31 ± 14 **a**	577 ± 255 **ac**	555 ± 186 **ac**	1112 ± 380 **bc**
	Disstream	N/A	0.010	211 ± 80 **ab**	114 ± 21 **a**	1317 ± 507 **b**	673 ± 192 **ab**	1377 ± 487 **b**
Pm	Rhizosphere (0.2–1.0m)	Next [1]	ns*	1848 ± 760	1460 ± 398	10106 ± 2104	10717 ± 374	11274 ± 8509
		Between [2]	ns*	165 ± 45	1075 ± 120	N/A	1810 ± 457	2675 ± 582
	Shallow gw (1.1–2.5m)	Next [1]	0.000	2987 ± 1286 **ab**	173 ± 14 **a**	12433 ± 3244 **b**	9771 ± 2091 **b**	4079 ± 1097 **b**
		Between [3]	0.004	1394 ± 959 **ab**	139 ± 15 **a**	1547 ± 500 **b**	693 ± 132 **b**	884 ± 227 **b**
	Deeper gw (7.0–11.8m)	Next (N/A)	N/A	N/A	N/A	N/A	N/A	N/A
		Between [3]	0.025	152 ± 10 **ab**	109 ± 30 **a**	407 ± 45 **b**	444 ± 178 **ab**	777 ± 464 **ab**
	Disstream	N/A	0.025	667 ± 170 **ab**	122 ± 14 **a**	1024 ± 279 **b**	1144 ± 344 **b**	1548 ± 820 **b**
PM	Rhizosphere (0.2–1.0m)	Next [1]	ns*	6963 ± 3539	3974 ± 1775	9494 ± 3319	7344 ± 550	3333 ± 1781
		Zoom in: CloseNext	ns*	1038 ± 853	5684 ± 824	9494 ± 3319	6818 ± 279	1900 ± 1830
		MidNext	ns*	12888 ± 2053	554 [4]	N/A	8395 [4]	6200 [4]
		Between [2]	ns*	15 ± 15	0.0 ± 0.0	N/A	3952 ± 1573	5721 ± 64
	Shallow gw (1.1–2.5m)	Next [1]	ns*	9742 ± 3799	5749 ± 2495	4819 ± 1279	4592 ± 1128	2080 ± 842
		Zoom in: CloseNext	0.045	5304 ± 992 **ab**	11177 ± 1288 **a**	6326 ± 178 **ac**	4055 ± 1359 **ac**	2136 ± 1162 **bc**
		MidNext	ns*	14179 ± 7176	322 ± 99	3312 ± 2289	5129 ± 2055	2024 ± 1482
		Between[3]	ns*	100 ± 35	89 ± 64	876 ± 478	223 ± 77	241 ± 123
	Deeper gw (7.0–11.8m)	Next (N/A)	N/A	N/A	N/A	N/A	N/A	N/A
		Between [3]	0.040	7.5 ± 7.5 **ab**	0.0 ± 0.0 **a**	51 ± 29 **b**	29 ± 19 **ab**	44 ± 32 **ab**
	Disstream	N/A	0.003	13.3 ± 8.2 **a**	10 ± 4.2 **a**	591 ± 216 **bc**	131 ± 17 **ac**	1040 ± 805 **bc**

[1] CloseNext and MidNext.
[2] MidBet.
[3] MidBet and FarBet.
[4] No SE available
* ns stands for not significant.

Table 6
Mean ± SE of the non-normalized cumulative CoECs [ng/L] for the compartments rhizosphere, shallow groundwater, deep groundwater, and the discharge to surface water, specified for sampling points located in between versus directly next to an infiltration pipe. Compartments found to differ significantly ($p<0.05$ based on the Benjamin- Hochberg method of the Dunn test) from other compartments for the same persistence mobility class are indicated with different letters.

