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Risk assessment of contaminants of emerging concern in the context of wastewater reuse for irrigation: An integrated modelling approach

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Abstract:

Direct reuse of reclaimed wastewater (RWW) in agriculture has recently received increasing attention as a possible solution to water scarcity. The presence of contaminants of emerging concern (CECs) in RWW can be critical, as these chemicals can be uptaken in irrigated crops and eventually ingested during food consumption.

In the present study, an integrated model was developed to predict the fate of CECs in water reuse systems where RWW is used for edible crops irrigation. The model was applied to a case study where RWW (originating from a municipal wastewater treatment plant) is discharged into a water channel, with subsequent irrigation of silage maize, rice, wheat and ryegrass. Environmental and human health risks were assessed for 13 CECs, selected based on their chemical and hazard characteristics. Predicted CEC concentrations in the channel showed good agreement with available measurements, indicating potential ecotoxicity of some CECs (estrogens and biocides) due to their limited attenuation. Plant uptake predictions were in good agreement with existing literature data, indicating higher uptake in leaves and roots than fruits. Notably, high uncertainties were shown for weakly acidic CECs, possibly due to degradation in soil and pH variations inside plants. The human health risk due to the ingestion of wheat and rice was assessed using the threshold of toxicological concern and the hazard quotient. Both approaches predicted negligible risk for most CECs, while sulfamethoxazole and 17α-ethinylestradiol exhibited the highest risk for consumers. Alternative scenarios were evaluated to identify possible risk minimization strategies (e.g., adoption of a more efficient irrigation system).

Keywords: dietary intake; micropollutants; model-based risk assessment; plant uptake

Declarations of interest: none

1. Introduction

Water scarcity induces monetary and job losses throughout all continents (Asano, 2002; Ding et al., 2011) and the situation is expected to worsen due to population growth, increase of water use per capita, climate change and other stress factors (IPCC, 2014; Gosling and Arnell, 2016). Following circular economy principles, the reuse of reclaimed wastewater (RWW) originating from urban wastewater treatment plants (WWTPs) is identified as one of the main measures to alleviate fresh water depletion (COM/2015/614). This can be a valid alternative to water supply for agricultural irrigation, the largest source of freshwater consumption worldwide (COM/2015/614). This approach has recently been promoted by the European Union, which also proposed minimum requirements for a safe reuse (COM/2018/337). This document acknowledges the need of assessing the risk (where relevant) associated to contaminants of emerging concern (CECs), whose threat for environment and human health is well recognized (Daughton and Ternes, 1999; Monteiro and Boxall, 2010).

Existing WWTPs are typically not designed for removal of CECs (e.g. pharmaceuticals, estrogens, biocides), which are generally released from households into sewer systems (Luo et al., 2014; Castiglioni et al., 2018). Hence, some CECs persist in RWW and can reach agricultural fields through irrigation, leading to accumulation in soil (Durán-Alvarez et al., 2009; Gibson et al., 2010) and contamination of groundwater (Siemens et al., 2008; Lesser et al., 2018). Irrigated crops can also accumulate CECs in roots (Miller et al., 2016) and translocate them towards edible plant organs such as leaves and fruits (Goldstein et al., 2014; Christou et al., 2017). Consequently, potential exposure of humans and organisms living in environmental recipients to CECs requires a careful assessment, and adverse effects can be quantified based on the estimated exposure concentrations (Piña et al., 2018). Besides being discontinuous in time and subject to uncertainty (due to e.g. analytics), empirical measurements of environmental CEC levels are site-specific and do not allow extrapolating contamination levels to other RWW reuse systems. In this case, modeling tools can contribute with valuable complementary information (e.g. filling temporal gaps between measurements), and account for the influence of site-specific conditions. The use of complex modelling tools, especially for integrated systems, can be challenged by parameter identifiability (Voinov and Shugart, 2013; Bach et al., 2014) and limited input data availability. These sources of uncertainty can be addressed by using statistical analysis methods (e.g., sensitivity and uncertainty analysis), allowing the identification of important model factors and the quantification of results uncertainty. So far, integrated models have shown the ability of evaluating the impacts of discharges from storm- and wastewater system on the chemical status of surface water (De Keyser et al., 2010). However, a dynamic chemical fate model capable of estimating CEC concentrations (and thereby risk) in different environmental compartments (surface water, soil, crops) under different water management and reuse scenarios is currently in high need.

The objective of this work was to develop a flexible integrated model to predict CEC fate in different types of RWW reuse systems, irrespective of size and complexity, and to assess environmental and human health risks. The model was: (i) applied to a real RWW reuse scenario, comprising a discharge channel and cultivation of four different types of crops (silage maize, rice, wheat and ryegrass); (ii) verified with site-specific measurements, where available, and literature data in different compartments; (iii) used to estimate the environmental risk associated to CEC occurrence in surface water, and human health risk following the ingestion of irrigated crops; (iv) used to evaluate alternative risk management and minimization scenarios, which were compared to the present situation and to a worst-case scenario (characterized by the absence of a WWTP).

2. Materials and methods

2.1 Fate model development and evaluation

A generic RWW reuse system was considered to include a surface water body, receiving RWW discharges, and cultivated fields with irrigation. The river water quality model extended with CEC fate processes (from the IUWS_MP library) (Vezzaro et al., 2014) and the coupled soil-plant model (CSPM) (Trapp and Matthies, 1998; Trapp, 2017) were identified as the state-of-the-art models (section 2.1.1) to describe CECs fate in the generic system. These models were extended (section 2.1.2) to increase their applicability and coupled (section 2.1.3). A sensitivity analysis (section 2.1.4) was also performed to identify the most significant parameters in the developed model.

2.1.1 State of the art models

The IUWS_MP library (Vezzaro et al., 2014) utilizes a conceptual approach to simulate river water quality, where water transport is simulated by a series of continuously stirred tanks reactors (CSTRs). Each CSTR consists of two compartments (bulk water and sediments), in which fate processes (abiotic and biotic degradation, sorption to suspended solids and colloids) occur.

The CSPM includes (i) a tipping bucket model to describe the movement of water and dissolved CECs through soil and (ii) a numerical four-compartment model to simulate CEC uptake and translocation through xylem and phloem flows, in roots, stem, leaves and fruits. Partitioning between plant tissues and soil, and xylem and phloem flows is described through a detailed intracellular model (Trapp, 2004; Trapp and Horobin, 2005; Trapp, 2009; Trapp 2017).

2.1.2 Model extensions

Many CECs are ionized at environmental pH, which affects their partitioning behavior (Franco et al., 2010). Hence, the equations described in Franco and Trapp (2008) were included in the IUWS_MP library to describe sorption of ionized monovalent acidic and basic compounds.

In the CSPM, phloem flow introduced to improve the dynamics of the internal plant circulation, through which weakly acidic CECs translocate from leaves through stem to fruits and roots (Gonzalez-Garcia et al., 2019; Kleier & Hsu, 1996).

Model structures were further modified to accommodate for temporal and spatial dynamics of environmental conditions (e.g., air, soil and water temperature, water and soil pH, sunlight intensity, etc.), which can substantially affect CEC fate (Kunkel and Radke, 2011; Matamoros and Rodriguez, 2017). Moreover, the CSPM was also modified to simulate complex types of irrigational systems, in which water can partially submerge the cultivations (e.g. rice). Particularly, the field capacity of the first soil layer was adjusted to simulate the saturation effect introduced by a standing water layer. The reader is referred to the Supplementary Material (SM) for a detailed description of the extensions of the IUWS_MP library and of CSPM model.

2.1.3 Model coupling and software selection

Predicted CEC concentrations were obtained twice a day (noon and midnight) from the river model (implemented in WEST 2014®, DHI A/S, Denmark) to consider high and low peaks, and input to the CSPM (implemented in Microsoft Excel), which provided daily outputs.

2.1.4 Identification of influential parameters

A sensitivity analysis (SA) was performed to identify: (i) the most influential model parameters for concentration predictions and (ii) non-sensitive model parameters uncertainties, which could be fixed to a default value without affecting model predictions uncertainties. As for the river model, a one-at-a-time (OAT) approach (Frey and Patil, 2002) was performed by varying each parameter ±5% from its default value. A total of 52 parameters were investigated. The variation in predicted concentrations was calculated as reported in Equation 1:

$$Deviation = \frac{1}{n}\sum_{i}^{n}\frac{y_i^{p,max} - y_i^{p,min}}{y_i^{p,default}} \qquad \text{(Eq. 1)}$$

where $y_i^{p,max}$, $y_i^{p,min}$, $y_i^{p,default}$ are the predicted concentrations obtained with the maximum, minimum and default values of the parameter *p* for i^{th} time step; *n* is the number of time steps in the simulation. Three CECs (i.e. diclofenac, triclosan and carbamazepine, see section 2.2.1) were chosen as benchmark for different physicochemical properties. Parameters influencing predicted concentrations were also assessed for four conventional pollutants (ammonia, nitrite, nitrate and phosphorus).

As for the SA of CSPM, partial rank correlation coefficients (PRCCs) (Saltelli et al., 1993) were calculated through the software Crystal Ball 11.1.2 (Oracle®). First, 1000 runs were conducted by varying separately plant and soil parameters. The parameters presenting |PRCCs| above 0.1 were selected and included into a second SA of 10000 runs. This time, parameters with |PRCCs| exceeding $\sqrt{1/n}$ (with *n* being the number of parameters varied in each simulation) were identified as relevant. The validity of the PRCCs was checked through the R^2 between the two sets of ranks (Sin et al., 2011). The second SA was carried out both with and without degradation in soil to better highlight its sensitivity on model variations.

2.2 Model testing

The developed model was tested on an existing Italian case study, where RWW from a municipal WWTP (flow = 3.5 m^3 s^{-1}) is the only source providing water through a surface water channel to subsequently irrigate crop fields. The channel extends for about 12 km and provides irrigation water for 90 farms with more than 40 km^2 of crop fields (Pizza, 2014). Cultivated crops include winter wheat and rice, which are sold for human food consumption; and silage maize and ryegrass that are used for animal feed production. Irrigation systems included surface irrigation, the dominant form of irrigation in southern European countries (Masseroni et al., 2017) for all the crops but rice, which is grown in paddies. In the area, crop rotation is a standard procedure and is performed each season.

2.2.1 Chemicals

Thirteen CECs of different classes of use were assessed: clarithromycin (CLA), sulfamethoxazole (SMX), diclofenac (DCF), ibuprofen (IBU), paracetamol (PAR), carbamazepine (CBZ), furosemide (FUR), 17-α ethinylestradiol (EE2), 17-β estradiol (E2), estrone (E1), perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS) and triclosan (TCS). These CECs were selected from an initial group of 80 CECs, for which measurements were available at the outlet of the WWTP (Castiglioni et al., 2018a, 2018b). Specifically, two criteria were used: i) selected CECs had to cover a broad range of physicochemical properties in terms of: air/water partitioning coefficient (K_{aw}), normalized organic carbon partitioning coefficients (K_{oc}), and ionization state at environmental pH; ii) selected CECs had to belong to different CEC classes (e.g. antibiotics, hormones, etc.) and to possibly exceed the predicted no-effect concentration (PNEC). Physicochemical properties (Table S2) and degradation rates (Tables S3-S15) of the selected CECs were collected from literature (see SM for sources) and/or retrieved from QSAR software (Advanced Chemistry Development Inc., 2015; National Food Institute, Technical University of Denmark, 2018).

2.2.2 System conceptualization

The RWW reuse system was conceptualized as shown in Figure 1. The channel was described by the river modules from the IUWS_MP library, resulting in 11 in-series CSTRs, each one approximately 500 m long. This length was selected in agreement with Benedetti et al. (2004) as a compromise between the need of simulating temporal dynamics in a realistic way and the required computational effort. Within the channel, nine equidistant locations were selected, each having irrigation water withdrawal that was proportional to the required water demand to harvest the closest crops. The water demand (m^3 d^{-1}) was defined as the product of the water consumption to harvest one unit of land and total land extension (Brouwer et al., 1992). Crop types and corresponding extensions were derived from georeferenced maps of the area (www.geoportale.regione.lombardia.it) and elaborated with QGIS 2.18. Periods of water withdrawal and crop rotation were simulated according to the irrigation calendars (Figure 1b) based on agronomic information of the area (Nelli and Sodi, 2007; Provincia di Milano, 2007; Borrelli et al., 2014; Moretti et al., 2015). Two water withdrawal scenarios were considered: (i) scenario *MR*, where silage maize and ryegrass were grown at the same time of rice and ryegrass and, (ii) scenario *MW*, where silage maize and ryegrass were grown at the same time of winter wheat. Moreover, different irrigation systems were simulated depending on crop types: (i) a monthly irrigation water pulse for silage maize, ryegrass and winter wheat and, (ii) a continuous irrigation for rice. Three types of soils were found predominantly in the study area, with more than one crop per type of soil (see Table S18). For this reason, crop simulations were repeated for different soils. The simulated soil structure was also adapted to match the identified stratigraphy for a soil depth of 1 m, splitting (if needed) the widest horizons over two layers.

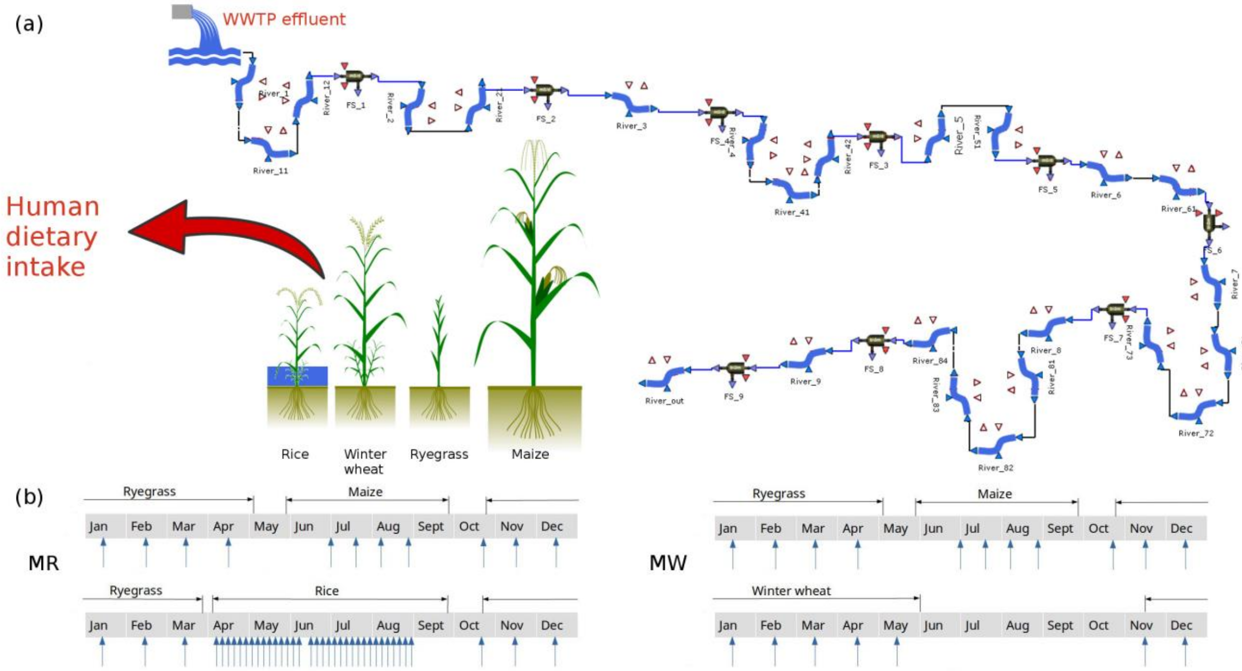

Figure 1. Outline of the wastewater reuse system (a) and irrigation calendars (b) for the two crop rotation scenarios.

2.2.3 Model input and parameters

Concentrations of conventional pollutants in RWW (i.e. ammonia, nitrite, nitrate and phosphorus) represented a 24-hour time-proportional composite sample and were retrieved from the laboratory measurements conducted by WWTP staff. CEC concentrations in RWW were obtained from previous measurements at the outlet of the WWTP (Castiglioni et al., 2018a, 2018b) and assumed constant over the year. Such assumption can be held valid for CECs (e.g., DCF and CBZ) that show low to no seasonal fluctuations in usage (Sui et al., 2011). For antibiotics such as CLA, for which seasonal fluctuations were observed (McArdell et al., 2003), measurements may reflect a worst-case scenario as campaigns were conducted during winter time. Environmental conditions (Tables S16-17) were directly obtained from public databases or indirectly estimated (e.g., potential evaporation, soil temperature, bulk density and water retention properties). Crop-specific data (Table S19) were collected from literature preferring, where available, local sources. Soil initial conditions (CECs concentrations and water content) were assumed equal to the pseudo-steady state reached using the median CECs. For more details, the reader is referred to SM.

2.2.4 Uncertainty propagation

The uncertainty associated to CEC concentrations in RWW and transformation rates (e.g., aerobic degradation in water, photodegradation and aerobic/anoxic degradation in sediments) were propagated to the predicted concentration in the surface water channel through a Monte-Carlo based Uncertainty Analysis (UA). Uniform, triangular or empirical parameter distributions were chosen based on literature values (Tables S3-S15). For every CEC, 2000 runs were performed.

Resulting uncertainties in the predicted CEC concentrations along the river were then propagated, together with soil degradation rates and influential crop parameters, to CSPM predictions. Specifically, triangular distributions were considered for soil degradation rates and CEC concentrations. Crop parameters were considered as uniformly distributed with a variation of ±10% from literature data (Felle, 2001). Attention was paid to avoid parameter combinations that may lead to non-realistic scenarios (Steinwand et al., 2001). 2000 latin-hypercube Monte Carlo runs were performed for each CEC and soil type (Table S18). Physicochemical properties (Table S2) of perfluorinated compounds exhibited a high degree of uncertainty due to analytical limitations (Wang et al., 2011), and were thus included in UA. More details on UA are provided in SM.

2.3 Model objectives

The three main objectives of the developed integrated model were:

I – Fate predictions and assessment of model performance: long term simulations (≥ 1 year) were performed to assess CECs fate in surface water, irrigated crops and groundwater. Assessment of model performance was carried out by comparing model predictions with site-specific measurements, where available (as for DCF) and/or literature data. For the surface water channel, further verification was made by deriving first-order attenuation rates by fitting predicted median concentrations at different locations and comparing to experimental literature data. In this case, overall attenuation derives from the combination of different biotic and abiotic degradation processes.

