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Long-term effects on the agroecosystem of using reclaimed water on commercial crops

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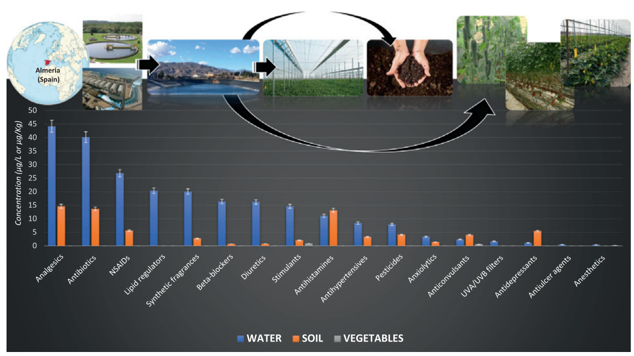
HIGHLIGHTS

- Data from 5 greenhouses irrigated with reclaimed water are presented.
- Irrigation water exhibited the highest levels of CECs followed by soils ≥ vegetables.
- Carbamazepine and caffeine were the only CECs in all water-soil-plant continuum.
- Lidocaine exhibited the greatest bioaccumulation factor in all crops.
- None of vegetables represented a risk to human health.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of reclaimed water for crop irrigation has been proposed as a suitable alternative for farmers in the coastal areas of Mediterranean countries, which suffer from greater water scarcity. In this work we study the impact on the water-soil-plant continuum of using reclaimed water for commercial crops irrigated over a long period, as well as the human risks associated with consuming the vegetables produced. Forty-four CECs were identified in the reclaimed water used for crop irrigation. Of these, twenty-four CECs were identified in the irrigated soil samples analysed. Tramadol, ofloxacin, tonalide, gemfibrozil, atenolol, caffeine, and cetirizine were the pharmaceuticals detected at the highest levels in the water samples (between 11 and 44 μg/L). The CECs with the highest average soil concentrations were tramadol (14.6 μg/kg), followed by cetirizine (13.2 μg/kg) and clarithromycin (12.7 μg/kg). In the irrigated vegetable samples analysed over the study period, carbamazepine, lidocaine, and caffeine were only detected at levels from 0.1 to 1.7 μg/kg. The CEC accumulation rate detected in the edible parts of the vegetables permanently irrigated with reclaimed water was very low (~1 %), whereas it was 33 % in the soils. The results revealed that consuming fruits harvested from plants irrigated for a long period with reclaimed water does not represent a risk to human health, opening the door to a circular economy of water. Nevertheless, for crop irrigation, future studies need to be conducted over longer periods and in other matrices to provide more scientific data on the safety of using reclaimed water.

1. Introduction

The availability of suitable quality water is essential for the growth of those economic sectors that depend on it, and for society in general. However, according to the latest data from UNESCO, it is estimated that, by

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2050, 40 % of the global population will be living under conditions of severe water scarcity (UNESCO, 2020). Using reclaimed water is a very important water supply alternative, offering significant environmental (extending the water life cycle), economic and social benefits (Delli Compagni et al., 2020). Therefore, this practice is being incorporated as an integral part of water resource management plans in many regions around the world (Singh, 2021).

In Europe, water reuse is a priority area within the Strategic Implementation Plan of the European Innovation Partnership on Water. At present, about 1 billion m^3 of treated urban wastewater is reused annually, accounting for approximately 2.4 % of overall treated urban wastewater effluents, yet this is <0.5 % of annual EU freshwater withdrawals. It is estimated that, by 2025, the wastewater reuse volume will reach 3222 Mm^3/year in Europe (Alcalde Sanza and Gawlik, 2014). Spain is the European leader in wastewater reuse, the annual volume of which is 347 hm^3/year, the main application being in agriculture, as is the case worldwide. Specifically, 71 % of the regenerated water volume is used for crop irrigation, 17 % for environmental use, 7 % for recreational use, 4 % for urban use, while only 0.3 % is used in industries (Jodar-Abellan et al., 2019).