	Rhizosphere (0.2–1.0m)		Shallow gw (1.1–2.5m)		Deeper gw (7.0–11.8m)	Disstream
	Between[2]	Next[1]	Between[3]	Next[1]	Between[3]	
pm[4]	3.4 ± 3.4 **a**	102 ± 49 **b**	23 ± 4.15 **ac**	124 ± 48 **b**	27 ± 5.30 **cd**	45 ± 6 **bd**
pM[4]	50 ± 28 **a**	3679 ± 911 **bd**	1425 ± 352 **be**	3816 ± 685 **d**	548 ± 133 **ae**	678 ± 160 **ce**
Pm[4]	1431 ± 377 **ac**	6754 ± 1817 **a**	880 ± 177 **cd**	5421 ± 1070 **a**	409 ± 122 **bd**	870 ± 198 **cd**
PM[4]	2422 ± 989 **a**	6268 ± 1180 **b**	329 ± 120 **a**	5438 ± 1081 **b**	28 ± 11 **cd**	319 ± 164 **ad**
82 Parent CoECs[4]	977 ± 310 **ac**	4201 ± 663 **b**	664 ± 114 **a**	3700 ± 460 **b**	253 ± 51 **c**	478 ± 82 **a**

[1] CloseNext and MidNext.
[2] MidBet.
[3] MidBet and FarBet.
[4] KW-χ2 p-value for all rows is equal to 0.000.

interquartile range between 50% and 100%. For the rhizosphere between the pipes, we find the same except for Pm, with an interquartile removal efficiencies range of 40 to 100%. Directly next to the pipes, we find no significant removal for all classes in both the rhizosphere and shallow groundwater and even significant accumulation for Pm. The accumulation in the shallow groundwater with a median of -25%, is highly influenced by some outliers with an accumulation of 200–4000% for CoECs 1H-benzotriazole, climbazole, DEET, gemfibrozil, and triclosan. The removal of CoECs belonging to the class Pm is hindered by hydrophobicity and persistency, thus drainage will have hardly any effect on this class of CoECs and degradation may take years (Picó et al., 2019). It was expected that Pm CoECs would show higher concentrations and possible accumulation over long-term drought conditions. Our data are supported by other studies showing that independent of the method of supply CoECs concentrations in sewage effluent and their physiochemical properties are the main factors governing their fate in agricultural water reuse systems (Ben Mordechay et al., 2022; Christou et al., 2017c; Delli Compagni et al., 2020).

Fig. 7C shows no buildup in the deeper groundwater and the discharge to the surface water and even significant removal for the polar CoECs (pM and the PM). For the two deeper groundwater sampling points that we were able to capture within this study (MidBet and