As for the uptake in crops, the bioconcentration factor (BCF, g_{dw}^{-1} $g^{-1}{}_{dw}$) was calculated as C_{organ}/C_{soil}, where C_{organ} and C_{soil} are the predicted dry weight concentrations in a given plant organ (root, stem, leaf, fruit) and in the first soil layer. There is currently limited consensus on calculation of BCFs since different approaches have been considered with respect to C_{soil} values (Polesel et al., 2015). For this reason, both the simulated maximum and median soil concentrations were used for the BCF calculation, corresponding to BCF_{max} and BCF_{median}, respectively. Calculated BCF was compared with literature (when not explicitly reported, empirical BCFs were derived from reported concentration data) except for CLA, which showed limited plant uptake (Limmer and Burken, 2014; Lamshoeft et al., 2018). Predicted leaching of CECs into groundwater was also compared with measurements from the nearby area.

II – Ecological and human health risk assessment: environmental risk assessment was carried out through the risk quotients (RQs) (Hernando et al., 2006; Kuzmanovic et al., 2013). RQs were calculated for each CEC as *PEC/PNEC*, where *PEC* is the predicted environmental concentration and *PNEC* the predicted no-effect concentration. *PNECs* were obtained from literature (Table S1) and *PEC*s were the predicted concentrations at the end of the surface water channel; specifically, maximum, median and minimum concentrations were predicted to obtain RQ_{max}, RQ_{median} and RQ_{min}, respectively. Two alert thresholds of RQ above 0.1 and 1 were identified as medium and high risk, respectively (Hernando et al., 2006). Monthly frequency of exceedance above the alert thresholds was calculated as additional risk indicator.

The human health risk associated to dietary intake was calculated with two different approaches: the threshold of toxicological concern (TTC) (Kroes et al., 2004; Malchi et al., 2014) and the hazard quotient (HQ) (Prosser et al., 2014b; Prosser and Sbiley, 2015). TTC values were obtained through the Cramer classes decision tree implemented in the Toxtree v3.1 software (Patlewicz et al., 2008) and used to calculate the crop ingestion required for posing a risk as (BW TTC)/ C_{fw}], where BW (kg) is the reference body weight (EFSA, 2012) and C_{fw} ($\mu g/kg_{dw}$) is the CEC concentration in the edible part, based on fresh weight. These values were then compared with typical Italian food consumption rates for infants and adults (Leclercq et al., 2009). HQs were calculated as the ratio between the estimated daily intake (EDI) and the admissible daily intake (ADI), which is the amount of CECs that can be consumed daily over a person's lifespan without evocating an adverse effect. The level of concern was set to 0.1 as dietary ingestion represents a single pathway of exposure (Prosser and Sibley, 2015). Hazard Index (HI) was also calculated as the sum of HQs to provide a conservative first-tier estimate of the mixture risk (Prosser and Sibley, 2015; Evans et al., 2015). Median and 97.5% percentile were derived for HQ, TTC and HI values from UA propagation. Further details on the two methods are given in SM.

III – *Management scenarios analysis*

Two agronomic management strategies were simulated to assess their potential for human health risk mitigation compared to the existing surface irrigation:

(i) the adoption of sprinklers, which require a lower investment cost than drip irrigation, and are a more efficient irrigation system than surface irrigation (i.e. irrigation efficiency increases from 60% to 75% according to Brouwer et al., 1989);

(ii) one week extension of the period without irrigation before harvest (also known as crop-drying stage). Waiting periods before harvest are a commonly required health safety measure in case of biosolids application (Prosser et al., 2014b).

The benefits in terms of human health risk reduction of the existing WWTP, although not specifically designed to remove CECs, were simulated in a specific scenario, where untreated wastewater was directly used for irrigation. Specifically, CEC concentrations measured in WWTP influent (Castiglioni et al., 2018a) were used as input to the river model and first order attenuation rates (calculated beforehand) were used to estimate *PECs* at the end of the channel. Based on *PECs* as input, the CSPM was then used to predict concentrations in fruits, allowing to estimate dietary intake and health risk for infants as shown earlier.

3. Results and discussion

3.1 Sensitivity analysis

Among the 52 parameters of the river model in the IUWS_MP library, 12 parameters (Figure S2) had an impact on predicted CEC concentrations. The fraction of CEC sorbed onto total suspended solids (TSS) showed higher sensitivity if compared to the dissolved fraction sorbed to colloids, mainly due to sedimentation parameters, in agreement with De Schepper et al. (2012). As to conventional pollutants, ammonium, nitrite and nitrate were impacted by microbial growth parameters, in agreement with Deksissa et al. (2004), while phosphorus was influenced by the sorption rate and sedimentation parameters (Figure S2).

For the CSPM model, variations of CECs concentrations were influenced by several soil and plants parameters (Figure S3), in agreement with previous modeling studies (Trapp, 2015) and experimental data (Chen et al., 2013; Goldstein et al., 2014; Dodgen et al., 2015; Lamshoeft et al., 2018). Notably, the effect of the Arrhenius temperature correction coefficient on soil concentrations ($|PRCC| > 0.9$) out-weighed the effect of the other parameters, as seen before (Legind et al., 2011). Predicted concentrations of the weakly acidic DCF showed considerable sensitivity to internal plant pH, which was further assessed.

3.2 Fate analysis

3.2.1 Surface water channel

Verification of IUWS_MP for conventional pollutants was adequate for the intended purpose, showing predicted concentrations in agreement with the measurements (≤ 0.75 log units) and being able to follow seasonal trends (Figure S4).

Along the water channel, model predictions (Figure 2 and Figures S5-14) showed that all the investigated CECs were almost entirely found as dissolved in the water phase (~ 98% of the load released from the WWTP). The only exception was CLA, for which the fractions on colloids and

TSS were, on average, equal to 6% and 17% of the total mass (Figure 2c). Most of the simulated CECs have lower sorption affinity than CLA ($logK_{ow}$ = 3.2), or they were negatively charged at the measured pH (i.e. electrical repulsion). These results were in good agreements with the measurements in the Ebro river (Ferreira da Silva et al., 2011), where most of the CECs were found as predominantly dissolved (84%, 87%, 95%, 95%, 95% of the total mass for DCF, CLA, PAR, CBZ and IBU, respectively). The width of concentration prediction bounds (about ± 200 % of the median) was mainly explained by the propagation of the uncertainties associated to the initial concentrations of CECs in RWW and by degradation rates. Low variation in predicted concentrations (~ 0.3 log units) resulted from the propagation of uncertainties of conventional pollutant parameters.

The temporal dynamics of predicted concentrations followed different daily and/or seasonal patterns depending on the simulated CEC. For example, photodegradation caused an important reduction in concentrations for DCF (52-89%) and FUR (25-87%) between night and day time, in agreement with the findings of Hanamoto et al. (2013). Predicted DCF concentrations during day time were also confirmed by the available measurements (Figure 2a). Photodegradation and biodegradation also caused seasonal patterns with the lowest concentrations during June, July and August (Figure 2a and 2b), when temperature and sunlight irradiation reached their maximum values (22-25 °C and up to 900 W m^{-2}, respectively). A considerable reduction was observed in summer months, as compared to December, for DCF (30-41%; summer median: 204-244 ng L^{-1}), and FUR (49-72%; summer median: 49.4-90.6 ng L^{-1}). Moreover, when rice was cultivated, median concentrations of DCF and FUR were 16% and 67% lower than when winter wheat was cultivated (orange and red lines in Figure 2). In fact, a high water withdrawal for rice cultivation led to a reduction of the water level and thus enhancing photodegradation and sedimentation since rates of these two processes are inversely proportional to the water depth (Schwarzenbach, 2003).

Due to the low tendency to photodegrade (median $k_{pho,nearsurf} \leq 23.1\ d^{-1}$) and the overall slow biodegradation in water (median $k_{bio,\ water} \leq 0.32\ d^{-1}$), the other CECs showed smaller daily fluctuations (intra-day variation: ≤ 10 %), seasonal trends (reduction in summer months compared to December: ≤ 11%) and variations due to water withdrawal (concentration decrease during rice cultivation: ≤ 4%) (see Figures S5-S14).

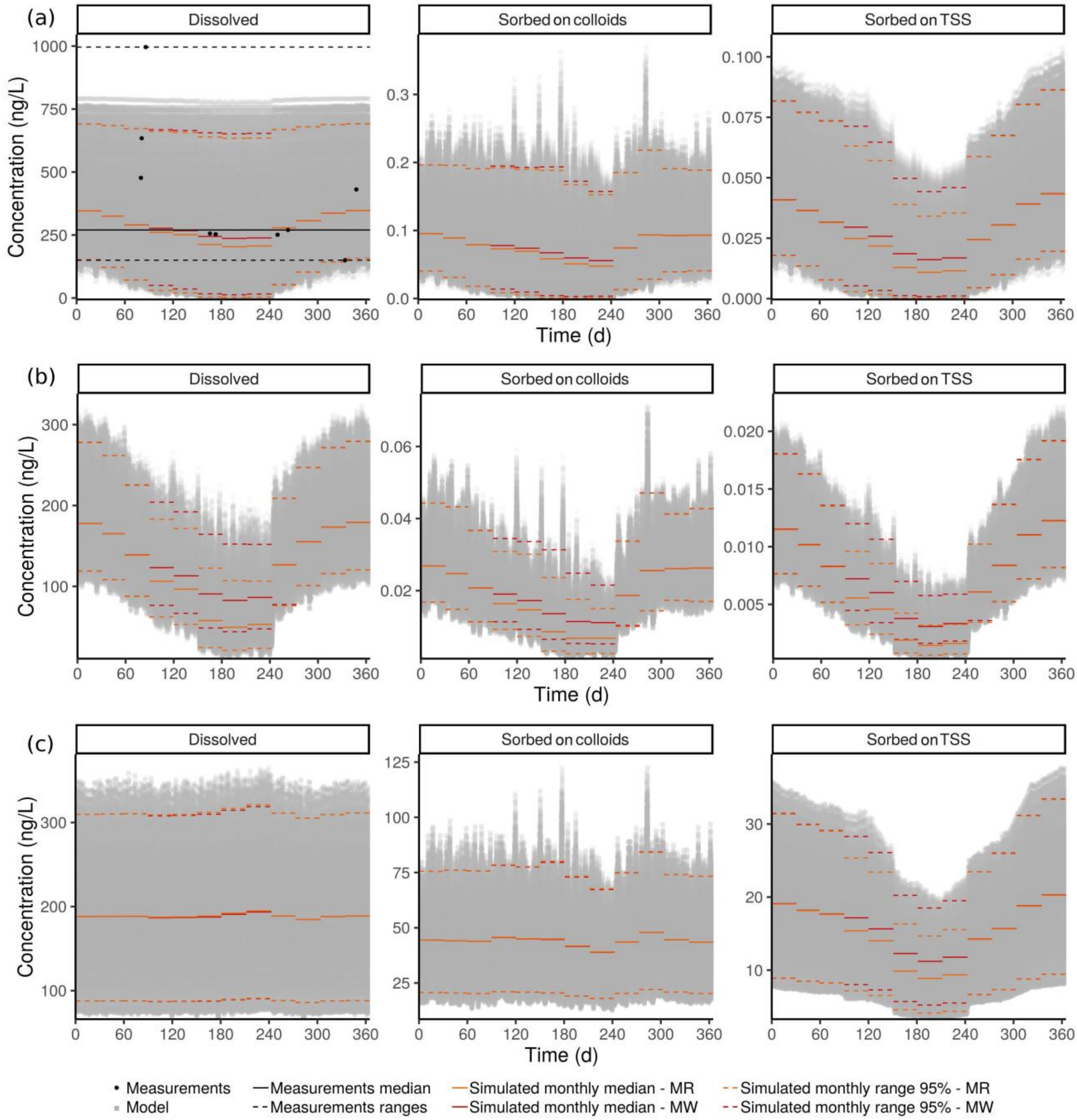

Figure 2. Annual variation (from January 1st to December 31st) of daytime DCF (a), FUR (b), CLA (c) concentrations at the end of the channel.

Predicted attenuation rates were in good agreement with literature data (Figure S15), with slight underestimation (≤ 1 order of magnitude). Differences might be due to the biofilm growth on submerged vegetation and sediment surface (Winkler et al., 2001; Sabaliunas et al., 2003; Kunkel and Radke, 2011; Writer et al., 2013), that enhances attenuation processes with respect to biodegradability processes accounted by our model.

Median attenuation rates varied throughout the year up to one order of magnitude due to different environmental conditions (temperature, sunlight intensity and water depth), with predicted maximum and minimum rates during July and December, respectively. Due to low CLA degradation (median $k_{pho,\ nearsurf}$ = 0.17 d^{-1}, median $k_{bio,\ water}$ = $3.85E^{-02}$ d^{-1}), CLA attenuation rate variations were mostly caused by sedimentation, which was enhanced by the lower summer water depth, in agreement with Castiglioni et al. (2006). Similar seasonal variations of the attenuation rates were also observed by Matamoros et al. (2017) and Labadie and Budzinski (2005).

3.2.2 Crops

In Figure 3a we report BCF_{max} predictions for three CECs in different plant compartments, where the maximum simulated soil concentration is used for normalization (see Figures S16-S19 for the BCF_{max} calculated with maximum soil concentrations for all the other CECs). Figure 3b-c presents BCF_{median} values for fruits and leaves of the investigated crops based on the simulated median soil concentration, given the larger data availability for plausibility check (see Figures S16-S19 for roots and stems $BCFs_{median}$). Box-plots were obtained by aggregating BCFs based on crop type (i.e. maize, rice, ryegrass and wheat), and resulting ranges (i.e. width of the whiskers) included both variability (of CEC concentrations in the irrigation water, soil pH and soil organic content SOM) and uncertainty of model input.

Within crops (Figure 3a), predicted results for weakly acidic CECs, such as DCF, PFOA, FUR and IBU, mainly show accumulation in roots, which can be partly attributed to phloem translocation. For these CECs, a considerable BCF variation (more than factor 100) was generally obtained. This could be attributed to pH variability within the plant cell organs (Vreugdenhil and Koot-Gronsveld, 1989; Felle, 2001), which can strongly affect speciation of ionizable CECs and, consequently, the extent of CECs adsorption and translocation within the plant (Trapp, 2004). Moreover, large BCF variations for PFOA and PFOS were also associated to $\log K_{ow}$ and K_{HSA} uncertainty, which affect in-plant translocation and in-soil bioavailability (Trapp, 2009). TCS also showed maximum accumulation in roots, but mainly due to its high lipophilicity, which limits partitioning into xylem (Hsu et al., 1990). Conversely, neutral and hydrophilic CECs, such as CBZ, translocated upwards through the xylem to the leaves (Collins et al., 2006; Miller et al., 2016), where they showed the highest accumulation. In this case, variations of BCF were mainly caused by SOM variability, which influenced sorption of CECs in neutral form, such as estrogens (E1, E2 and EE2), TCS, PAR and CBZ (Goldstein et al., 2014), affecting bioavailability and uptake. SMX presented a more uniform accumulation among the plant organs due to both high phloem and xylem mobility (Kleier and Hsu, 1996; Goldstein et al., 2014). Regardless of the type of CEC, rice was generally the crop showing the highest uptake (Figure 3a), given that the irrigation system constantly floods the crop over the irrigational period, thus enhancing CECs loading. Conversely, the other crops were intermittently irrigated, and degradation and growth dilution lower uptake between irrigation events.

Box-plot medians (Figure 3b-c) were generally close (within 1 order of magnitude) to measurements, while for estrogens and PAR few to no measurements were available. Conversely, CBZ, TCS and SMX (having the highest data availability) showed measured values overall lower than predicted BCF_{median}. This may be due to metabolization within the plant compartments, which has been experimentally observed for CBZ in leaves (Riemenschneider et al., 2016; Goldstein et al., 2014; Malchi et al., 2014), for TCS in roots (Macherius et al., 2012) and for SMX (Dodgen et al., 2013; Bircher et al., 2015; He et al., 2017; Li et al., 2018). In the model, metabolization within plants was assumed negligible since no kinetic data are available within the existing literature to account for such process. The approach used with respect to in-plant metabolism represents a realistic worst-case scenario. Moreover, in-plant metabolism does not always lead to degradation of the chemical but may lead to the formation of (i) conjugated metabolites that are prone to be transformed back to their parent analogue (Macherius et al., 2012); (ii) other metabolites that may be as hazardous as their respective parent (e.g., the case of carbamazepine metabolites; Malchi et al., 2015).

BCF calculation was highly affected by in-soil degradation, since it increases the differences between maximum and median soil concentration (hence, the difference between BCF_{max} and BCF_{median}). In particular, BCF_{median} variation for estrogens was the most affected (≥ 2 orders of magnitude) by in-soil degradation rates. The effect was more pronounced for maize, as the longer time between irrigation events allows for larger variations of the median soil concentration than for other crops. Overall, these results further confirm the need for a standard methodology for BCF calculation to allow for inter-study comparison of empirical results.

The model also predicted mass loss above 10^{-4} mg m^{-2} $season^{-1}$ from soil to groundwater for CBZ, SMX, IBU, PFOS and PFOA (Figure S20), in agreement with the high GW concentrations measured in the area (Castiglioni et al., 2018b). Losses to groundwater were also predicted for DCF and FUR, while measurements were below detection limits, possibly due to further degradation outside the model boundary. Castiglioni et al. (2018b) also found traces of CLA and TCS in the groundwater, in disagreement with model predictions that showed almost complete accumulation in the surface soil layers, as confirmed by Chen et al. (2013) and Xu et al. (2009). The chemicals might stem from other sources (e.g. house imhoff tanks located in rural area) or reach groundwater by macropore transport.