One of the advantages of using reclaimed wastewater is that less fertilizer has to be applied; this is because reclaimed wastewater contains nitrogen, phosphorus and potassium as well as micronutrients (Singh, 2021). However, this practice can affect soil salinity, potentially inducing a water absorption deficit in the plant (Shakir et al., 2017). Furthermore, as has been reported by several authors, the treated waters contain a wide range of organic contaminants known as contaminants of emerging concern (CECs), including pharmaceutical and personal care products (PPCPs) and pesticides (Martínez Bueno et al., 2012; Ofrydopoulou et al., 2022; Renau-Pruñonosa et al., 2020). The bio-physico-chemical properties of these molecules determine their fate in the water-soil-plant continuum. In this regard, over recent years, several studies have reported that using reclaimed water for crop irrigation might be an important pathway for organic contaminants to be introduced into agricultural production, and then subsequently enter the food chain, potentially posing a risk to health and to the environment (Christou et al., 2019; Picó et al., 2019). Nonetheless, most of these works were carried out in field trials at concentration levels higher than those expected in reclaimed water (under controlled greenhouse conditions) or on a specific group of organic contaminants (pharmaceutical products) (Beltrán et al., 2020; Christou et al., 2017; González García et al., 2019; Martínez-Piernas et al., 2019). To date, scarce scientific data are available regarding CEC concentrations in commercially grown crops. In a recent publication, Ben Mordechay et al. (2021) reported data on CECs in crops collected from 445 commercial fields irrigated with reclaimed wastewater in Israel.

Until 2020, water use in the European Union was regulated by Directive 2013/39 & Commission Implementation Decision (EU) 2018/840, and by Directive 91/271/EE. However, these frameworks did not sufficiently specify the conditions and parameters for using reclaimed water for crop irrigation. Consequently, a new regulation has recently been established by the European Commission regarding the minimum water reuse requirements for agricultural irrigation (Regulation 2020/741/EU, 2020). Nevertheless, this only regulated the physicochemical and microbiological parameters; again, CECs were not considered, creating commercial difficulties for agricultural products cultivated with reclaimed water.

Considering all of the above, the goal of the current work was to evaluate the impact of the long-term use of reclaimed water for crop irrigation under real agronomic conditions. The specific objectives were: (1) to develop, validate and apply an analytical approach based on a multi-residue analysis of environmental samples (water and soil) and food samples; and (2) to identify those contaminants that, due to their physicochemical properties, may pose a greater risk to health from being consumed in the edible part of the plant and/or from their environmental impact. For that, a multiresidue method based on QuEChERs (Quick, Easy, Cheap, Effective and Rugged) extraction coupled to liquid chromatography tandem mass spectrometry (LC–MS/MS) was the procedure used. The risk to human health was estimated based on the daily human intake values found of each detected target compound and compared with reported acceptable daily intake values (ADI), both in the conventional as well vegetarian diet. To the best of the authors' knowledge, this is the first time that such a large panel of target organic pollutants have been investigated (a total of 293 substances: 49 pharmaceutical products and 244 pesticides) on commercial crops permanently irrigated with reclaimed water in greenhouses in Spain. Therefore, the current work aspires to meet one of the main challenges facing European society (The Strategic Implementation Plan of the European Innovation Partnership on Water), providing improved scientific-technical knowledge regarding the long-term effects on the water-soil-plant continuum of using reclaimed water for crop irrigation.