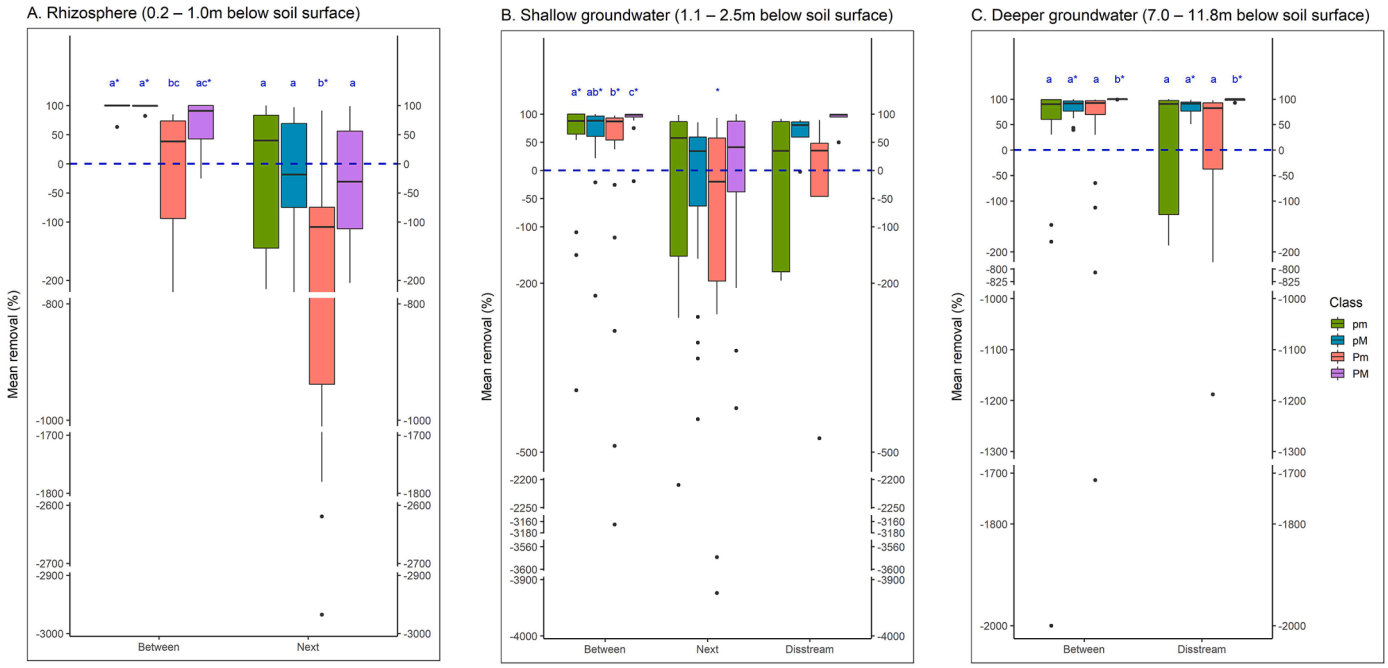

Fig. 7. Box-and-whisker plot illustrating the mean removal percentage calculated with the normalized concentrations, specified per class for (A) the rhizosphere, (B) the shallow groundwater, and (C) the deeper groundwater. Positive removal means that concentrations are lowered compared to the STP effluent while negative removal points to a buildup of concentrations in that compartment. Persistence-mobility classes (pM = low persistency and high mobility) found to differ significantly ($p<0.05$ based on the Benjamin- Hochberg method) from other classes within each group ("Between", "Next", "Disstream") are indicated with different letters. Removal efficiencies found to significantly differ from a 0 ($p<0.05$ based on the Wilcoxon test) are indicated with the * symbol.

FarBet) we observe the highest removal efficiencies for all classes. The long residence time in the groundwater enhances the removal of CoECs (Sopilniak et al., 2018).

3.4. Public health implications

A barrier to the reuse of STP effluent in agricultural irrigation is the perceived risk this reuse may pose to human health and the environment, related to CoECs present in the effluent. Risk assessment involves the identification of both hazards and exposure. While all irrigation techniques (i.e. surface, spray/sprinkler, drip irrigation, and SSI) have the potential to contaminate croplands, the SSI systems limit the direct exposure of STP effluent to crops and workers by supplying irrigation water underground through shallow groundwater. As stated by Revitt et al. (2021) the likelihood of CoECs reaching the root zone is largely dependent on a prior storage and transport buffer, which is one attribute that makes SSI better compared to conventional irrigation systems.

Several studies have discussed the need to develop a quantitative approach to assess the risks and benefits associated with STP effluent reuse in different irrigation systems and highlighted the need for quantitative datasets (Christou et al., 2017a; Dingemans et al., 2020; Revitt et al., 2021). Relatively few studies focus on quantitative data in the context of direct reuse of STP effluent under real farming conditions (Ben Mordechay et al., 2021; Revitt et al., 2021).

This is the first study to quantitatively assess direct effluent reuse in a real-scale sub-surface irrigation system for a broad range of CoECs. As such, the results provide valuable insights into the presence, transport, and fate of a broad range of CoECs in SSI systems under natural aerobic and anaerobic conditions, which is an understudied area (Biel-Maeso et al., 2018; Revitt et al., 2021). We differentiate between CoECs removal during a normal and extremely dry year, dilution by precipitation and groundwater by comparing sampling points next to and in between infiltration pipes, and removal due to degradation and sorption processes. We also take care to identify the CoECs potential to accumulate in the soil compartments.

The transformation products formed during SSI are an important issue since it has been reported that transformation products can sometimes represent a higher toxicity concern than parent substances (Murrell et al., 2021). All in all, higher numbers and concentrations of CoECs are found in the SSI field as compared to the reference field. However, also relatively high net removal efficiencies are shown in our nature-based treatment benefiting the surface waters that would otherwise receive the STP effluent directly, but care must be taken to monitor the CoECs that are (moderately) hydrophobic as these significantly accumulate around infiltration pipes and show no significant removal in the rhizosphere.