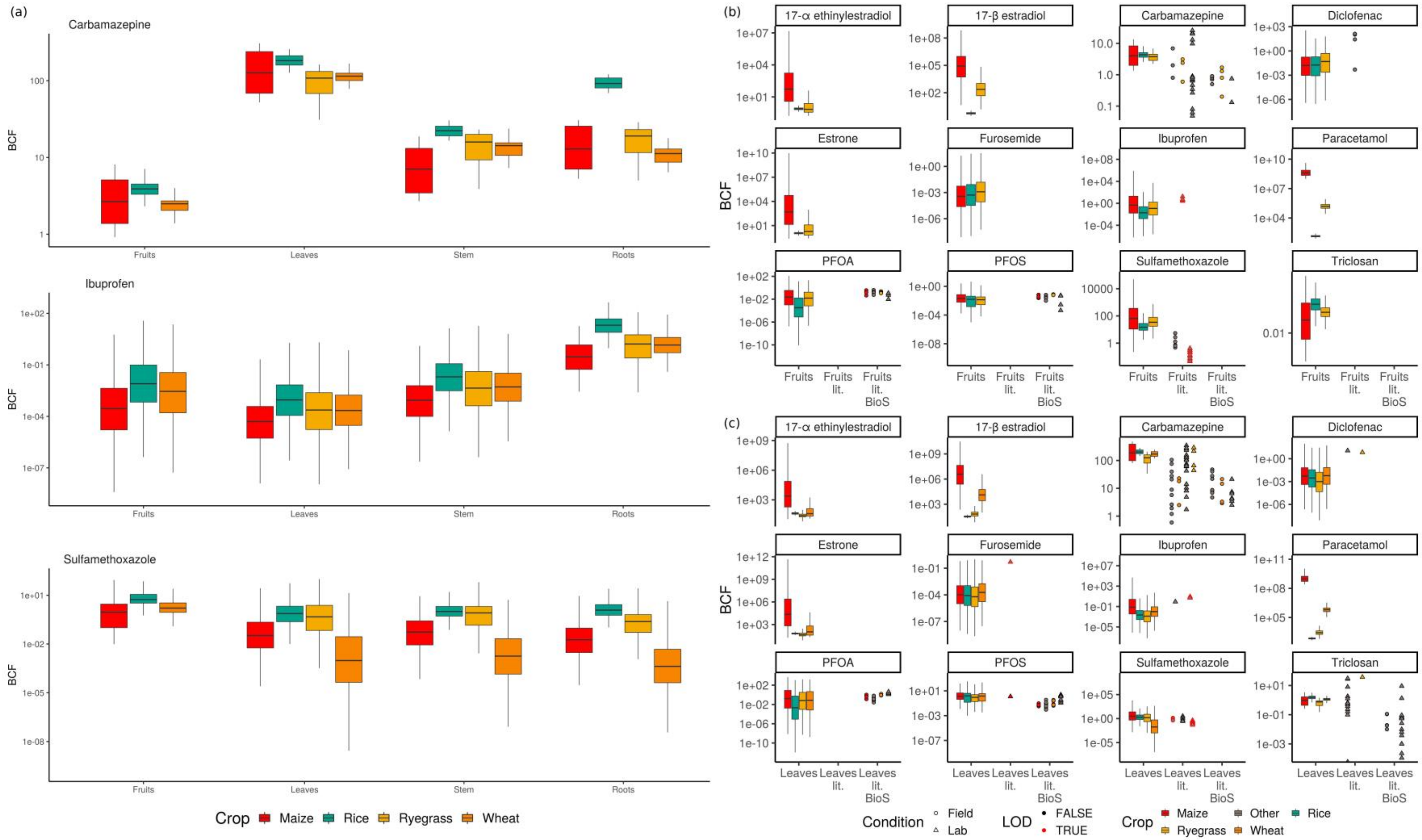

Figure 3. (a) Bioconcentration factors (BCFs, g_{dw}/g_{dw}) for CBZ, IBU and SMX in different crops and soil types. BCFs were calculated with respect to maximum soil concentrations (COLOR FIGURE). (b, c) Fruit and leaf BCFs (g_{dw}/g_{dw}) for all evaluated CECs in silage maize, winter wheat and rice in different soil types, and comparison with literature values (lit.). BCFs were calculated with respect to median soil concentrations. BioS indicates experimental studies conducted with the use of biosolids. Red borders indicate the use of a LOD value in the calculations. Refs: Bizkarguenaga et al. (2016), Blaine et al. (2013), Carter et al. (2014), Christou et al. (2017), Fu et al. (2016), Goldstein et al. (2014), Hurtado et al. (2017), Malchi et al. (2014), Mordechay et al. (2018), Navarro et al. (2017), Pannu et al. (2012), Shenker et al. (2011), Wen et al. (2014), Winker et al. (2010), Wu et al. (2010, 2012), Yager et al. (2014), Yoo et al. (2011).

3.3 Risk assessment

3.3.1 Ecological risk

Three estrogens (E1, E2 and EE2), two antibiotics (SMX and CLA), one non-steroidal anti-inflammatory drug (IBU) and one antiseptic (TCS) showed RQ_{median} above the alert thresholds at least once over the 1-year simulation. EE2 displayed the highest risk both in terms of magnitude and frequency of exceedance, with a daily median concentration always above the PNEC (RQ_{median} ~ 27), and a maximum concentration during winter corresponding to a RQ_{max} of 46. Predicted RQ_{median} for E2, CLA and TCS were approximately 1.5, with an average monthly frequency of exceeding the corresponding PNECs of 0.95, 0.79 and 0.77, respectively. IBU, E1 and SMX showed RQ_{median} below 1, although a non-negligible ecological risk (RQ_{max} ranging between 0.15 and 0.45) was shown. Other investigated CECs had an RQ below 0.1, showing low or negligible ecological risk (see Table S22). These results, in good agreement with what found by Riva et al. (2019) in the surrounding area, highlight that certain CECs may negatively affect aquatic organisms at a medium distance (approximately 12 km) from the WWTP.

3.3.2 Human health risk from dietary uptake

The estimated consumption of rice and wheat required to exceed TTCs (Table S23) showed unrealistic values (>2 kg/d per person) for all the CECs but SMX. For this compound a consumption of 10 g/d and 50 g/d (considering the 97.5^{th} rice concentration percentile) might imply potential genotoxic effects (Malchi et al., 2015) on infants and adults, respectively. Conversely, SMX had an HQ below the alert threshold of 0.1 in accordance with the work of Christou et al. (2017). Consequently, experimental measurements should be performed in rice to clarify a possible risk related to SMX. The calculated negligible human health risk is in good agreement with the findings of Malchi et al. (2014) and Riemenschneider et al. (2016).

As for the predicted risk by the HQ approach (Table 1), results indicated negligible risk for all the CECs, although an HQ (infants) of 0.3 was calculated for EE2. A comparison with the TTC could not be done, since this latter approach is not valid for classes of compounds such as estrones (Kroes et al., 2004).

To conclude, the HI value (sum of all individual HQs, see Table 1) was below 1, showing no potential risk for human health from the investigated CECs. Moreover, the risk from indirect exposure (possible biotransfer of CECs from forage to milk and beef and, subsequently to humans) was not quantified since available empirical models (Travis and Arms, 1988; Hendriks et al., 2007) failed to properly describe fate of ionisable compounds and were not validated for the CECs here considered. Mechanistic models (Rosenbaum et al., 2009; Trapp et al., 2008) predict bioaccumulation in milk and meat solely for chemicals with strong partitioning into lipids, which is not the case for the investigated compounds.

Table 1. HQs and HIs for crops irrigated with water withdrawn at the end of the channel. P97.5 stands for values calculated with the 97.5th percentile CEC concentration.

ECs	Rice		Wheat		Total	
	Median	P97.5	Median	P97.5	Median	P97.5
Infants						
SMX	2.94E-03	2.03E-02	1.86E-04	1.58E-03	3.12E-03	2.19E-02
DCF	2.66E-06	6.35E-04	6.14E-08	1.26E-05	2.72E-06	6.48E-04
IBU	1.12E-09	5.27E-07	1.21E-10	5.94E-08	1.24E-09	5.86E-07
PAR	7.12E-07	1.05E-06	5.64E-08	9.08E-08	7.69E-07	1.14E-06
CBZ	2.62E-03	3.91E-03	2.21E-03	2.80E-03	4.84E-03	6.71E-03
FUR	5.37E-08	8.49E-05	1.25E-07	9.82E-05	1.79E-07	1.83E-04
EE2	2.77E-02	2.57E-01	1.95E-03	3.85E-02	2.97E-02	2.95E-01
E2	1.07E-05	2.53E-05	8.72E-07	2.02E-06	1.15E-05	2.73E-05
E1	5.23E-04	4.82E-03	4.06E-05	7.80E-04	5.63E-04	5.60E-03
PFOS	6.98E-06	2.75E-04	5.44E-06	1.24E-04	1.24E-05	4.00E-04
PFOA	2.23E-08	1.22E-04	1.17E-06	2.66E-04	1.19E-06	3.88E-04
TCS	6.19E-09	1.79E-08	2.57E-09	1.04E-08	8.76E-09	2.83E-08
			Hazard Index		3.82E-02	3.31E-01
Adults						
SMX	4.45E-04	3.08E-03	8.88E-05	7.52E-04	5.34E-04	3.83E-03
DCF	4.03E-07	9.63E-05	2.93E-08	6.03E-06	4.33E-07	1.02E-04
IBU	1.70E-10	7.99E-08	2.93E-08	6.03E-06	2.27E-10	1.80E-07
PAR	1.08E-07	1.59E-07	2.69E-08	4.33E-08	1.35E-07	2.20E-07
CBZ	3.98E-04	5.93E-04	1.06E-03	1.33E-03	1.45E-03	1.93E-03
FUR	8.14E-09	1.29E-05	5.96E-08	4.69E-05	6.78E-08	5.97E-05
EE2	4.20E-03	3.89E-02	9.32E-04	1.84E-02	5.13E-03	5.73E-02
E2	1.62E-06	3.84E-06	4.16E-07	9.63E-07	2.03E-06	4.80E-06
E1	7.93E-05	7.30E-04	1.94E-05	3.72E-04	9.86E-05	1.10E-03
PFOS	1.06E-06	1.31E-04	2.60E-06	5.94E-05	3.65E-06	1.90E-04
PFOA	3.38E-09	1.85E-05	5.58E-07	1.27E-04	5.62E-07	1.46E-04
TCS	9.38E-10	2.71E-09	1.23E-09	4.96E-09	2.17E-09	7.67E-09
			Hazard Index		7.22E-03	6.47E-02

3.4 Risk management strategies

The adoption of a more efficient irrigation system (i.e. sprinklers) led to a calculated reduction of the human health risk due to the lower CECs load that reach the crops. Particularly, median HQs for infants decreased by 25% for EE2 and SMX. In the model simulations, direct deposition of chemicals on leaf surfaces due to sprinkling has not been considered and may lead to an additional uptake of chemicals via this pathway, while significant uptake into grains via surface deposition is unlikely. However, weak acids could reach the grains by phloem transport. We are not aware of studies addressing this process. On the other hand, the adoption of a crop-drying stage before rice harvest did not show any substantial reduction (< 2%) in the median rice concentrations of EE2 (from $3.71 \cdot 10^{-4}$ ng/g_{dw} to $3.65 \cdot 10^{-4}$ ng/g_{dw}) and SMX (from $5.21E^{-01}$ ng/g_{dw} to $5.12E^{-01}$ ng/g_{dw}). In fact, at the later stages of crop growth the transpiration rate is minimum (Hidayati et al., 2016), consequently resulting in limiting the predicted CECs uptake during this stage. To best of our knowledge no experimental studies compared the CECs uptake under different irrigation systems preventing further verification of the model results.

Although not explicitly designed to remove CECs, the existing WWTP showed to be crucial for guaranteeing human health safety. In the scenario where the WWTP was absent, only few CECs (PFOS, PFOA, DCF, FUR and CBZ) had a HQ median risk below 0.1, while it was substantially above 1 for all the other CECs. For example, HQ_{median} of TCS increased from 1.43 to 429, reaching in the worst-case scenario an HQ_{max} of 842. Predicted rice concentrations increased up to 3 orders of magnitude, especially for TCS, IBU, E1 and PAR, which are efficiently removed (>99%) by the WWTP (Castiglioni et al., 2018b). These results were in agreement with the work of Goldstein et al. (2014) and Wu et al. (2014), in which higher CECs concentrations in TWW led to higher accumulation in crops. The risk for infants associated to SMX and PAR (considering the 97.5^{th} percentile of the concentration in rice) showed a required ingestion to exceed TTC lower than 1 g d^{-1} and the HQs of E1, EE2 and SMX were 0.34, 0.26 and 0.33, respectively. Median and 97.5^{th} percentile for infants HIs increased up to 8 times, reaching values of 0.27 and 0.95. respectively. These results further indicate that irrigation with untreated wastewater requires specific attention when considering the risk posed by CECs.

4. Conclusions

This study proposed a new integrated model for simulating the fate of different contaminants of emerging concern under dynamic conditions when reclaimed wastewater is reused for irrigation purposes. By extending and integrating existing fate models, the model showed capability and flexibility in describing the fate of 13 contaminants, covering a wide range of physicochemical properties, across different compartments and over long time intervals.

Model predictions for contaminant occurrence in irrigation water and crops were generally verified with measured data, thus allowing for the evaluation of ecological and human health risk posed by wastewater discharge and reuse. Although dependent on the approach used, sulfamethoxazole and 17α-ethinylestradiol were associated to potential health risk from dietary intake of irrigated crops, particularly rice. While the existing wastewater treatment plant contributes significantly to reduce the overall risk, further reductions can be obtained by adopting more efficient irrigation practices.

Overall the proposed integrated approach represents a valuable decision support tool for assessing the safety of reclaimed wastewater reuse practices within the circular economy, particularly when considering recent developments in the regulation (EC, 2018).

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Risk assessment of contaminants of emerging concern in the context of wastewater reuse for irrigation: An integrated modelling approach

Supplementary Material

Number of pages: 32; Number of Tables: 24; Number of Figures: 20;

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SI.1 Models extension

SI.1.1 IUWS_MP

CECs are often ionized at environmentally relevant pH (Franco et al., 2010). While sorption of neutral chemicals occurs due to Van der Waals forces, in the presence of ions, the process is dominated by the stronger electrical forces. Hence, neutral molecules, anions and cations present different sorption behaviors which are furthermore affected by the degree of ionic speciation (Franco and Trapp, 2008). The Koc formula was updated accordingly to Franco et al. (2013) as shown in Eq. S1.

$$Koc_{acid} = \Phi_n 10^{0.54\ logKow+1.11} + \Phi_i 10^{0.11\ logKow+1.54} \qquad \text{(Eq. S1)}$$
$$Koc_{base} = 10^{logDow+2.78}$$

The sorption of the charged and neutral fractions of monovalent chemicals is described as a function of Kow or Dow, pK_a and, in case of acids, also the solution pH. Φ_n and Φ_i are respectively the neutral and anionic CECs fractions calculated at pH_{opt} = pH - 0.6. The range of applicability is $pK_a < 10$ for monovalent acids and $pK_a > 4$ for monovalent bases (Franco et al., 2013).

Environmental properties are intrinsically dynamic (Kunkel and Radke, 2011; Matamoros and Rodriguez, 2017) and the use of constant values would not properly describe realistic conditions. Hence, the use of external measurement inputs was allowed for the following properties:

- Sunlight intensity
- Water pH
- Air temperature
- Water temperature
- Wind speed

Irrigation is, also, seasonal dependent (Portmann et al., 2008). For this reason, the flow splitters, used to simulate the water withdrawal, were, thus, enhanced to describe a dynamic pattern throughout the year.

SI.1.2 Coupled soil-plant model (CSPM)

Figure S1 shows the modelled flows mainly responsible for CECs traslocation inside the plants.

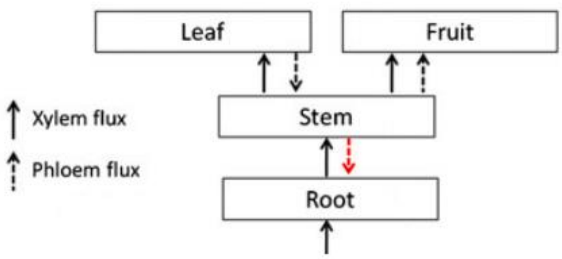

Figure S1. Modelled CECs flows inside the plants. In red the new phloem flux added.

As multiple crops are commonly grown on the same field within the same year (Borrelli et al., 2014), the model was extended to describe the succession of two different crops within the same year. Furthermore, an extra input was added to the model to account for the water and CECs mass added to the first soil layer through irrigation and the time-step used in the solution scheme was refined to prevent numerical issues.

Soil pH is not constant with depth, especially in agricultural field in which the surface layers are extensively plowed and fertilized (Zhang et al., 2017b). Therefore, a pH value was given to each of the five soil layers present in the model. Moreover, soil temperatures vary throughout the year due to the fluctuations of air temperature and solar radiation. As depth increases, temperatures are more uniform throughout the year, compared to the overlying layers (Xing and Spitler, 2017). Hence, a daily temperature was added for each of the layers 2-5, while the surface layer temperature was assumed equal to the air above.

SI.2 Chemicals

Table S1. PNECs of selected CECs.

		PNEC value (ng/L)	Reference
clarithromycin	CLA	200	Zhao et al. (2017b)
sulfamethoxazole	SMX	890	Huang et al. (2018)
diclofenac	DCF	9800	Zhao et al. (2017b)
ibuprofen	IBU	18	Huang et al. (2018)
paracetamol	PAR	367	Riva et al. (2019)
carbamazepine	CBZ	9000	Zhao et al. (2017b)
furosemide	FUR	45100	Riva et al. (2019)
17-β estradiol	E2	2	Caldwell et al. (2012)
estrone	E1	6	Caldwell et al. (2012)
17-α ethinylestradiol	EE2	0.1	Caldwell et al. (2012)
perfluorooctanoic acid	PFOA	1.07E06	Gredelj et al. (2018)
perfluorooctane sulfonate	PFOS	1.6E04	Gredelj et al. (2018)
triclosan	TCS	2.6	Gredelj et al. (2018)

SI.2.1 CECs physicochemical properties and degradation rates

Table S2 presents the physicochemical values used during the simulations. QSAR estimates of CLogP and ECOSAR of PFOS and PFOA were discarded as not reliable (Arp et al., 2006).

Table S2. Physicochemical properties of the selected CECs. All properties from Advanced Chemistry Development Inc. (2015), unless noted. (b) indicates a basic pK_a

CEC	Mol mass (g/mol)	pK_a	Vapor P (mmHg)	Log(Sw) (M)	Log(Kow)	Log(Koc)	Log(K_{HSA})
CLA	747.95	8.5 (b)	0	-3.29	3.2		2.77
SMX	253.28	5.7	1.9E-09	-2.62	0.89	2.34[28], 1.79[28], 1.3[28], 1.4[28], 2.06[28], 3.47[28]	2.86

Table S2. Cont.