2. Materials and methods

2.1. Reagents and materials

Ultrapure water was obtained from Fisher Scientific (Fair Lawn, NJ, USA). Methanol, HPLC-grade acetonitrile, and LC-MS-grade acetonitrile were purchased from Honeywell (Charlotte, North Carolina). Formic acid was supplied by Fluka Analytical (Steinheim, Germany). QuEChERS salts (anhydrous magnesium sulphate, sodium chloride, sodium hydrogen citrate sesquihydrate and sodium citrate tribasic dihydrate) were obtained from Sigma-Aldrich (Steinheim, Germany) while C-18 sorbent was supplied from Supelco (Bellefonte, PA, USA). An automatic axial extractor (AGITAX®) was purchased from CirtaLAb, S.L., Spain. The centrifuge was supplied by Ortoalresa (Daganza, Madrid, Spain). Carbendazim-d^3, dichlorvos-d^6, malathion-d^{10} and caffeine-^{13}C were used to check the extraction efficiency while dimethoate-d^6 was selected to check the analytical efficiency.

The analytes were acquired from Sigma-Aldrich (Steinheim, Germany) at analytical grade (>98 %), except for hydrochlorothiazide, betahistine, sulpiride, famotidine, pantoprazole, clonazepam, and diazepam, which were obtained in pill form. In the Supplementary Material section (Table S1), detailed information is given on the physicochemical properties of the compounds selected in this study. Individual stock solutions of each organic emerging contaminant were prepared at 2000–10,000 mg/L in MeOH, placed in amber screw-capped glass vials, and stored in the dark at -40 °C. Standard working solutions were prepared daily in ACN at 1000 mg/L by diluting the stock solution; this working solution was then used for identification and quantification purposes.

2.2. Sampling site and sample collection

The province of Almería is situated in the southeast of Spain (the Western Mediterranean area). Almería is the main production area of horticultural products for Spain and Europe (Caparrós-Martínez et al., 2020). It produces >3.5 MT of fruit/vegetables per year, mostly grown under plastic (35,000 ha), of which 2.7 MT are exported (76 %). Among the typical crops cultivated in Almería are tomato (*Solanum lycopersicum*), cucumber (*Cucumis sativus*), pepper (*Capsicum annuun*), melon (*Cucumis melo*), eggplant (*Solanum melongena*) and zucchini (*Cucurbita pepo*). According to data published by the Government of Andalusia, 48 % of Almerian farmers use reclaimed water as the only supply source, and the remaining 52 % mix it with conventional water from local water sources and wells (Segura and Fernández, 2014).

Irrigation water samples were directly collected from the water treatment plant of the General Community of Water Users of Almería (CGUAL). Reclaimed wastewater effluents and desalinated seawater are mixed and treated using an ultrafiltration and sodium hypochlorite disinfection process prior to distribution. The reclaimed water complies with the main European Directives on water reuse requirements (Directive 2013/39/EU, 2013; Directive 91/271/EEC, 1991; Regulation 2020/741/EU, 2020). Vegetable and soil samples were obtained from greenhouses managed by CGUAL farmers over two agricultural seasons (from September 2021 to May 2022). A total of 22 irrigation water samples were collected weekly in glass bottles (2 L). Four different crops (cucumber, tomato, pepper, and zucchini) were analysed. The vegetable samples were collected in plastic bags and transferred to the laboratory, where they were triturated. The irrigated soil samples were taken from the top 10 cm layer. They were collected in glass bottles and transferred to the laboratory. There, they were sifted through a 0.5 mm diameter sieve and dehydrated in an oven at 30 °C for 24 h. All the samples were frozen and stored at −20 °C prior to analysis.