For these persistent moderately hydrophobic CoECs we determined the risk characterization ratio's (RCRs) and ΣRCR. None of the single-chemical RCRs are > 1 (Table 7). The ΣRCR of this persistent moderately hydrophobic group is also much smaller than one for both the rhizosphere and the shallow groundwater. Both values imply sufficiently safe ambient exposures. Possible solutions to successfully further minimize the exposure of crops and deep groundwater to CoEC, especially those belonging to the Pm class, in SSI reuse systems using STP effluent may consist of implementation of further STP upgrading through redesigning of the existing treatment processes (Kahl et al., 2017), optimizing operating conditions of the existing biological process (He et al., 2021) or implementing an effective additional tertiary treatment (Licciardello et al., 2018; Rizzo et al., 2019). As a future perspective, to facilitate risk management in the context of STP effluent reuse in SSI systems, standardized emission scenarios should be developed for this use, supporting the systematic assessment of risks posed by (un)regulated chemical substances released from STPs.

4. Conclusion

- Apart from sub-surface irrigation providing a robust barrier against drought, it also helps to significantly remove most CoECs.
- After a drought period the SSI system needs more time to reset to background concentrations, whereas after a normal hydrological

Table 7
Risk characterization ratio's (RCRs) for persistent moderately hydrophobic CoECs.

Pm (Persistent moderately hydrophobic) CoECs	Cas number	Primary pseudo mode of action[1,2]	Acute EC50 SSD midpoint concentration [μg/L][2]	Chronic NOEC SSD midpoint concentration [μg/L][2]	Average normalized concentration at the sampling location CloseNext on the 23rd of October 2018 [μg/L]		Acute RCR(Average normalized concentration/ Acute EC50 SSD midpoint)		Chronic RCR(Average normalized concentration/ Chronic NOEC SSD midpoint concentration)	
					Rhizosphere	Shallow gw	Rhizosphere	Shallow gw	Rhizosphere	Shallow gw
1H-benzotriazole[3]	95-14-7	*unknown*	54954	6989	25	17	4,63E−04	3,11E−04	3,64E−03	2,45E−03
Atrazine[3]	1912-24-9	chlorotriazine	1905	90	N/A	N/A	N/A	N/A	N/A	N/A
Azinophos-ethyl	2642-71-9	organothiophosphate	20	2	N/A	0	N/A	1,01E−03	N/A	1,00E−02
Chloroxuron	1982-47-4	phenylurea	3162	314	N/A	0	N/A	0,00E+00	N/A	0,00E+00
Climbazole[3]	38083-17-9	conazole	759	122	0	0	2,45E−04	1,51E−04	1,53E−03	9,44E−04
Clomazone	81777-89-1	unclassified herbicides	8128	987	N/A	0	N/A	0,00E+00	N/A	0,00E+00
Cyanazine[3]	21725-46-2	chlorotriazine	5370	11	N/A	N/A	N/A	N/A	N/A	N/A
DEET[3]	134-62-3	insect repellents	107152	10705	3	3	3,06E−05	2,96E−05	3,06E−04	2,96E−04
Desmetryne[3]	1014-69-3	methylthiotriazine	6761	680	0	0	0,00E+00	0,00E+00	0,00E+00	0,00E+00
Dimefuron[3]	34205-21-5	*unknown*	302	N/A	N/A	0	N/A	0,00E+00	N/A	N/A
Dimethametryn	22936-75-0	methylthiotriazine	5370	533	N/A	0	N/A	0,00E+00	N/A	0,00E+00
Dimethanamid-p	163515-14-8	amide	7762	1007	0	0	1,38E−05	4,03E−06	1,06E−04	3,10E−05
Ethofumesate	26225-79-6	benzofuranyl alkylsulfonate	22387	3983	0	0	0,00E+00	0,00E+00	0,00E+00	0,00E+00
Fipronil[3]	120068-37-3	pyrazole	27	2	0	0	4,31E−03	3,88E−03	6,41E−02	5,76E−02
Fluometuron	2164-17-2	phenylurea	7079	329	N/A	0	N/A	0,00E+00	N/A	0,00E+00
Fluoxastrobin (, trans-)	361377-29-9	*unknown*	708	133	N/A	N/A	N/A	N/A	N/A	N/A
Gemfibrozil[3]	25812-30-0	Cardiovascular Drugs	34674	87	1	0	2,48E−05	6,69E−06	9,92E−03	2,67E−03
Linuron	330-55-2	phenylurea	646	25	0	0	3,10E−05	1,18E−05	8,10E−04	3,08E−04
Methabenzthiazuron	18691-97-9	urea	1660	167	N/A	N/A	N/A	N/A	N/A	N/A
Methoxyfenozide	161050-58-4	moulting hormone agonists	2570	535	N/A	N/A	N/A	N/A	N/A	N/A
Metolachlor-s	87392-12-9	*unknown*	4571	458	N/A	N/A	N/A	N/A	N/A	N/A
Neburon	555-37-3	phenylurea	871	88	0	0	2,95E−05	1,18E−05	2,93E−04	1,17E−04
PFOA[3]	335-67-1	*unknown*	42658	4596	0	0	2,26E−06	2,30E−06	2,10E−05	2,13E−05
Prometon[3]	1610-18-0	methoxytriazine	28840	2851	0	N/A	1,56E−07	N/A	1,58E−06	N/A
Simetryne[3]	1014-70-6	methylthiotriazine	1413	142	0	0	0,00E+00	0,00E+00	0,00E+00	0,00E+00
Teflubenzuron	83121-18-0	chitin synthesis inhibitor	13804	1375	N/A	0	N/A	3,40E−06	N/A	3,41E−05
Terbacil	5902-51-2	uracil	69183	54	N/A	0	N/A	0,00E+00	N/A	0,00E+00
Terbumeton[3]	33693-04-8	methoxytriazine	19055	1899	0	N/A	2,36E−07	N/A	2,37E−06	N/A
Triclosan[3]	3380-34-5	Polar narcosis	112	26	N/A	N/A	N/A	N/A	N/A	N/A
ΣRCR							**0,01**	**0,01**	**0,08**	**0,07**