DCF	296.15	4.4	1.59E-07	-5.1	4.4		4.91
IBU	206.28	4.3	1.39E-04	-3.99	3.4		4.74
PAR	151.06	10.2	1.43E-06	-0.99	0.46	1.55[1]	2.43
CBZ	236.27	-	5.78E-07	-3.33	2.3		3.91
FUR	330.74	3.5	0	-3.66	2.03		5.27
E2	272.38	10	9.8E-09	-4.64	3.36		4.41
E1	270.37	9.9	1.54E-08	-3.95	3.13		1.06
EE2	296.40	10	3.7E-09	-4.7	3.54		3.55
PFOA	414.07	2.4, 0.5, 3.8[5], 0.5[6], 1.31[7], 1.01[4], <1[15], 2.5[12], 2.8[3], 0.9[8], 0[9], 0[13], -0.21[10], 2.14[11]	3.14E-02[13], 3.11E-03[13], 3.14E-02[13], 2.4E-03[14], 2.25E-04[14], 9.02E-02[19], 1.5E-01[19]	-4.54, -1.98[2], -2.01[11], -2.09[2], -1.64[2], -2.73[8]	4.6, 7.75, 4.3[14], 5.3[8], 4.59[14], 1.92[13], 6.26[15]	2.06[17], 1.9[17], 2.17[17], 1.1[15], 3.2[15], 1.47[27]	5.02, 4.0[20], 3.4[20], 3.42[21], 4.34[22], 3.57[23], 4.38[24], 5.16[24], 4.5[24]
PFOS	500.13	-5.7, -3.7, -3.41[8], 0.14[10], -3.3[12]	2.6E-02[14], 2.54E-01[14], 2.34E-03[19], 1.13E-01[15]	-5.05, -3.84[8], -3.79[15]	2.59, 7.03, 5.25[14], 5.26[14], 2.45[16], 4.67[15]	1.6[15], 4.8[15], 2.57[17], 2.57[17], 3.1[17], 1.82[18]	5.02, 7.1[20], 3.4[20], 3.51[25], 3.6[25], 3.66[23], 5.12[23], 3.7[26]
TCS	289.54	8.8	4E-06	-4.46	4.76		4.81

References: 1: ECHA (2006), 2: Jensen et al. (2008), 3: Brace (1962), 4: Igarashi and Yotsuyanagi (1992), 5: Burns et al. (2009), 6: Vierke et al. (2013), 7: López-Fontán et al. (2005), 8: Wang et al. (2011), 9: Goss (2008), 10: Ahrens et al. (2012), 11: Nielsen (2012), 12: EFSA Scientific Commitee (2008), 13: Ding and Peijnenburg (2013), 14: Arp et al. (2006), 15: Rayne and Forest (2009b), 16: Jing et al. (2009), 17: Higgins and Luthy (2006), 18: Stevens and Coryell (2007), 19: Bhhatarai and Gramatica (2011), 20: Beesoon and Martin (2015), 21: Han et al. (2003), 22: Hebert and MacManus-Spencer (2010), 23: Chen and Guo (2009), 24: Bischel et al. (2010), 25: Wu et al. (2009), 26: Li et al. (2009), 27: Rahman et al. (2014), 28: Barron et al. (2009).

Table S3. CLA degradation rates.

Near-surface photodegradation		Biodegradation					
		Sediments		Water		Soil	
$K_{pho,nearsurf}$ (d^{-1})	Reference	$K_{bio,sed}$ (d^{-1})	Reference	$K_{bio,wat}$ (d^{-1})	Reference	$K_{bio,soil}$ (d^{-1})	Reference
0.23	Calza et al. (2013)	2.31E-03 – 2.31E-04	JRC (2003)	Negligible	Alexy et al. (2004)	< 6.93E-4 – 7.80E-3	Kodešová et al. (2016)
0.13	Gozlan and Koren (2016)			< 6.6E-03	Calza et al. (2013)		
				< 9.9E-02	Hanamoto et al. (2013)		
				3.56E-3 – 1.39E-3	Falås et al. (2013)		

Table S4. SMX degradation rates. (an) for anaerobic or anoxic conditions.

Near-surface photodegradation		Biodegradation					
		Sediments		Water		Soil	
$K_{pho,nearsurf}$ (d^{-1})	Reference	$K_{bio,sed}$ (d^{-1})	Reference	$K_{bio,wat}$ (d^{-1})	Reference	$K_{bio,soil}$ (d^{-1})	Reference.
4.62 – 5.33	Baena-Nogueras et al. (2017)	6.86E-2 – 0.14	Lai and Hou (2008)	8.66E-3	Poirier-Larabie et al. (2016)	6.08E-02 – 7.7E-02, 3.79E-2 – 4.53E-2 (an)	Lin and Gan (2011)
1.28E-2	Poirier-Larabie et al. (2016)	0.63	Radke et al. (2009)	Negligible	Baena-Nogueras et al. (2017)	4.5E-03 – 0.15	Kodešová et al. (2016)
0.71 – 4.33	Andreozzi et al. (2003)	5.1E-02 – 7E-02, 4.15E-02 (an)	Zhang et al. (2013)	1.24E-2 – 1.38E-2	Adamek et al. (2016)	0.2 – 0.73	Li et al. (2015b)
11.55, 2.77 – 5.78	Lam and Mabury (2005)	2.04E-02	Li et al. (2015c)	2.54E-3	Radke et al. (2009)	0.35	Liu et al. (2010)
9.90 – 17.33	Ryan et al. (2011)	3.65E-2	Lam et al. (2004)	Negligible	Al-Ahmad et al. (1999)		
23.1 – 2.89	Niu et al. (2013)	3.09E-2 – 5.42E-02	Xu et al. (2011)	6.08E-2	Zhang et al. (2013)		
7.22E-02 – 0.75	Boreen et al. (2004)	4.53E-03	Su et al. (2016)				
2.39 – 6.93	Bahnmüller et al. (2014)						
2.17 – 2.77	Oliveira et al. (2019)						
0.39 – 1.73	Bonvin et al. (2013)						
4.08	Willach et al. (2018)						

Table S5. DCF degradation rates. (an) for anaerobic or anoxic conditions.

Near-surface photodegradation		Biodegradation					
		Sediments		Water		Soil	
$K_{pho,nearsurf}$ (d^{-1})	Reference	$K_{bio,sed}$ (d^{-1})	Reference	$K_{bio,wat}$ (d^{-1})	Reference	$K_{bio,soil}$ (d^{-1})	Reference
17.33	Buser et al. (1998)	3.73E-03 – 0.13	Kunkel and Radke (2008)	Negligible	Baena-Nogueras et al. (2017)	2.34E-2 – 0.14	Lin and Gan (2011)
86.64	Poiger et al. (2001)	3.45E-02, 1.54E-2 – 1.84E-02 (an)	Koumaki et al. (2017)	4.08E-3	Buser et al. (1998)	3.39E-2 – 0.23	Xu et al. (2009)
1.73	Poirier-Larabie et al. (2016)	2.39E-02 – 7.7E-02	Radke and Maier (2014)	9.9E-03	Poirier-Larabie et al. (2016)	1.73	Grossberger et al. (2014)
99.02 – 115.52	Baena-Nogueras et al. (2017)	8E-3 – 2.6E-2	Gröning et al. (2007)				
34.66	Packer et al. (2003)						
0.35 – 3.47	Andreozzi et al. (2003)						
2.31 - 23.1	Koumaki et al. (2015)						
231.05	Zhang et al. (2017a)						
266.59 – 277.26	Zhang et al. (2011)						
6.93	Vochezer (2010)						
11.55	Radke et al. (2010)						

Table S6. IBU degradation rates. (an) for anaerobic or anoxic conditions.

Near-surface photodegradation		Biodegradation					
		Sediments		Water		Soil	
$K_{pho,nearsurf}$ (d^{-1})	Reference	$K_{bio,sed}$ (d^{-1})	Reference	$K_{bio,wat}$ (d^{-1})	Reference	$K_{bio,soil}$ (d^{-1})	Reference
1.68E-03 – 2.77E-02	Yamamoto et al. (2009)	3.65E-02 – 9.9E-02, 1.27E-03 – 3.35E-03 (an)	Conkle et al. (2012)	1.2E-02	Baena-Nogueras et al. (2017)	4.56E-02 – 6.66E-02	Lin and Gan (2011)
7.97E-02	Fono et al. (2006)	0.43, 9.52E-03 – 2.11E-02 (an)	Koumaki et al. (2017)	3.47E-02	Buser et al. (1999)	0.11 – 0.76	Xu et al. (2009)
5.13E-02	Baena-Nogueras et al. (2017)	0.14 – 0.28	Kunkel and Radke (2008)	3.47E-02 – 3.69E-02	Yamamoto et al. (2009)	2.28E-02 – 4.06E-04	Carr et al. (2011)
0.58 – 0.72	Packer et al. (2003)	8.56E-02 – 2.26, 1.47e-02	Radke and Maier (2014)			0.86	Grossberger et al. (2014)
6.30	Peuravuori and Pihlaja (2009)	> 0.12	Löffler et al. (2005)				
1.81E-02	Koumaki et al. (2015)	0.36 – 0.39	Li et al. (2015c)				
1.12	Lin and Reinhard (2005)						
6.93	Jakimska et al. (2014)						

Table S7. PAR degradation rates.

Near-surface photodegradation		Biodegradation					
		Sediments		Water		Soil	
$K_{pho,nearsurf}$ (d^{-1})	Reference	$K_{bio,sed}$ (d^{-1})	Reference	$K_{bio,wat}$ (d^{-1})	Reference	$K_{bio,soil}$ (d^{-1})	Reference
0.58 – 17.32	Baena-Nogueras et al. (2017)	0.77	Lam et al. (2004)	1.2E-02 – 0.33	Yamamoto et al. (2009)	>0.69	Li et al. (2014)
0.33	Carlos et al. (2012)	0.31	Lin et al. (2010)	2.47E-02	Baena-Nogueras et al. (2017)	3.65 – 3.85	Li et al. (2015b)
0.3 – 0.46	Yamamoto et al. (2009)	0.22	Löffler et al. (2005)				
Negligible	Kawabata et al. (2013)						
2.69E-02	Peuravuori (2012)						
4.95E-02 – 0.69	De Laurentiis et al. (2014)						
0.95 – 2.47	Li et al. (2017b)						

Table S8. CBZ degradation rates. (an) for anaerobic or anoxic conditions.

Near-surface photodegradation		Biodegradation					
		Sediments		Water		Soil	
$K_{pho,nearsurf}$ (d^{-1})	Reference	$K_{bio,sed}$ (d^{-1})	Reference	$K_{bio,wat}$ (d^{-1})	Reference	$K_{bio,soil}$ (d^{-1})	Reference
0.17	Calza et al. (2013)	2.63E-03 – 4.2E-03, 1.58E-03 – 2.47E-03 (an)	Conkle et al. (2012)	2.97E-03 – 5.55E-03	Yamamoto et al. (2009)	4E-03 – 1.5E-02	Li et al. (2013)
6.93E-03 – 3.47E-02	Andreozzi et al. (2013)	Negl – 1.2E-02	Radke and Maier (2014)	Negligible	Baena-Nogueras et al. (2017)	< 6.93E-04 – 5.37E-03	Kodešová et al. (2016)
7.92E-03 – 0.2	Yamamoto et al. (2009)	2.11E-03	Löffler et al. (2005)	1.1E-03 – 2.2E-03	Durán-Álvarez et al. (2015)	< 3.47E-03 – 4.28E-03	Grossberger et al. (2014)
Negligible – 1.39	Baena-Nogueras et al. (2017)	Negl	Li et al. (2015c)	< 6.6E-03	Calza et al. (2013)		
0.34	Carlos et al. (2012)	8.45E-03	Lam et al. (2004)				
0.22 – 0.77	Dong et al. (2015)						
0.16	Durán-Álvarez et al. (2015)						
1.71E-02	Peuravuori and Pihlaja (2009)						
0.87	Doll and Frimmel (2003)						
0.14 – 2.77	Lam and Mabury (2005)						
1.26E-02	De Laurentiis et al. (2012)						

Table S9. FUR degradation rates.

Near-surface photodegradation		Biodegradation					
		Sediments		Water		Soil	
$K_{pho,nearsurf}$ (d^{-1})	Reference	$K_{bio,sed}$ (d^{-1})	Reference	$K_{bio,wat}$ (d^{-1})	Reference	$K_{bio,soil}$ (d^{-1})	Reference
86.64	Hanamoto et al. (2013)	4.33E-02 – 4.62E-02	Li et al. (2015c)	< 0.1	Hanamoto et al. (2013)	4.91E-03 – 1.65E-02	Polesel et al. (2015b)
69.31	Yagi et al. (1991)	3.47E-02 – 4.95E-02	Radke and Maier (2014)	8.11E-04*	Khan and Ongerth (2004)		
34.66	Jakimska et al. (2014)	1.33E-02 – 4.62E-02	Fenner et al. (2016)				

*: calculated correcting degradation rate with canal TSS

Table S10. E2 degradation rates. (an) for anaerobic or anoxic conditions.

Near-surface photodegradation		Biodegradation					
		Sediments		Water		Soil	
$K_{pho,nearsurf}$ (d^{-1})	Reference	$K_{bio,sed}$ (d^{-1})	Reference	$K_{bio,wat}$ (d^{-1})	Reference	$K_{bio,soil}$ (d^{-1})	Reference
2.77 – 17.32	Liu et al. (2017)	5.1E-02 – 5.33E-02, 1.75E-02 – 2.6E-02 (an)	Robinson et al. (2017)	~ 1E-03	Bradley et al. (2009)	6.3	Colucci and Topp (2002)
2.17 – 2.77	Leech et al. (2009)	2.57	Mashtare et al. (2013)	7.97E-02 – 3.47	Jurgens et al. (2002)	0.17 – 0.46	Carr et al. (2011)
1.73 – 2.77	Chowdhury et al. (2011)	3.3E-02	Czajka and Londry (2006)	0.12 – 0.23	Liu et al. (2011)	0.46 – 3.15	Colucci et al. (2001)
2.17 – 2.77	Whidbey et al. (2012)	6.3, 1.05 – 1.87 (an)	Jurgens et al. (2002)				
8.66	Lin and Reinhard (2005)	>1E-02	Bradley et al. (2009)				
0.13	Jurgens et al. (2002)	1.87 – 7.7	Zhang et al. (2016)				
0.83 – 1.24	Li et al. (2017a)						
2.89 – 5.78	Silva et al. (2016b)						

Table S11. EE2 degradation rates.

Near-surface photodegradation		Biodegradation					
		Sediments		Water		Soil	
$K_{pho,nearsurf}$ (d^{-1})	Reference	$K_{bio,sed}$ (d^{-1})	Reference	$K_{bio,wat}$ (d^{-1})	Reference	$K_{bio,soil}$ (d^{-1})	Reference
0.16	Matamoros et al. (2009)	6.42E-03	Wu et al. (2015a)	Negligible	Wu et al. (2015a)	0.83	Colucci and Topp (2002)
3.85	Ren et al. (2016)	0.16	Mashtare et al. (2013)	4.08E-02	Jurgens et al. (2002)	3.34E-03 – 3.07E-02	Carr et al. (2011)
0.72	Zuo et al. (2013)	Negligible	Czajka and Londry (2006)	6.42E-03	Zuo et al. (2013)	2.15E-02 – 0.37	Colucci and Topp (2001)
3.46	Whidbey et al. (2012)			< 4.95E-02	Matsuoka et al. (2005)		
6.93	Lin and Reinhard (2005)			Negligible	Liu et al. (2011)		
0.13	Jurgens et al. (2002)						
0.73 -3.46	Ren et al. (2017a)						
2.4E-02 – 0.5	Atkinson et al. (2011)						
0.89 – 7.7	Silva et al. (2016b)						
0.77	Grzybowski and Szydlowski (2014)						
0.63 – 0.69	Ren et al. (2017b)						
1.39	Wu et al. (2015a)						

Table S12. E1 degradation rates. (an) for anaerobic or anoxic conditions.

Near-surface photodegradation		Biodegradation					
		Sediments		Water		Soil	
$K_{pho,nearsurf}$ (d^{-1})	Reference	$K_{bio,sed}$ (d^{-1})	Reference	$K_{bio,wat}$ (d^{-1})	Reference	$K_{bio,soil}$ (d^{-1})	Reference
2.31	Atkinson et al. (2011)	6.8E-02 - 0.24, 3.14E-02 – 4.41E-02 (an)	Robinson et al. (2017)	6.36E-02 – 6.93	Jurgens et al. (2002)	1.22E-02 – 0.22	Carr et al. (2011)
4.33 – 7.7	Silva et al. (2016a)	1.93E-02	Mashtare et al. (2013)	0.17 – 3.47	de Mes et al. (2005)	0.41 – 1.14	Colucci et al. (2001)
2.48 – 4.33	Caupos et al. (2011)	1.65, 4.88E-02 – 6.03E-02 (an)	Jurgens et al. (2002)				
13.86 – 34.66	Chowdhury et al. (2011)	>1E-02	Bradley et al. (2009)				
2.48 – 4.33	Lin and Reinhard (2005)						

*: calculated correcting degradation rate with canal TSS

Table S13. PFOA degradation rates.

Near-surface photodegradation		Biodegradation					
		Sediments		Water		Soil	
$K_{pho,nearsurf}$ (d^{-1})	Reference	$K_{bio,sed}$ (d^{-1})	Reference.	$K_{bio,wat}$ (d^{-1})	Reference	$K_{bio,soil}$ (d^{-1})	Reference
4.22E-04	Vaalgaama et al. (2011)	Negligible	Liou et al. (2010)	Negligible	Liou et al. (2010)	Negligible	Liou et al. (2010)
<1.98E-03	Giesy et al. (2010)						

Table S14. PFOS degradation rates.

Near-surface photodegradation		Biodegradation					
		Sediments		Water		Soil	
$K_{pho,nearsurf}$ (d^{-1})	Reference	$K_{bio,sed}$ (d^{-1})	Reference	$K_{bio,wat}$ (d^{-1})	Reference	$K_{bio,soil}$ (d^{-1})	Reference
1642	Brooke et al. (2004)	Negligible	Avendano et al. (2015)	Negligible	Avendano et al. (2015)	Negligible	Avendano et al. (2015)

Table S15. TCS degradation rates.

Near-surface photodegradation		Biodegradation					
		Sediments		Water		Soil	
$K_{pho,nearsurf}$ (d^{-1})	Reference	$K_{bio,sed}$ (d^{-1})	Reference	$K_{bio,wat}$ (d^{-1})	Reference	$K_{bio,soil}$ (d^{-1})	Reference
23.1 - 115.52	Baena-Nogueras et al. (2017)	7.2E-03	Wu et al. (2015a)	Negligible	Wu et al. (2015a)	3.85E-02	Wu et al. (2015a)
23.1	Koumaki et al. (2015)	6.36E-02, Negligible (an)	Koumaki et al. (2018)	1.92E-02	Baena-Nogueras et al. (2017)	4.42E-02 – 5.48E-02	Xu et al. (2009)
3.15	Durán-Álvarez et al. (2015)	1.22E-02 – 1.29E-02	NICNAS (2009)	0.69E-02 – 2.1E-02	Durán-Álvarez et al. (2015)	9.78E-03 – 1.74E-03	Carr et al. (2011)
3.3	Latch et al. (2005)					1.2E-02 – 2.17E-02	Wu et al. (2009)
69.31	Lindström et al. (2002)						
23.1	Singer et al. (2002)						
34.66 – 69.31	Tixier et al. (2002)						
4.62	Mezcua et al. (2004)						
3.01	Martínez-Zapata et al. (2013)						
231.04	Sanchez-Prado et al. (2006)						
0.2	Wu et al. (2015a)						

SI.3 Model parameters and model inputs

The environmental conditions used in RWQM1s1_MP are shown in Table S16. All values were taken from ARPA (Agenzia Regionale Protezione Ambiente) measurements databases for the year 2016. Regarding the CSPM, the model layers were adapted to the stratigraphy of the various soils with the parameters shown in Table S17. Photodegradation in rice paddies was assumed to be negligible due the sediment in suspension and plants shading. Eventual surface runoff of water was not modeled.