2.3. Sample extraction

The water samples were analysed by direct injection after a centrifugation step at 3500 rpm for 5 min to remove suspended solid particles. The vegetable and soil samples were extracted using two procedures that had been previously reported and validated by our research group (García Valverde et al., 2021; Martínez Bueno et al., 2022). Each sample was extracted in triplicate. Briefly, 10 g of sample was weighed in a 50-mL PTFE centrifuge tube. To rehydrate the soil samples, 5 mL of distilled water was added. After this, a deuterated standard mixture was added to check the extraction procedure (caffeine-^{13}C, carbendazim-d^{3}, dichlorvos-d^{6} and malathion-d^{10}). Next, 10 mL of acidified ACN (0.5 % v/v, formic acid) was added to the samples to improve the extraction. The samples were shaken for 6 min in an automatic axial extractor at room temperature (AGITAX®, CirtaLAb, S.L., Spain). After that, 4 g of anhydrous $MgSO_4$, 1 g of $Na_3Citrate·2H_2O$, 1 g of NaCl and 0.5 g of $Na_2HCitrate·1.5H_2O$ were added. The samples were shaken again and then centrifuged at 3500 rpm for 5 min. Subsequently, 5 mL of the supernatant was transferred to a 15 mL polyethene tube, to which 750 mg of anhydrous $MgSO_4$ and 125 mg of C18 were added. After this, the tubes were vortexed for 30 s. The last step was to centrifuge the tubes once more. Prior to injection, 100 μL of each extract was evaporated and reconstituted with 100 μL of ACN:water solution (10:90, v/v), which contained dimethoate-d^{6} as the surrogate injection standard.

2.4. Sample analysis

For target analysis purposes, a wide-scope method harmonized with DG SANTE 11312/2021 guidelines was employed. Samples were analysed on a Sciex high-performance liquid chromatography system (Exion HPLC 6500+) connected to a mass spectrometer equipped with a turbo spray ion-drive source (LC-ESI-TripleQuad-MS/MS, Sciex) operating in positive and negative mode. Chromatographic separation was performed on a Zorbax Eclipse Plus C8 of 1.8 μm × 2.1 mm × 100 mm (Agilent). The mobile phases were 0.1 % formic acid in ultrapure water (solvent A) and ACN (solvent B) at a constant flow rate of 0.3 mL/min. The gradient programme was 10 % of B and 90 % of A for 0.5 min (the initial conditions) after a linear gradient up to 100 % of B in 11.5 min; B was kept at 100 % for 4 min and, finally, the mobile phase returned to 10 % B and 90 % A. The total run time was 18 min, and the injection volume was 5 μL. The ionization settings used were: ion spray voltage, 5000 V and −4500 V (for the positive and negative ionization modes, respectively); GS1, 50 psi; GS2, 40 psi; curtain gas, 20 (arbitrary units) and temperature, 500 °C. Nitrogen was used as the nebulizer gas and collision gas.

To optimize the target compounds, an individual standard solution at 200 μg/L was used. The chromatographic and mass spectrometer conditions for each compound were obtained with these individual solutions. In full-scan mode, the solutions were infused directly into the MS system and the precursor ion was selected by choosing the most intense ion. The analyses were performed in multiple reaction monitoring (MRM) mode. Then, the optimal collision energies (CEs) were selected using the two most intense transitions in product-ion mode. Consequently, the quantifier ion (SRM1) was the ion with the most intense and the qualifier ion (SRM 2) was the ion with the second most intensity. The optimal mass spectrometric parameters for each target compound using LC-MS/MS are shown in Table S2 in the Supplementary Material section.

Data analysis was performed with Sciex Analyst version 1.7.3 software for data acquisition/processing and SCIEX OS version 2.0.0.45330 software for data quantification. In addition, an SRM schedule with a retention time window of 0.4 min was applied during the acquisition and quantification.

2.5. Target compounds

The analytes chosen in the present study were selected based on previously published data on the presence of CECs in treated water (Martínez Bueno et al., 2012; Ofrydopoulou et al., 2022). A total of 293 target compounds were selected from the following categories: 49 pharmaceutical products belonging to 19 different therapeutic classes and 244 pesticides belonging to 5 different pesticide types (acaricides, biocides, herbicides, insecticides, and nematicides). More information about the target compounds can be found in the Supplementary Material section (Table S1).