[1] The word pseudo indicates that the mode of action is not identified as the real biochemical mechanism of action, but rather as a use classification.
[2] Source: Posthuma et al. (2019).
[3] Pm CoEC was also detected in the 24-H effluent samples.

year with a precipitation surplus and drainage in winter, most CoECs are removed.

- ➢ CoECs of the class Pm however significantly buildup in the rhizosphere and shallow groundwater next to infiltration pipes.
- ➢ CoECs belonging to the class pM show a high seasonal dependence. This is true for rhizosphere and shallow groundwater but not the deeper groundwater indicating that these CoECs break down.
- ➢ CoECs belonging to the pm class show no change amongst their removal in a dry versus normal year. This also holds true for the PM class, except shortly for the deep groundwater. This indicates that the PM CoECs go with the flow of the water and that pm CoECs are degraded easily in the system.

In summary, the removal efficiency is highly dependent on the persistency-mobility class of a compound, the seasonal drought conditions, and the compartment of the SSI system. Thus, when adopting a SSI STP effluent reuse system, relatively high removal efficiencies are shown benefiting the surface waters that would otherwise receive the STP effluent directly but care must be taken to monitor the CoECs that are (moderately) hydrophobic as these significantly accumulate around infiltration pipes and show no significant removal in the rhizosphere.

CRediT authorship contribution statement

D.M. Narain-Ford: Conceptualization, Data curation, Visualization, Project administration, Formal analysis, Investigation, Methodology, Writing – original draft. **A.P. van Wezel:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing. **R. Helmus:** Methodology. **S.C. Dekker:** Conceptualization, Writing – review & editing. **R.P. Bartholomeus:** Conceptualization, Funding acquisition, Investigation, Supervision, Writing – review & editing.

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

Supplementary data to this article are available from the Mendeley data repository (Narain-Ford et al., 2022): https://data.mendeley.com/datasets/4x77nynfnx/1.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2022.119303.

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