Table S16. Measurements and parameters used to characterize environmental conditions for the RWQM1s1_MP model

Parameter	Source	Notes
Wind speed at 10 m above ground	ARPA	Hourly measurements
Air temperature	ARPA	Hourly measurements
Sunlight intensity	ARPA	Hourly measurements
Water temperature	ARPA	Monthly measurements at end of canal
pH	ARPA	Canal measurements average ±1 daily fluctuation (Simonsen and Harremoës, 1978)
TWW entering the canal	Mazzini et al. (2013)	Daily flow variations and rain events neglected
TWW CECs concentrations	Castiglioni et al. (2018a, 2018b)	Converted dissolved to total concentrations thanks to equations in Chapra (1997)
Algae, heterotrophs and nitrifying bacteria concentrations		Initially left as default and then calibrated
Algae and bacterial growth parameters	Vanrollenghem et al. (2001)	
Phosphorous sorption and desorption	Chapra (1997)	

Table S17. Environmental parameters and sources used for the CSPM. LOSAN is a publicly available soil database provided by ERSAF (Ente Regionale per i Servizi all'Agricoltura e alle Foreste), CRA-CMA stands for Unità di Ricerca per la Climatologia e la Meteorologia applicate all'Agricoltura

Parameter	Source	Notes
Soil organic carbon	LOSAN	
Soil layer pH	LOSAN	
FC and PWP	LOSAN	Estimated from granulometries using correlations by Rawls et al. (1982)
Soil layers bulk density	LOSAN	Estimated from horizon-specific pedo-transfer functions from SOILQUALIMON report (Brenna et al., 2010)
Air temperature	ARPA	
Rainfall	ARPA	
Relative humidity	ARPA	
Potential evaporation	CRA-CMA	Obtained thanks to correction of potential evapotranspiration using $K_{c,ini}$ (1.05 rice, 0.3 other crops) (Legind et al., 2012; Polesel et al., 2015; Allen et al., 1998)
Soil layer temperature	CRA-CMA	Extrapolated from measurements at depths of 10 and 50 cm thanks to the sinusoidal functions in Xing and Spitler (2017).

SI.3.1 Soil properties

Table S18. Modeled soil properties.

Horizon bottom depth (cm)	pH	Organic carbon (%)	Field capacity (L/L)	Wilting point (L/L)	Bulk density (g/cm3)
Soil 1: silage maize and ryegrass					
13	7.3	4.9	0.36	0.14	1.09
38	6.9	0.64	0.23	0.10	1.52
60	7.8	0.64	0.31	0.13	1.32
75	7.6	0.5	0.38	0.21	1.80
100	7.5	0.37	0.32	0.14	1.59
Soil 2: silage maize and ryegrass, winter wheat					
20	6.6	1.27	0.24	0.09	1.45
40	6.6	1.27	0.24	0.09	1.45
60	6.7	0.16	0.18	0.09	1.48
80	6.7	0.16	0.18	0.09	1.48
100	6.7	0.16	0.18	0.09	1.48
Soil 3: rice and ryegrass, winter wheat					
35	6.1	2	0.26	0.11	1.33
45	6.9	0.72	0.21	0.08	1.49
67.5	7.2	0.63	0.16	0.06	1.41
90	7.2	0.63	0.16	0.06	1.41
100	7.4	0.44	0.23	0.12	1.49

Pseudo-steady state concentrations of the layers in each modeled soil were obtained with median concentration in TWW as irrigation concentration and median soil degradation rate and used as initial concentrations. For the crop rotation consisting of rice and ryegrass and winter wheat, the soil concentrations at the end of the rice and ryegrass years were used as represented the worst case soil concentration.

SI.3.2 Plant parameters

Table S19. Parameters used for crop modeling. Parameters not noted were left as default.

	Value	Reference	Notes
Maize			
Irrigation	400 mm/season	Borrelli et al. (2014)	
Germination date	20-05	Borrelli et al. (2014)	
Harvest date	30-09	Borrelli et al. (2014)	
Transpiration coefficient	60 L/kg fw	Legind et al. (2012)	
Water content roots	0.84 g/g	Wang et al. (1991)	
Final root mass	2.58 kg fw/m^2	Legind et al. (2012)	
Growth rate	0.081 1/d	Legind et al. (2012)	
Final stem mass	3.61 kg fw/m^2	Legind et al. (2012)	
Final leaf mass	0.96 kg fw/m^2	Legind et al. (2012)	
Final fruit mass	1.78 kg fw/m^2	Legind et al. (2012)	
Water content fruit	0.76	USDA (2018)	
Ryegrass			
Irrigation	210 mm/season	FAO (2007)	Calculated subtracting rainfall from water requirements
Germination date	9-12 with silage maize – 30/10 with rice	Borrelli et al. (2014), Nelli and Sodi (2007)	
Harvest date	14-05 with silage maize – 31/03 with rice	Borrelli et al. (2014), Nelli and Sodi (2007)	
Final root mass	2.35 kg fw/m^2		Assumed equal to winter wheat since same family (Poaceae)
Final stem mass	1.8 kg fw/m^2	Tabaglio et al. (2007), Abraha and Savage (2008)	Calculated assuming water content = 0.8
Final leaf mass	2.2 kg fw/m^2	Tabaglio et al. (2007), Abraha and Savage (2008)	Calculated assuming water content = 0.8
Initial fruit mass	1E-05 kg fw/m^2	Martiniello (1999)	To halt fruit development

Table S19. Cont.

Winter wheat			
Irrigation	100 mm/season	Polesel et al. (2015)	
Germination date	1-03	Legind et al. (2012)	
Harvest date	15-07	Legind et al. (2012)	
Final root mass	2.35 kg fw/m^2	Legind et al. (2012)	
Final stem mass	0.78 kg fw/m^2	Legind et al. (2012)	
Final leaf mass	1.81 kg fw/m^2	Legind et al. (2012)	
Final fruit mass	1.45 kg fw/m^2	Legind et al. (2012)	
Rice			
Irrigation	21.6 mm/day	Nelli and Sodi (2007)	
Germination date	6-04	Nelli and Sodi (2007)	
Harvest date	30-09	Nelli and Sodi (2007)	
Transpiration coefficient	52	Van der Vorm (1980)	
Roots/Stem/Leaf growth rate	0.068	Confalonieri and Bocchi (2005)	
Fruit growth rate	0.13		Doubled compared to plant growth rate similarly to what observed for winter wheat and to match model ripening with agronomic data
Final root mass	3.30	Confalonieri and Bocchi (2005)	
Final stem mass	1.76	Confalonieri and Bocchi (2005)	
Final leaf mass	1.92	Confalonieri and Bocchi (2005)	
Final fruit mass	0.94	Confalonieri and Bocchi (2005)	
Water content root	0.95	Zhang and Webster (2002); Henry et al. (2012)	Calculated based on fresh weight measurements and roots to shoots ratio
Water content fruit	0.23	Rice Knowledge Bank (2017)	

The ratio of phloem to xylem flux for PAR, SMX, IBU and FUR was set to 0.05, a median value between day and night. For the other CECs such ratio was set to 0 as considered non phloem-systemic based on the distinction by Kleier and Hsu (1996) relying on CECs Kow and pK_a. The phloem systemicity of DCF and PFOA was treated as uncertain as potentially affected by plant-specific parameters.

SI.4 Uncertainty propagation

The preliminary uncertainty analysis (UA) of the IUWS_MP model for traditional pollutants was carried out varying the parameters in Table S20. Parameters uncertainty was based on Reichert and Vanrollenghem (2001) considering two classes of confidence: poorly known parameters were varied by 50% (Class 2), while better known parameters were varied by 20% (Class 1). CBZ, DCF and TCS, CECs with different physicochemical characteristics, were chosen amongst the thirteen selected to be tested. Random parameters combinations were obtained through 1000 Latin hypercube samplings for each CEC.

Table S20. Uncertainty classes of parameters for the uncertainty analysis of the traditional pollutants submodel.

Parameter	Class	Parameter	Class
Heterotrophic bacteria input concentration	2	First stage nitrifiers (AOBs) input concentration	2
Phosphate adsorption rate	2	Algae input concentration	2
Saturation coefficient for aerobic growth of heterotrophs on dissolved organic substrate	2	Mean particle diameter	2
Slope	1	Saturation coefficient for growth of AOBs on ammonia	2
Maximum aerobic specific growth rate for heterotrophic biomass	1	Manning n value	1
Top canal width	1	Maximum aerobic specific growth rate for AOBs	1
Depth of canal filled to bank	1		

Successively, the uncertainty regarding the organic micropollutants IUWS_MP submodel and CSPM parameters on CECs concentrations were assessed through a Monte Carlo UA varying the parameters in Table S21. When no anoxic sediment biodegradation rates were found in literature, the aerobic values decreased by an order of magnitude were used. In case only one or two values were found, uniform distributions were used considering either a 10% variation or the range between the two values. The uncertainty of IUWS_MP was estimated thanks to 1000 runs for each water water withdraw scenario. The choice of the number of CSPM runs was based on the comparison of the percentiles from simulations consisting of an increasing amount of runs to the ones resulting from a 5000 runs simulation. As the percentiles from a 2000 runs simulation with Latin hypercube sampling differed negligibly from the 5000 runs simulation, the mentioned settings were chosen for the remaining simulations.

Table S21. Varied parameters during the IUWS_MP and CSPM Monte Carlo uncertainty analyses

Parameter	Distribution	Source	Notes
TWW CEC concentrations	Triangular	Castiglioni et al. (2018a, 2018b)	Inf: minimum value/LOD Mode: median value/0.5*LOQ Sup: maximum value/LOQ
Water aerobic biodegr. rate Sediment aerobic biodeg. rate Sediment anoxic biodegr. rate Soil dissipation rate Photodegradation rate	Empirical, triangular	Tables S4 – S16	Choice based on the quantity of experimental values found. Values outside 1.5*IQR (interquartile range) considered as outliers. Triangular distributions based on extreme values and medians
pK_a Kow Solubility Vapor pressure K_{HSA} Kaw (only perfluorinated chemicals)	Empirical, triangular	Table S3	Choice based on the quantity of experimental values found
Irrigation concentration	Triangular	Surface water model	Inf: 2.5th percentile canal conc. Mode: modal canal conc. Sup: 97.5th percentile canal conc.
pH in cytosol pH in vacuole pH in phloem pH in xylem	Uniform	Felle (2001), Felle et al. (2005), Johannes et al. (2001), Tournaire-Roux et al. (2003)	10% variation is comparable to observed fluctuations
Transpiration coeff. Root mass Root growth rate Stem growth rate Leaves growth rate Fruits growth rate	Uniform		Variation equal to 10% to avoid numerical errors
Arrhenius temperature correction coeff.	Lognormal	EFSA (2007)	Median: 1.099 95th percentile: 1.144

Other parameters were varied during the analysis of specific CECs to either prevent numerical errors (SMX, PAR, E2), include uncertainty (PFOA, DCF) and improve model results (CLA, PFOS):

- PFOA and DCF phloem flux was set in 50% of the runs as 0;
- CLA's Koc was set to 10176 L/kg to match the value from the equations in Franco and Trapp (2008);
- SMX and PFOS KOC was varied as the other physicochemical properties;

- The soil structure during PAR simulations was modified to 3 layers of 33 cm whose soil properties were calculated as weighted average of the original layers. The dissipation rate was, also, set to the minimum value and the Koc from ECHA (2006) was used;
- The dissipation rate of E2 was limited to 1 d^{-1}.

Successively, the monthly medians of the total CECs concentrations taken at four locations along the canal were fitted with a first-order dissipation rate thanks to the use of Matlab R2016a and the estimated traveling times provided by IUWS_MP model. Yearly best- and worst-case attenuation rates were calculated for all the modeled CECs and compared to literature as a further validation.

Such attenuation rates and influent CECs concentrations (Castiglioni et al., 2018a) were used to estimate the expected concentrations along the canal in case of the absence of the upstream WWTP. Best- and worst-case scenarios were calculated respectively using low concentrations and high rates, and high concentrations and low rates. The median scenarios were obtained thanks to the median concentrations and the mean between the two attenuation rates.

The fruit CECs concentrations in case of the absence of the WWTP were estimated thanks to the expected median concentrations at the end of the canal which were used to reach a pseudo-steady state in the coupled soil-plant model. Successively, the median CECs concentration of the first layer at pseudo-steady state was multiplied by the median or the 97.5th percentile BCFs, calculated from the previous Monte Carlo uncertainty analyses, to estimate of the median and 97.5th percentile fruit concentration.

SI.5 Sensitivity analyses (SA)

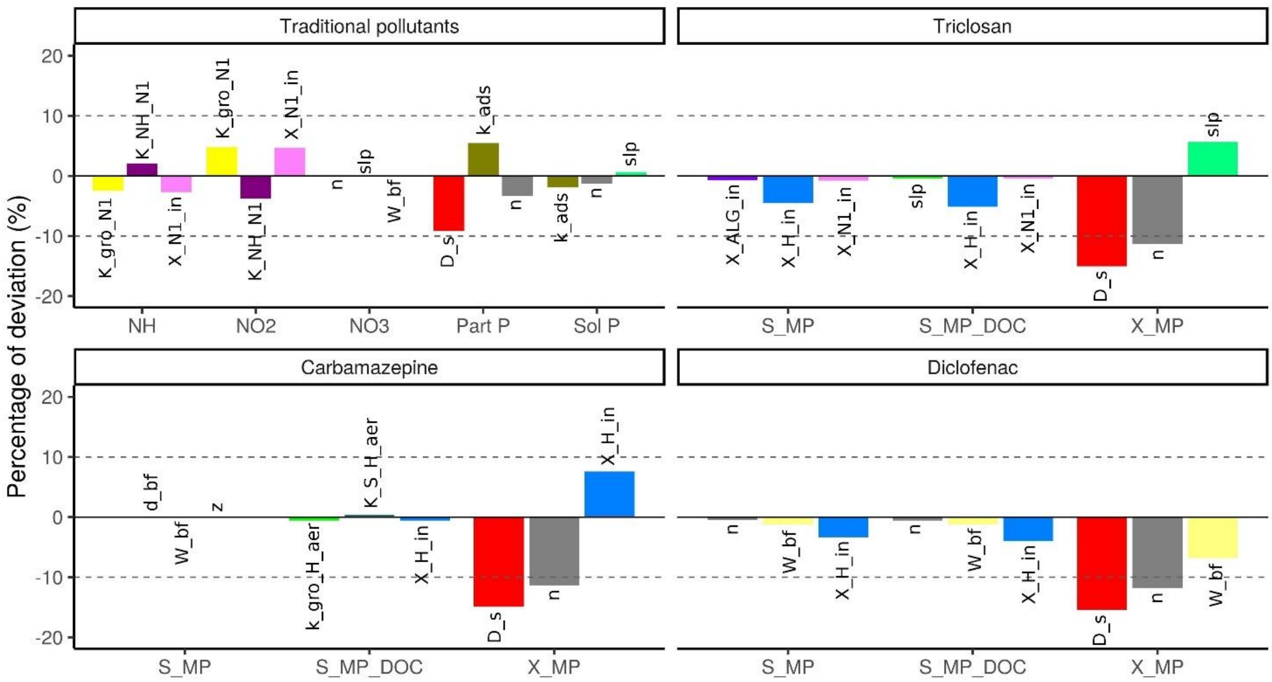

Figure S2. Deviation caused by increments of the parameters in the traditional pollutants submodel. S_MP, S_MP_DOC and X_MP indicate respectively the following fractions of a CEC: dissolved, sorbed on colloids and sorbed on TSS.

	C fruit			C leaves			C stem			C roots			C soil, L1			C soil, L2			C soil, L3			C soil, L4			C soil, L5			Leaching		
	CBZ	DCF	TCS	CBZ	DCF	TCS	CBZ	DCF	TCS	CBZ	DCF	TCS	CBZ	DCF	TCS	CBZ	DCF	TCS	CBZ	DCF	TCS	CBZ	DCF	TCS	CBZ	DCF	TCS	CBZ	DCF	TCS
Temp correction coeff			1		1	1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	
Initial water content L2-5																-1		-1	-1		-1	-1		-1	-1		-1	2		2
Soil field capacity														-1	-1	-1		-1		-1		-1	-1	-1	-1	-1	-1	2	2	2
Soil pH		2			2			2			2						-1			-1										
pH inside cytosol		2			2			2			2																			
pH inside phloem		2	2					2																						
pH inside xylem		1			2			2			2																			
Final root mass										2																				
Fruit growth rate	2		2																											
Leaf growth rate	2																-1											2	-1	2
Root growth rate	2		2	2		2											-1											2	-1	2
Soil organic carbon	2		2				-1		-1	2		-1	-1		-1	-1			-1		-1	-1		-1						
Transpiration coeff	2		2	2		2			-1	2		-1					-1					-1		-1	-1		-1	2	-1	2
Water % stem and leaves				2		2	2		2																					
Ratio Phloem to xylem flux	2		2						-1																					
Water % roots												2																		
Layers thickness														-1			-1													
Soil bulk density													-1						-1			-1								

2 WITH and NO degradation 1 Only WITH degradation -1 Only NO degradation

Figure S3. Coupled soil-plant model sensitive parameters in presence or absence of degradation.