2.6. Analytical performance and quality control

To confirm and quantify the target compounds, the requirements on mass spectrometric confirmation set by EU regulations (Commission Decision 2002/657/EC, 2002) were considered. The four criteria were: SRM1 with an s/n ≥ 10; SRM2 with an s/n ≥ 3; a retention time ± 0.1 min with reference to the standard; and a value of ±30 % when comparing the fragment ion area with the precursor ion area (the ion ratio).

The validation of the analytical approaches was performed according to EU quality control procedures, DG-SANTE/11312/2021 (European Commission DG-SANTE, 2021). The linearity, matrix effect, sensitivity, trueness (in terms of recovery), precision (in terms of method repeatability and reproducibility) and selectivity were evaluated for each matrix studied (water, fruit, and soil).

A control was injected prior to analysis to check the performance of the HPLC, the analytical column, and the QqQ-MS/MS system. This control contained a selection of analytes at 2 μg/L. The analytical procedure was checked at two different stages of the process. During the extraction, caffeine-^{13}C, carbendazim-d^{3}, malathion-d^{10} and dichlorvos-d^{6} were added to check the extraction efficiency. To check the analytical stage, dimethoate-d^{6} was added while the injection vials were being prepared. To evaluate the selectivity and specificity of the method, different blank samples of water, fruit and soil were extracted. No other peaks caused by matrix co-eluting interferences were detected for the target analytes in a time range of ±0.2 min.

2.7. Bioconcentration factor (BCF) and human exposure

The plant uptake was estimated using the bioconcentration factor (BCF) (González García et al., 2019; Martínez Bueno et al., 2022). The BCF values were calculated through the average concentration of each target compound detected in the edible part of the plant (cucumber, pepper, tomato, and zucchini) compared to the average concentration of each target compound in the irrigation water.

In addition, human exposure was estimated to gauge the daily human intake of each target compound. This value was obtained by multiplying the average concentration of each contaminant in the edible part of the plant (μg/kg) and the volume of fresh vegetables consumed per capita in Spain in 2021 (kg/day). According to the most recent data reported, the annual consumption of fresh vegetables in 2020 in Spain was around 2.9 billion kg (Trenda, 2022). Tomato, pepper, zucchini, and cucumber were the most consumed vegetables with consumption volumes per capita of 13.3, 4.8, 4 and 2 kg/person/year, respectively (36.4, 13.2, 11 and 5.5 g/day). Human exposure was calculated as follows:

$$\text{Human exposure} = C \times D \times T$$

with C standing for the concentration of CECs in the vegetables (μg/kg in fresh weight, fw), D being the amount of vegetables consumed daily per capita (kg/day) and T being the exposure time of these contaminated vegetables (days).

3. Results and discussion

3.1. Method validation

A validation study was carried out for each matrix studied (water, fruit and soil). Due to the difficulty in obtaining a "blank" of the reclaimed water (without CECs or below their LOQ levels), the water sample was previously analysed and the signal of the target analytes was subtracted to calculate the validation data.

To simplify the validation step, the guidance from the European Union (European Commission DG-SANTE, 2021) was used to classify the plant commodities according to their physicochemical properties. Cucumber, tomato, pepper, and zucchini are commodities with similar water contents. Therefore, the tomato matrix was selected to perform the validation study in vegetables. The analytical performance data for each compound/matrix combination are summarized in Table S3. The LOQ values were evaluated for each analyte/matrix combination. Overall, the LOQ values were below 0.5 μg/kg for >80 % of the analytes studied in the tomato and soil matrices. In the reclaimed water, a total of 209 compounds out of 293 (71 %) presented a LOQ ≤ 0.5 μg/L. Less than 2 % of the target compounds presented LOQ values at 10 μg/L in the matrices under study. All of these were pesticides, except for the analgesic acetaminophen in the water matrix and the antiulcer agent pantoprazole in the tomato matrix. Specifically, four pesticides presented LOQ values at 10 μg/L in the water matrix (acephate, cyazofamid, cyhalophos-butyl and MCPB), two in the tomato matrix (cyhalophos-butyl and procymidone), and five in soil matrix (acephate, cyhalophos-butyl, fluopyram, propiconazole and tolfenpyrad).

The linearity of the method was evaluated based on the linear regression and correlation coefficient (r^2). Matrix-matched calibration curves at 7 levels (from 0.1 to 100 μg/L or μg/kg) were prepared to study the linearity in each matrix. All the analytes presented a good response with correlation coefficients higher than 0.99 in all cases.

The calibration curves in the matrix and solvent were compared to evaluate the matrix effect (ME). Signal suppression was the most common effect found in the soil and vegetable matrices (>95 %), while the enhancement/suppression effect was similar for the reclaimed water (see Table S3). A ME ≤ 20 % was considered a weak matrix effect, between 20 % and 50 % a moderate matrix effect, and >50 % a strong effect. According to our results, no matrix effect was observed for >90 % and 70 % of the target analytes in the reclaimed water and the soil matrix, respectively. However, the number of compounds that presented matrix effects was greater in the tomato matrix — >75 % of the contaminants presented a moderate or strong matrix effect. Some authors have explained this issue as being caused by several enzymes/sugars present in the plant (Picó et al., 2019).

Recovery studies were carried out per quintuplet (n = 5) using spiked samples at different levels (1, 5, 10 and 50 μg/kg). The response of each contaminant in the spiked matrix extract was compared with the response detected in the spiked samples. Recoveries were considered acceptable when consistent results were obtained within the 70 to 120 % range. The recoveries obtained were satisfactory considering the wide range of contaminants being studied and their different properties. More than 75 % of the target compounds presented satisfactory recovery values within the 70–120 % range in the soil and tomato samples spiked at 1 μg/kg. The percentage of compounds was higher than 90 % when the soil and tomato samples were spiked at concentration levels above 10 μg/kg. The results demonstrate the method's good performance at low concentration levels. Only 13 compounds out of 293 presented poor recoveries in the soil matrix at any concentration (<37 %) — 4 pharmaceutical products (ciprofloxacin, famotidine, ofloxacin and ranitidine) and 9 pesticides (alfuzosin, cyromazine, formetanate hydrochloride, matrine, matrine-n-oxide, phosmet, prothioconazole, pyridalyl and pyridate). In tomato, 3 pharmaceuticals (ciprofloxacin, erythromycin, and ranitidine) and 7 pesticides (2,4-D, dodine, fluazifop-p, haloxyfop, matrine, matrine-n-oxide and propiconazole) presented the lowest recovery values (<39 %). For more details, see Table S3 in the Supplementary Material section.

Repeatability and reproducibility (intra and inter-day precision) were calculated for each analyte/matrix from the results obtained from five injections of a blank sample spiked at two levels: 1 and 10 μg/L, covering the different concentrations of the average linearity range of the target compounds. The results were acceptable with %RSD values between 1 % and 20 % for all the matrices.