SI.6 Fate analysis

SI.6.1 Traditional pollutants

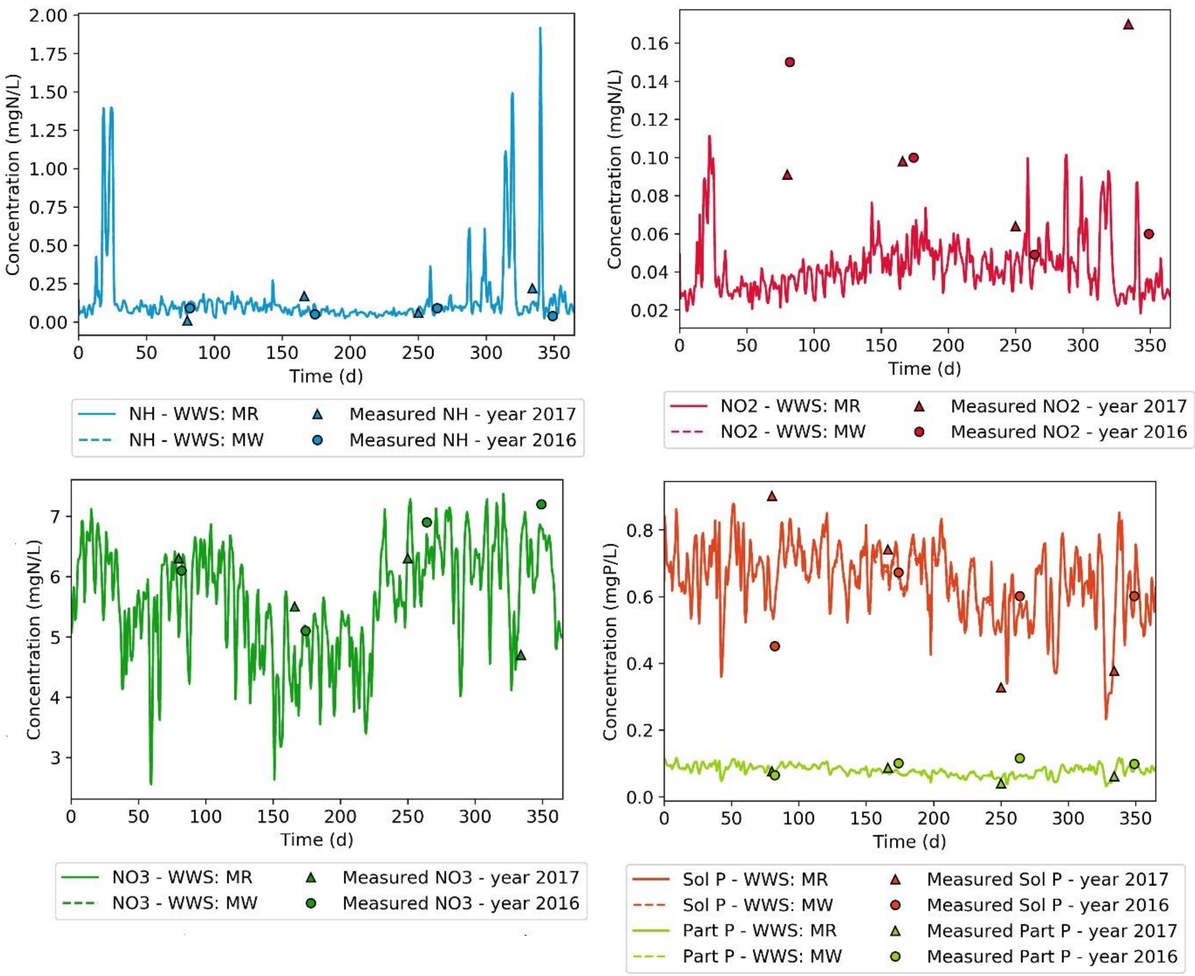

Figure S4. Traditional pollutants calibrated concentrations and measured values in canal. NH = ammonium, NO2 = nitrite, NO3 = nitrate, Sol P = soluble phosphorus, Part P = particulate phosphorus.

SI.6.2 Uncertainty of CECs concentrations in canal

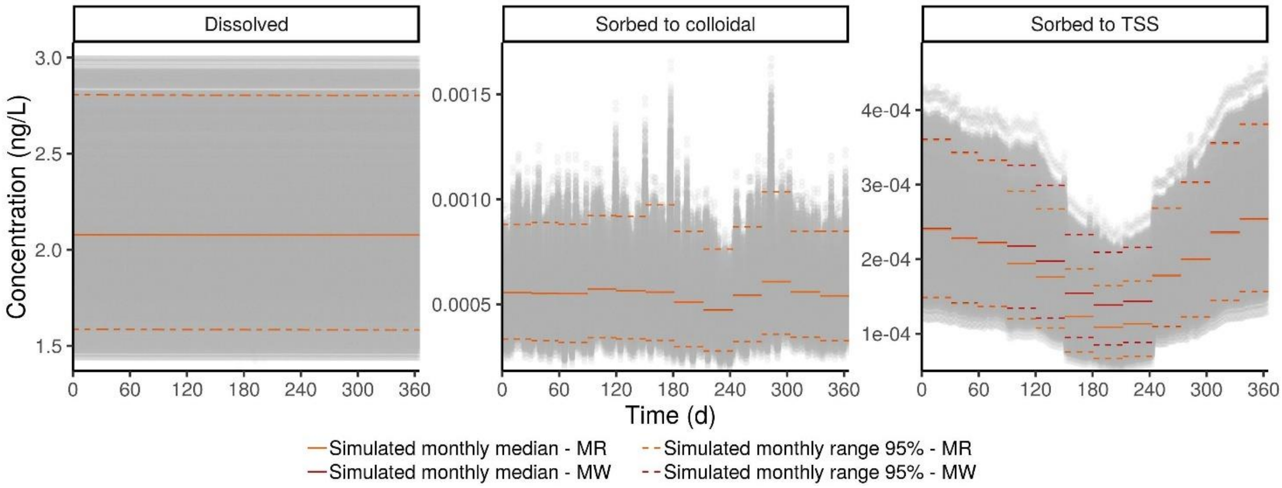

Figure S5. PFOS midday predicted concentration ranges. Days starting from January 1st until December 31st.

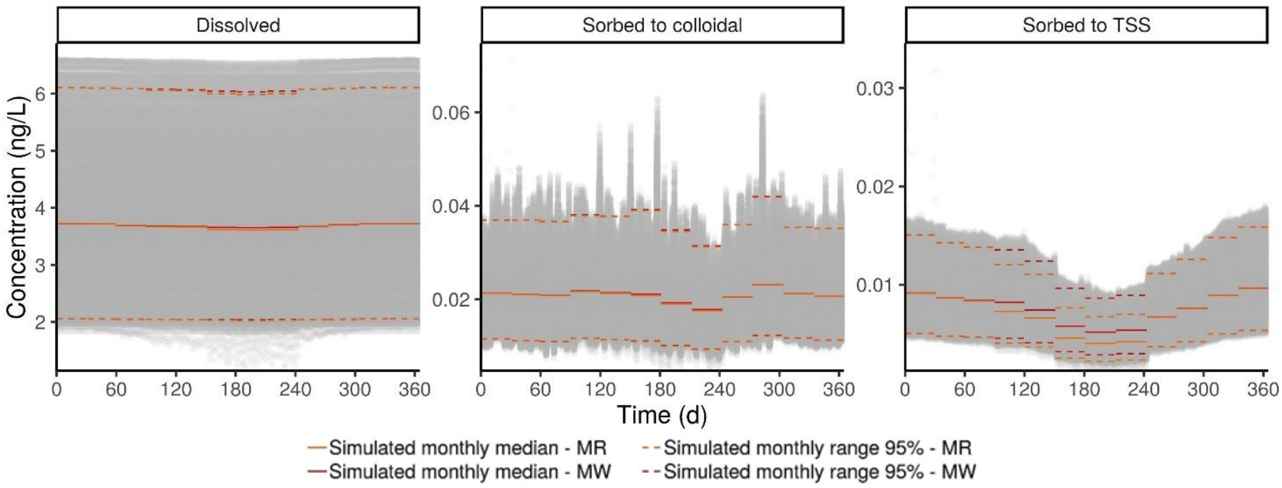

Figure S6. TCS midday predicted concentration ranges. Days starting from January 1st until December 31st.

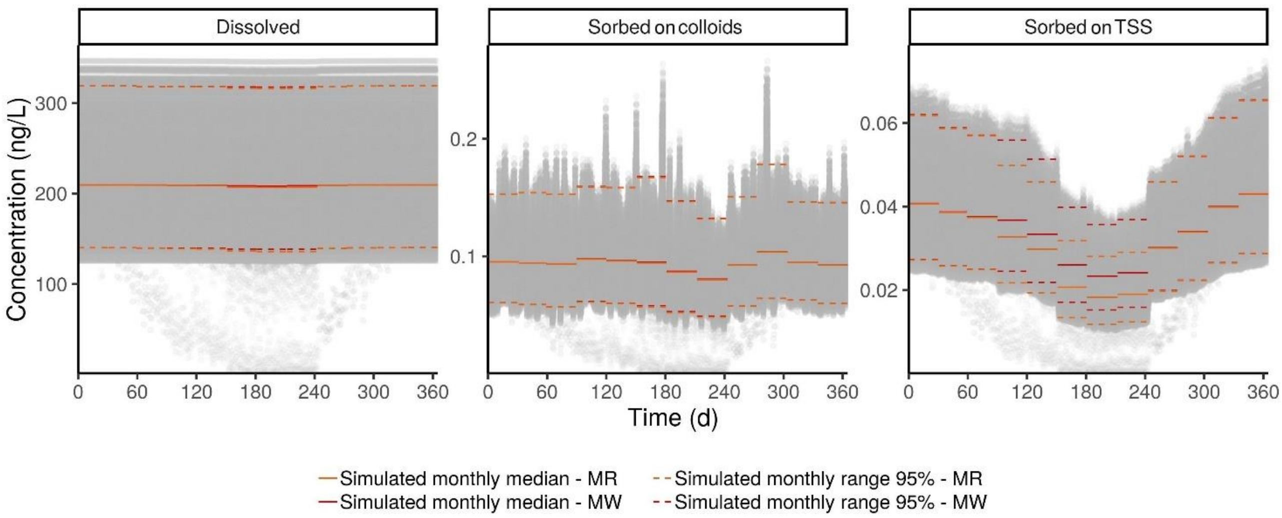

Figure S7. CBZ midday predicted concentration ranges. Days starting from January 1st until December 31st.

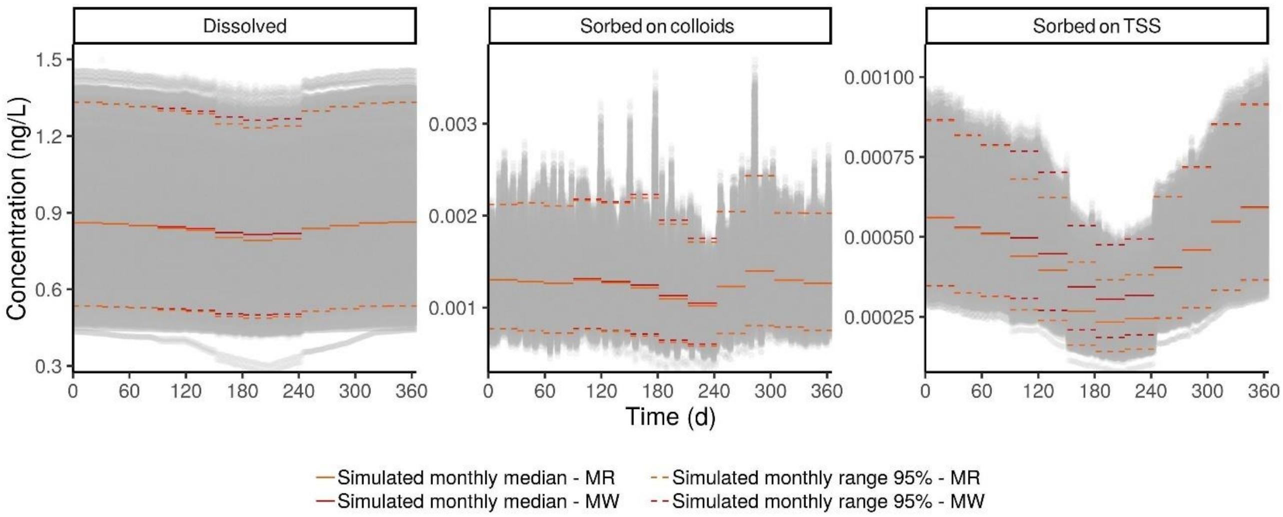

Figure S8. E1 midday predicted concentration ranges. Days starting from January 1st until December 31st.

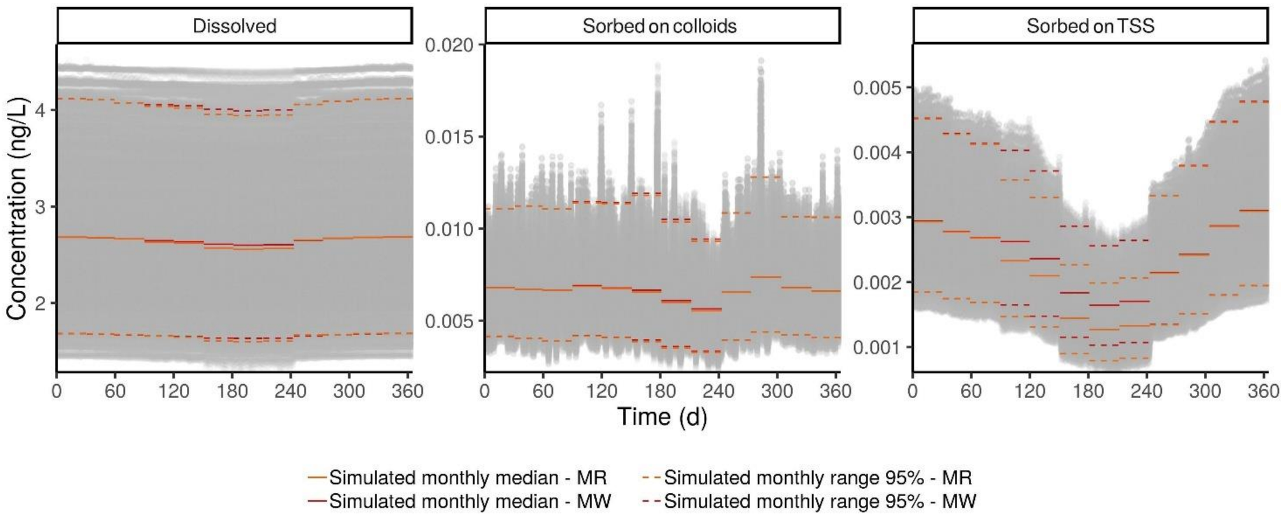

Figure S9. EE2 midday predicted concentration ranges. Days starting from January 1st until December 31st.

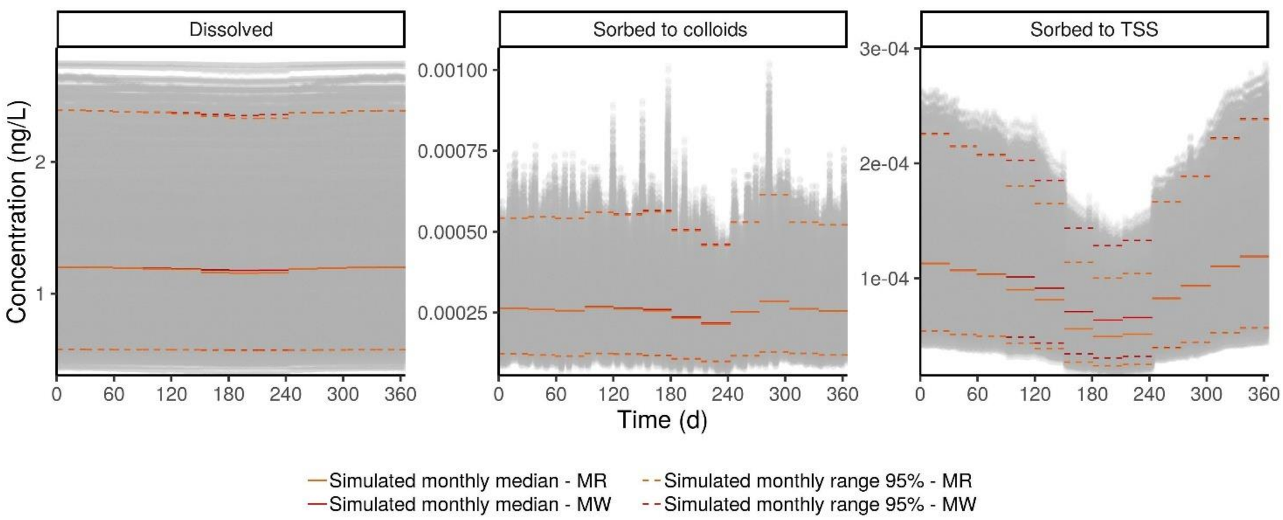

Figure S10. IBU midday predicted concentration ranges. Days starting from January 1st until December 31st.

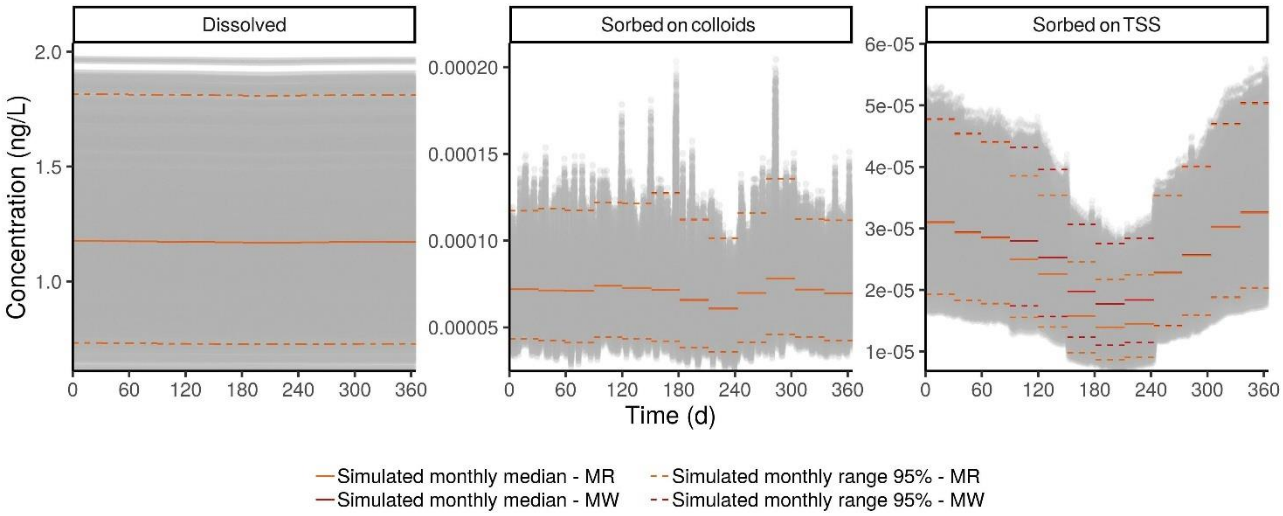

Figure S11. PAR midday predicted concentration ranges. Days starting from January 1st until December 31st.

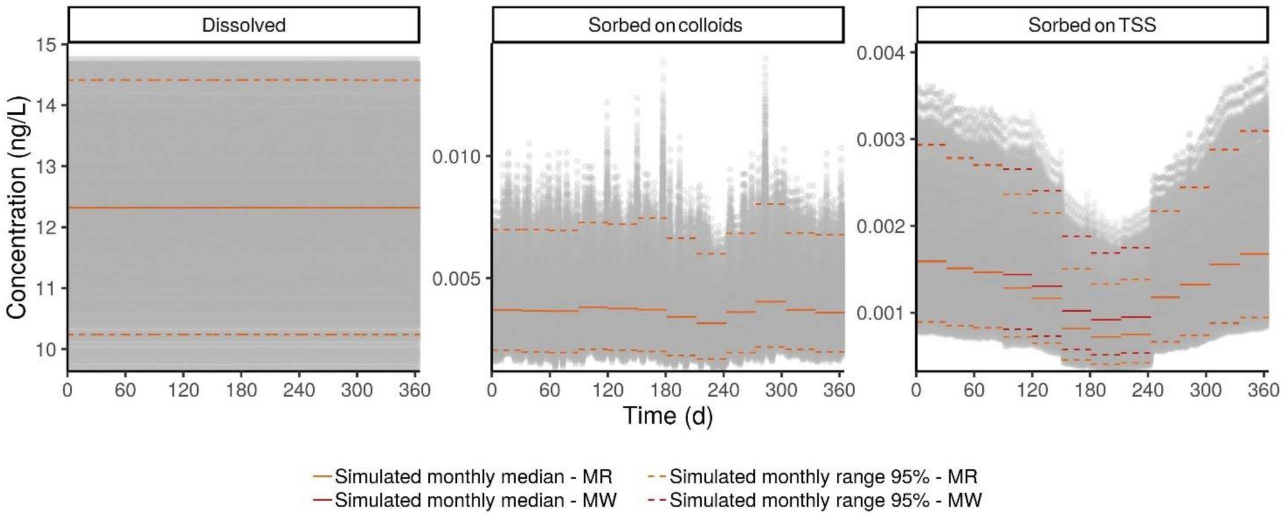

Figure S12. PFOA midday predicted concentration ranges. Days starting from January 1st until December 31st.

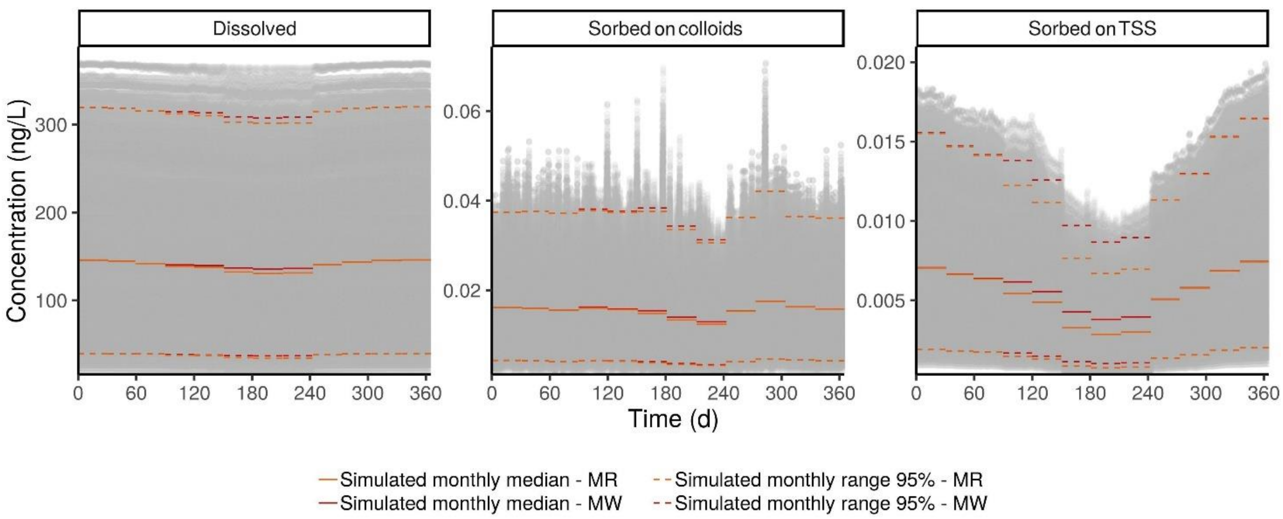

Figure S13. SMX midday predicted concentration ranges. Days starting from January 1st until December 31st.

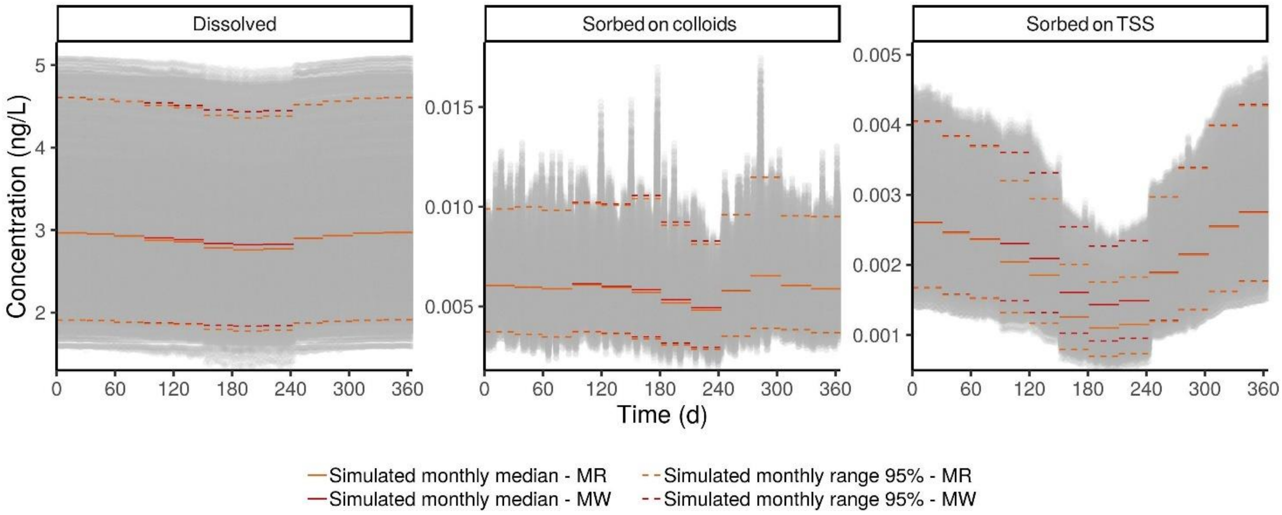

Figure S14. E2 midday predicted concentration ranges. Days starting from January 1st until December 31st.

SI.6.3 Attenuation along the canal

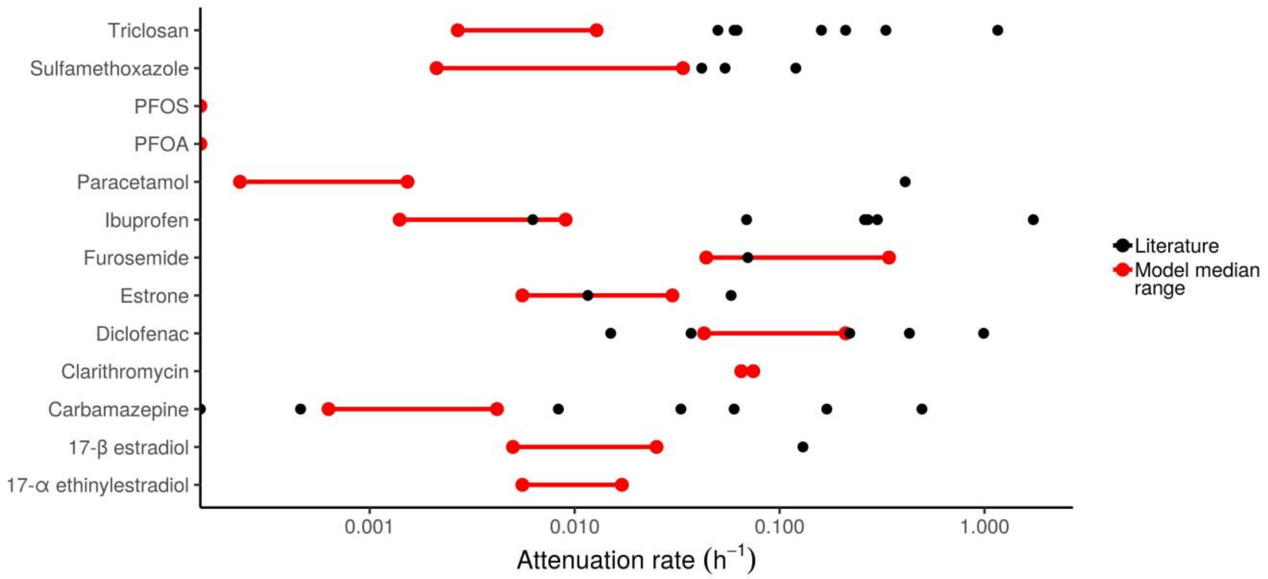

Figure S15. Predicted median attenuation rates compared to attenuation rates from literature. References: Acuña et al. (2015), Bester (2005), Fono et al. (2006), Guillet et al. (2019), Kunkel and Radke (2011), Lin et al. (2006), Morrall et al. (2004), Matamoros and Rodríguez (2017), Radke et al. (2010), Sabaliunas et al. (2003), Tixier et al. (2003), Williams et al. (2003), Writer et al. (2012, 2013).

SI.6.4 Bioconcentration factors

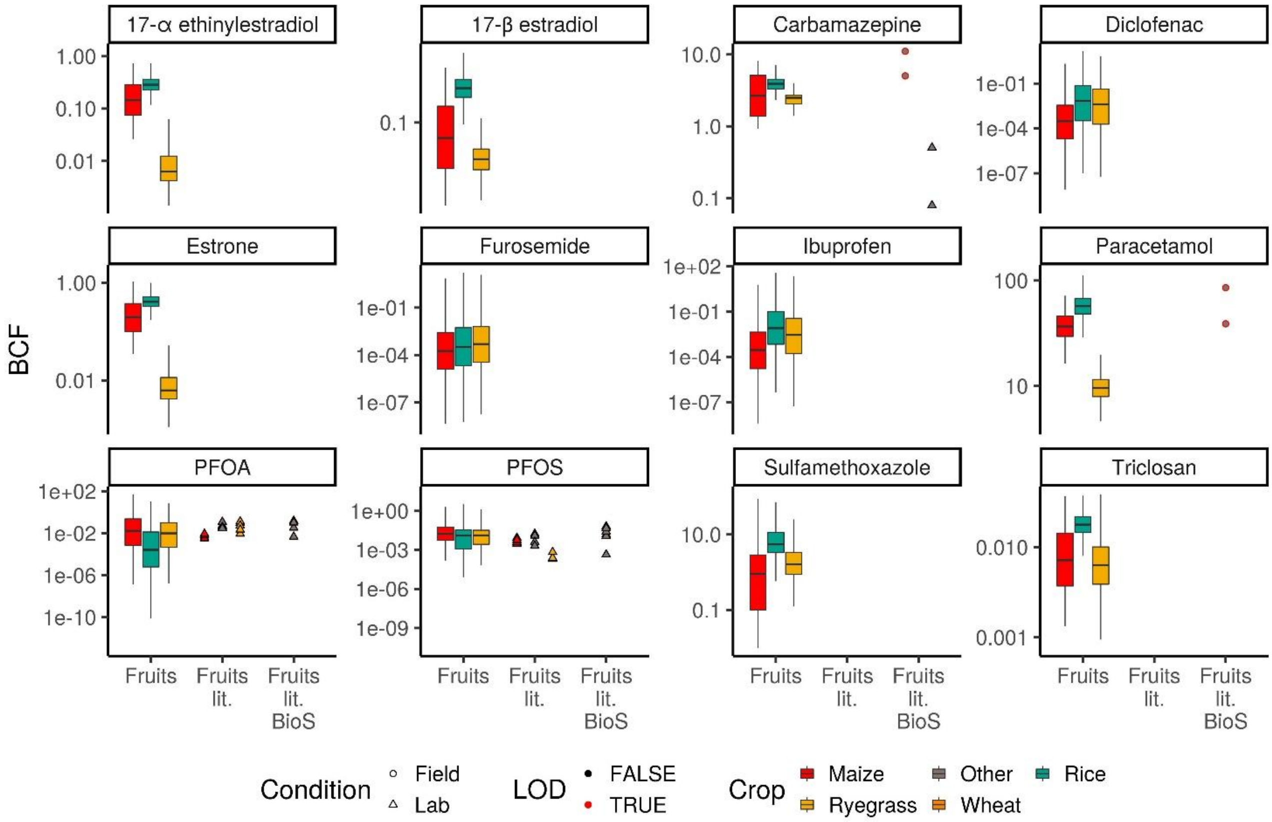

Figure S16. Fruit BCFs (gdw/gdw) for silage maize, winter wheat, ryegrass and rice with respect to maximum soil concentrations and literature (lit.) values. All simulated soils are shown. BioS indicates experimental studies conducted with the use of biosolids. Red borders indicate the use of an LOD value in the calculation of the BCF. References (including fruit BCFs in Figure 3): Blaine et al. (2013, 2014), Christou et al. (2017), Goldstein et al. (2014), Lechner and Knapp (2011), Mordechay et al. (2018), Navarro et al. (2017), Pannu et al. (2012), Prosser et al. (2014), Sabourin et al. (2012), Shenker et al. (2011), Stahl et al. (2009), Wen et al. (2014), Wu et al. (2010, 2012), Yager et al. (2014)

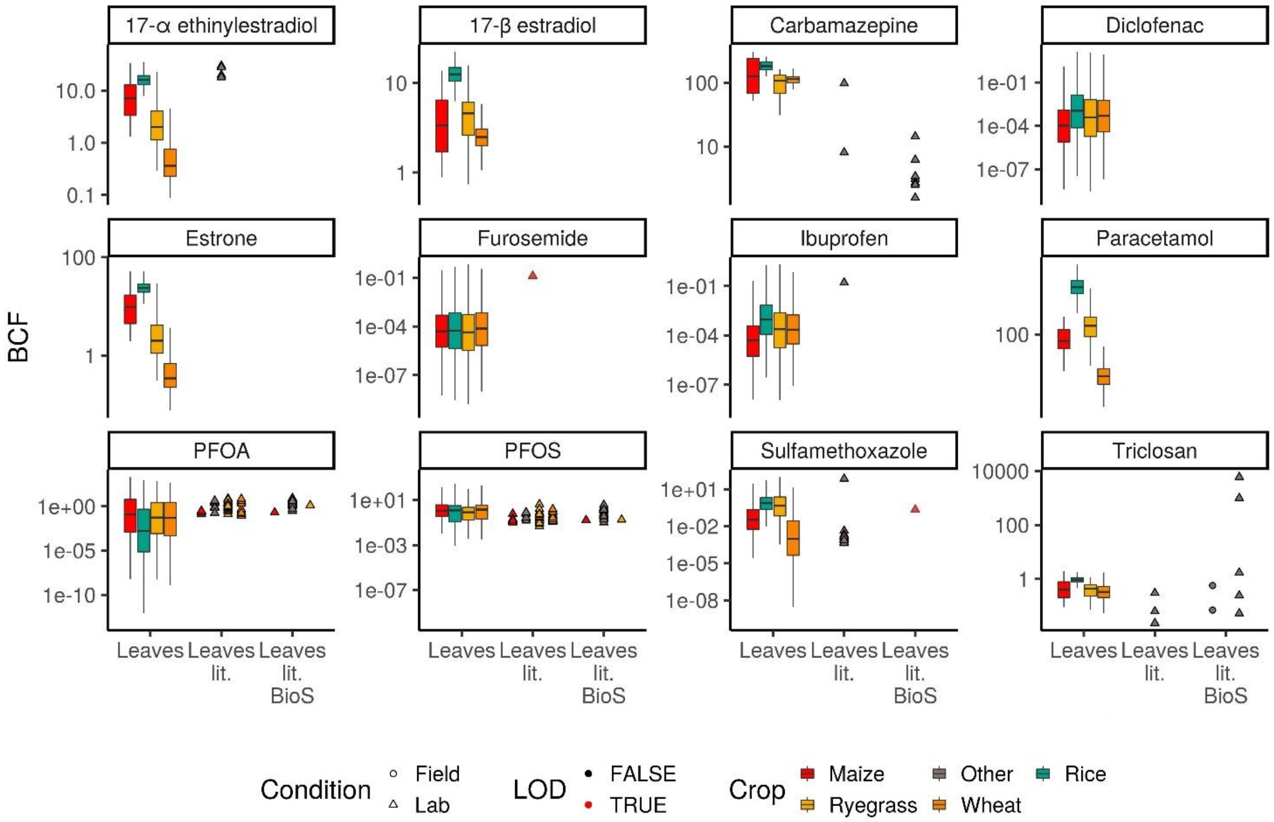

Figure S17. Leaf BCFs (gdw/gdw) for silage maize, winter wheat, ryegrass and rice with respect to maximum soil concentrations and literature (lit.) values. All simulated soils are shown. BioS indicates experimental studies conducted with the use of biosolids. Red borders indicate the use of an LOD value in the calculation of the BCF. References (including leaf BCFs in Figure 3): Aryal and Reinhold (2011), Bizkarguenaga et al. (2016), Blaine et al. (2013, 2014), Carter et al. (2014), Chitescu et al. (2012), Fu et al. (2016), Goldstein et al. (2014), Holling et al. (2012), Hurtado et al. (2017), Karnjanapiboonwong et al. (2011), Lechner and Knapp (2011), Macherius et al. (2012), Malchi et al. (2014), Mordechay et al. (2018), Navarro et al. (2017), Pannu et al. (2012), Prosser et al. (2014), Shenker et al. (2011), Stahl et al. (2009), Wen et al. (2014, 2016), Winker et al. (2010), Wu et al. (2010, 2012), Yoo et al. (2011), Zhao et al. (2014, 2017).

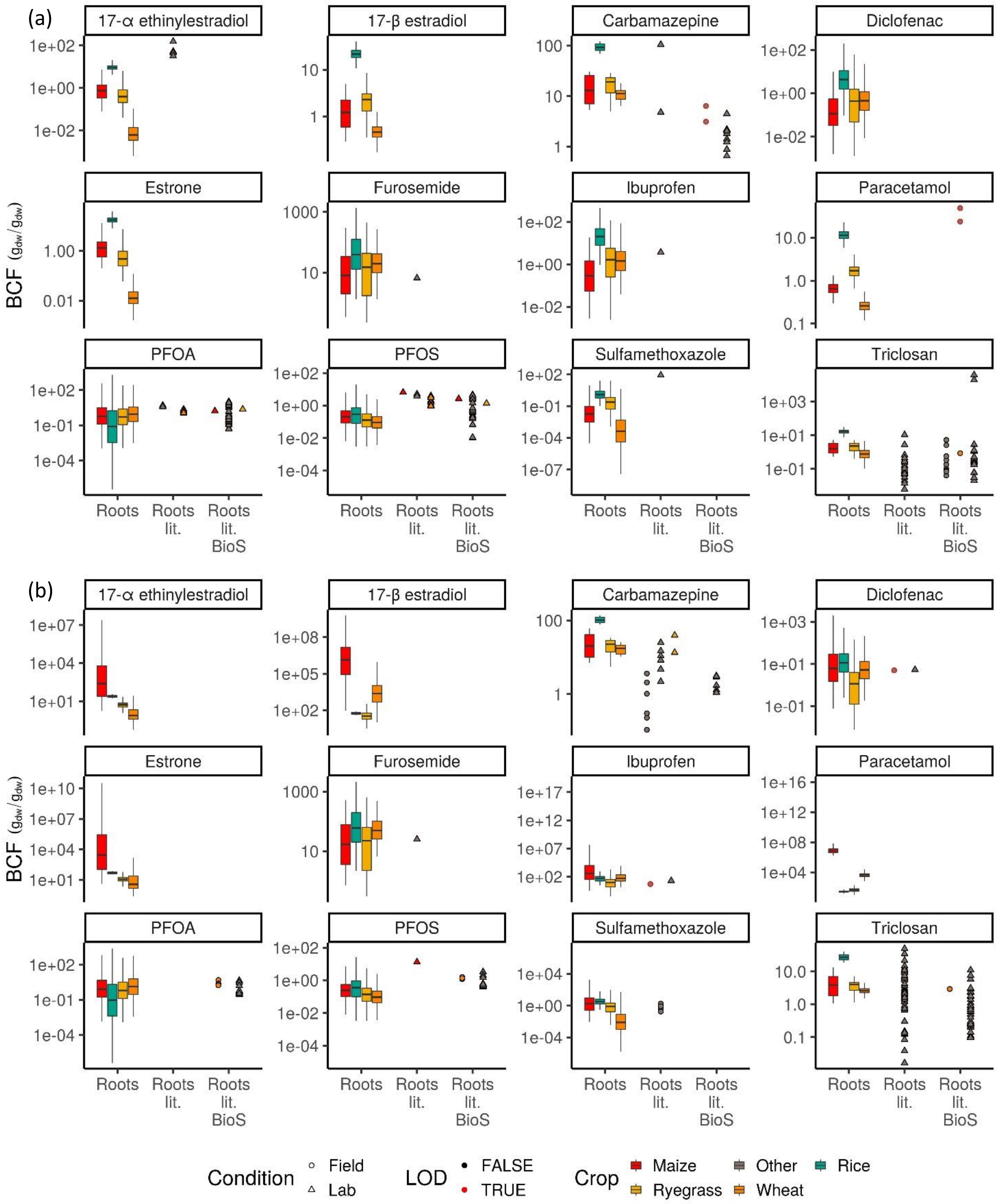

Figure S18. Root BCFs (g_{dw} /g_{dw}) for silage maize, winter wheat, ryegrass and rice with respect to maximum (a) or median (b) soil concentrations and literature (lit.) values. All simulated soils are shown. BioS indicates experimental studies conducted with the use of biosolids. Red borders indicate the use of an LOD value in the calculation of the BCF. References: Aryal and Reinhold (2011), Bizkarguenaga et al. (2016), Blaine et al. (2014), Carter et al. (2014), Fu et al. (2016), Holling et al. (2012), Hurtado et al. (2017), Karnjanapiboonwong et al. (2011), Lechner and Knapp (2011), Macherius et al. (2012), Malchi et al. (2014), Pannu et al. (2012), Prosser et al. (2014), Sabourin et al. (2012), Shenker et al. (2011), Wen et al. (2014, 2016), Winker et al. (2010), Wu et al. (2010, 2012), Yager et al. (2014), Zhao et al. (2014, 2017).

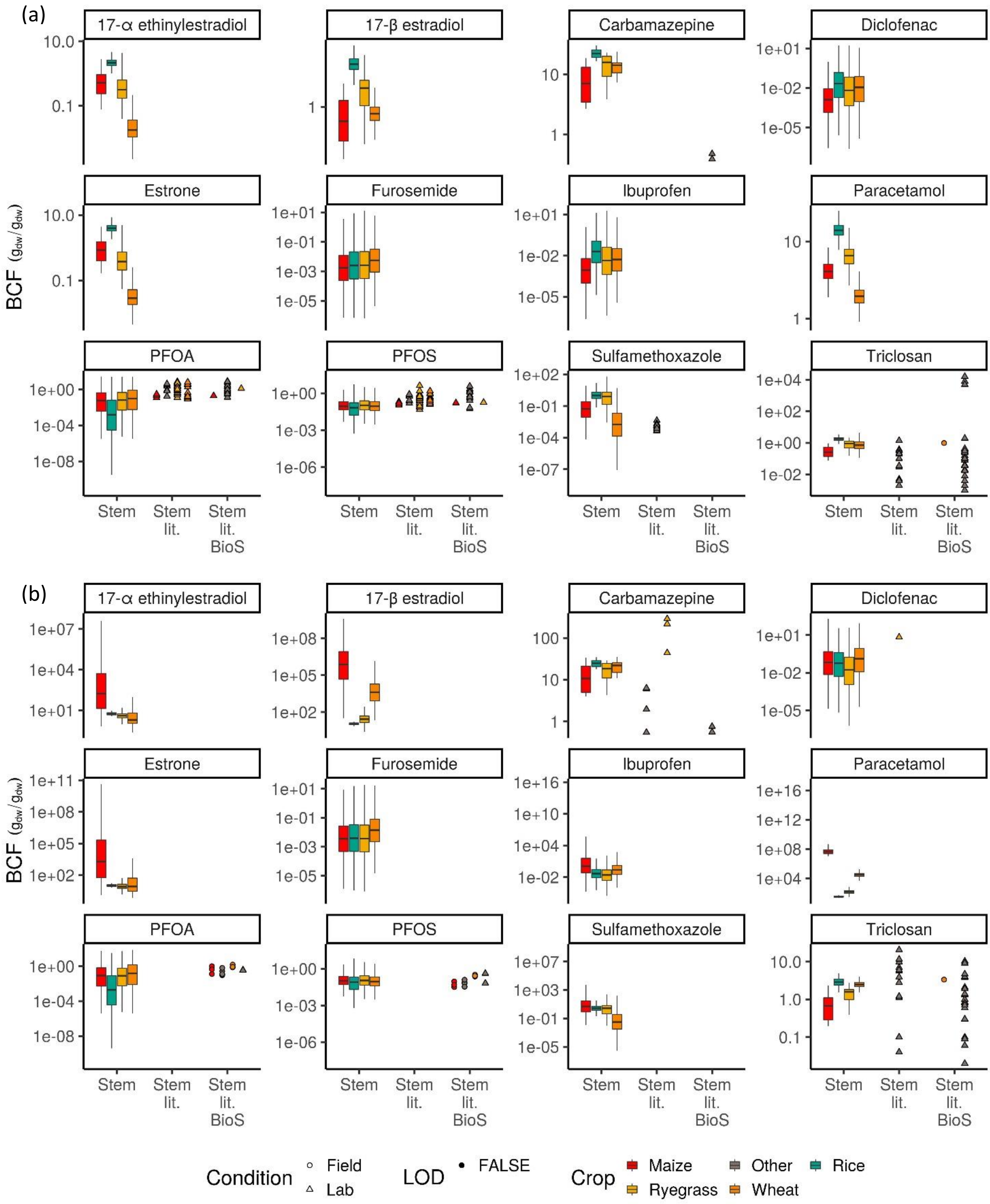

Figure S19. Stem BCFs (g_{dw}/g_{dw}) for silage maize, winter wheat, ryegrass and rice with respect to maximum (a) or median (b) soil concentrations and literature (lit.) values. All simulated soils are shown. BioS indicates experimental studies conducted with the use of biosolids. References: Aryal and Reinhold (2011), Blaine et al. (2013, 2014), Carter et al. (2014), Chitescu et al. (2012), Lechner and Knapp (2011), Navarro et al. (2017), Prosser et al. (2014), Shenker et al. (2011), Stahl et al. (2009), Wen et al. (2014, 2016), Winker et al. (2010), Wu et al. (2010), Yager et al. (2014), Yoo et al. (2011), Zhao et al. (2014, 2017).

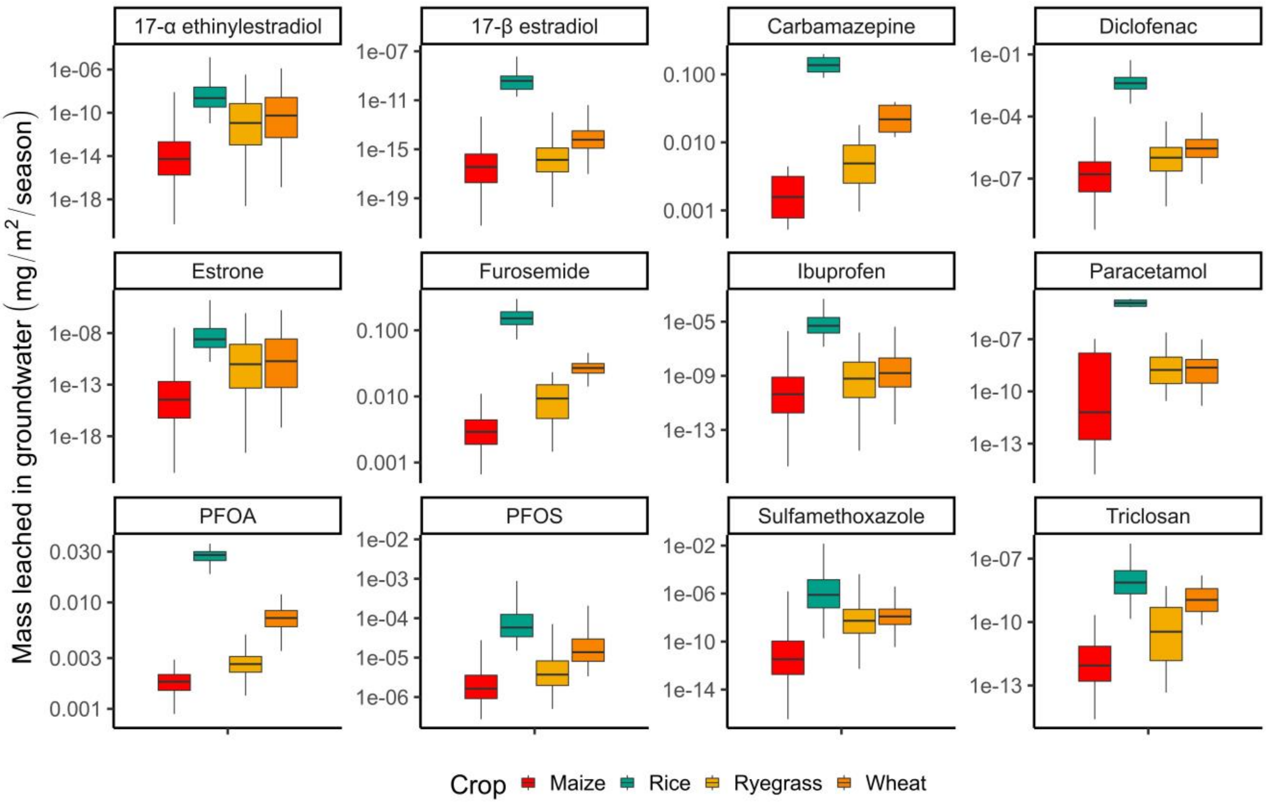

Figure S20. Total leached mass during each crop growing season.

SI.7 Risk assessment

SI.7.1 Environmental risk – Results

Table S22. Maximum, median and minimum RQs at the end of the canal and monthly frequency to exceed a given RQ.

CEC	Max/Median/Min RQ	Monthly frequency of exceedance (%)											
		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
RQ above 0.1													
SMX													
	0.42/0.16/0.018	74.1	73.9	73.5	73.5	73.4	72.7	72.4	72.6	73.7	73.9	74.2	74.1
IBU													
	0.15/0.07/0.021	16.9	16.7	16.5	16.4	16.3	15.9	15.8	15.9	16.2	16.4	16.7	16.8
E1													
	0.25/0.14/0.046	91.7	91.5	91.3	90.8	90.5	89.2	88.4	88.8	90.6	91.2	91.5	91.7
RQ above 1													
CLA													
	2.63/1.34/0.48	80	79.8	79.7	79.4	79	78.3	77.9	78	78.9	79.3	80	80.4
EE2													
	45.88/26.74/12.86	100	100	100	100	100	100	100	100	100	100	100	100
E2													
	2.57/1.48/0.65	95.8	95.6	95.4	95.1	94.9	94.1	93.6	93.8	95	95.3	95.7	95.8
TCS													
	2.56/1.43/0.44	77.9	77.7	77.6	77.3	77.1	76.5	76.5	76.6	77.3	77.6	77.7	77.9

SI.7.2 Human health risk – Methods

Following the precautionary principle, human health risk was calculated with the assumption of no degradation between harvest and consumption and the complete bioaccessibility and bioavailability of the ingested CECs.

To calculate the ingestion required to exceed the threshold of toxicological concern (*TTC*), *TTC* was set equal to 30, 9.1, 1.5 and 0.0025 µg kg_{bw}^{-1} d^{-1}, depending on the Cramer classes (I, II and III or genotoxic alerts) which the CEC belongs to (Kroes et al., 2004; Malchi et al., 2014).

Regarding the calculation of the hazard quotient (HQ), the ADI values were either found in Prosser and Sibley (2015) or in the reports produced by EFSA (2008), Environment Protection and Heritage Council of Australia (2008) and EMEA (2000) and, eventually, corrected as reported in Malchi et al. (2015).

SI.7.3 Human health risk – Results

Table S23. Consumption (kg/d) required to exceed TTC for crops irrigated with water withdrawn at the end of the canal. P97.5 stands for values calculated with the 97.5th percentile CEC concentration.

CEC	Infants				Adults			
	Rice		Wheat		Rice		Wheat	
	Median	P97.5	Median	P97.5	Median	P97.5	Median	P97.5
SMX	0.07	0.01	1.92	0.23	0.38	0.05	11.2	1.32
DCF	> 100	73.51	> 100	> 100	> 100	> 100	> 100	> 100
IBU	> 100	> 100	> 100	> 100	> 100	> 100	> 100	> 100
PAR	3.06	2.08	72.22	44.84	17.83	12.15	> 100	> 100
CBZ	8.59	5.77	19.03	15.06	50.12	33.65	> 100	87.84
FUR	> 100	> 100	> 100	> 100	> 100	> 100	> 100	> 100
PFOA	> 100	> 100	> 100	> 100	> 100	> 100	> 100	> 100
PFOS	> 100	> 100	> 100	> 100	> 100	> 100	> 100	> 100
TCS	> 100	> 100	> 100	> 100	> 100	> 100	> 100	> 100

Table S24. HQs and His for crops irrigated with water withdrawn at the end of the canal. P97.5 stands for values calculated with the 97.5th percentile CEC concentration.

CEC	Rice		Wheat		Total	
	Median	P97.5	Median	P97.5	Median	P97.5
Infants						
SMX	2.94E-03	2.03E-02	1.86E-04	1.58E-03	3.12E-03	2,19E-02
DCF	2.66E-06	6.35E-04	6.14E-08	1.26E-05	2.72E-06	6.48E-04
IBU	1.12E-09	5.27E-07	1.21E-10	5.94E-08	1.24E-09	5.86E-07
PAR	7.12E-07	1.05E-06	5.64E-08	9.08E-08	7.69E-07	1.14E-06
CBZ	2.62E-03	3.91E-03	2.21E-03	2.80E-03	4.84E-03	6.71E-03
FUR	5.37E-08	8.49E-05	1.25E-07	9.82E-05	1.79E-07	1.83E-04
EE2	2.77E-02	2.57E-01	1.95E-03	3.85E-02	2.97E-02	2.95E-01
E2	1.07E-05	2.53E-05	8.72E-07	2.02E-06	1.15E-05	2.73E-05
E1	5.23E-04	4.82E-03	4.06E-05	7.80E-04	5.63E-04	5.60E-03
PFOS	6.98E-06	2.75E-04	5.44E-06	1.24E-04	1.24E-05	4.00E-04
PFOA	2.23E-08	1.22E-04	1.17E-06	2.66E-04	1.19E-06	3.88E-04
TCS	6.19E-09	1.79E-08	2.57E-09	1.04E-08	8.76E-09	2.83E-08
				Hazard Index	3.82E-02	3.31E-01
Adults						
SMX	4.45E-04	3.08E-03	8.88E-05	7.52E-04	5.34E-04	3.83E-03
DCF	4.03E-07	9.63E-05	2.93E-08	6.03E-06	4.33E-07	1.02E-04
IBU	1.70E-10	7.99E-08	2.93E-08	6.03E-06	2.27E-10	1.80E-07
PAR	1.08E-07	1.59E-07	2.69E-08	4.33E-08	1.35E-07	2.20E-07
CBZ	3.98E-04	5.93E-04	1.06E-03	1.33E-03	1.45E-03	1.93E-03
FUR	8.14E-09	1.29E-05	5.96E-08	4.69E-05	6.78E-08	5.97E-05
EE2	4.20E-03	3.89E-02	9.32E-04	1.84E-02	5.13E-03	5.73E-02
E2	1.62E-06	3.84E-06	4.16E-07	9.63E-07	2.03E-06	4.80E-06
E1	7.93E-05	7.30E-04	1.94E-05	3.72E-04	9.86E-05	1.10E-03
PFOS	1.06E-06	1.31E-04	2.60E-06	5.94E-05	3.65E-06	1.90E-04
PFOA	3.38E-09	1.85E-05	5.58E-07	1.27E-04	5.62E-07	1.46E-04
TCS	9.38E-10	2.71E-09	1.23E-09	4.96E-09	2.17E-09	7.67E-09
				Hazard Index	7.22E-03	6.47E-02

SI.8 References

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