3.2. Irrigation water analysis

All the field-collected irrigation water samples contained CECs. A total of forty-four compounds were detected in the irrigation water samples analysed. Table 1 shows the detection frequencies (%), concentration ranges, and average concentrations (μg/L) of all the CECs detected in the irrigation water samples analysed. Tramadol, ofloxacin, tonalide, gemfibrozil, atenolol, caffeine, and cetirizine were the pharmaceutical products quantified at the highest concentrations, with mean values between 44.1 and 11.1 μg/L. On the other hand, the most frequently detected pesticides were the fungicide carbendazim and the insecticides acetamiprid and imidacloprid, with detection frequencies higher than 75 % and concentration levels up to 1.5, 35.7 and 9.2 μg/L, respectively. The herbicides, terbutryn and diuron were the least detected pesticides (<25 %). As can be seen in Table 1, a total of 14 contaminants were detected in all the water samples analysed. Among them were the antibiotic ofloxacin (a mean of 33.5 μg/L), the NSAIDs ketoprofen and mefenamic acid (means of 10 and 0.3 μg/L, respectively), the β-blocker propranolol (a mean of 0.6 μg/L), the anticonvulsant lamotrigine (a mean of 1 μg/L), the antihypertensives valsartan and irbesartan (means of 4.8 and 2.0 μg/L, respectively), the lipid regulator gemfibrozil (a mean of 16.9 μg/L), the diuretic hydrochlorothiazide (a mean of 5.8 μg/L), the antipsychotic drugs amisulpride and sulpiride (means of 0.3 and 3.1 μg/L, respectively), the antihistamine cetirizine (a mean of 11.1 μg/L), the anaesthetic lidocaine (a mean of 0.4 μg/L), and the insecticide imidacloprid (a mean of 1.8 μg/L). Other CECs with high detection frequencies were atenolol (95 %), galaxolide (95 %), telmisartan (91 %), venlafaxine (91 %), acetamiprid (91 %) and bezafibrate (86 %). Fig. 1 presents the data collected. In general, pharmaceutical products were detected at higher concentration levels than pesticides, with average total loads of 227.8 μg/L and 8.1 μg/L, respectively. The average total loads according to the different groups were: 44.1 μg/L for analgesics, 40.1 μg/L for antibiotics, 26.8 μg/L for NSAIDs, 20.4 μg/L for lipid regulators, 20.1 μg/L for synthetic fragrances, 16.4 μg/L for β-blockers, 16.2 μg/L for diuretics, 14.6 μg/L for stimulants, 11.1 μg/L for antihistamines, 8.4 μg/L for antihypertensives and 8.0 μg/L for pesticides (see Fig. 1). With regard to pesticides, none of the compounds included in the list of priority substances were detected at concentrations above their LOQs, except for diuron and terbutryn (Directive 2013/39/EU, 2013). However, neither exceeded the maximum limits permitted 1.8 μg/L and 0.34 μg/L, respectively. The most relevant CECs detected in the irrigation water samples analysed are discussed below.

Antibiotics are a group of drugs widely prescribed to treat bacterial infections. They can be expelled into the environment via effluents from hospitals, pharmaceutical industries, and wastewater treatment plants (WWTPs). Moreover, it is known that WWTPs provide only a low removal efficiency (Martínez Bueno et al., 2012). In a study carried out on Spain's surface water, the authors reported ofloxacin concentration levels of up to 0.4 μg/L (Martínez Bueno et al., 2010). In our study, six antibiotics were detected. Ofloxacin was detected in all the analysed samples at concentrations ranging from 5.6 to 130.7 μg/L, an average concentration of 33.5 μg/L. In contrast, clarithromycin, metronidazole, trimethoprim and sulfamethoxazole were detected at concentrations that were an order of magnitude lower than ofloxacin, with averages of 3.4, 1.4, 1.1 and 0.7 μg/L, respectively. A previously published study by Rodriguez-Mozaz et al. (2015) reported concentration levels similar to our results for clarithromycin, sulfamethoxazole, and trimethoprim (0.92, 0.64 and 0.97 μg/L, respectively).

Around 10 % of patients worldwide are diagnosed with chronic pain each year (Ahmed et al., 2021). Analgesics are used to provide pain relief. Tramadol is a typical analgesic although paracetamol is the most used. To date, there have been few studies evaluating tramadol. In our study, tramadol was detected at a detection frequency of 73 % and its average

Table 1
CECs in irrigation water (μg/L) and irrigated soil samples (μg/kg). Soil data per each crop are presented in Tables S4.

Compound	Irrigation water			Irrigated soils		
	Detection frequency (%)	Concentration range (μg/L)	Average concentration (μg/L)	Detection frequency (%)	Concentration range (μg/kg)	Average concentration (μg/kg)
PPCPs						
Antibiotics						
Clarithromycin	82	<LOQ–7.6	3.4	75	<LOQ–17.0	12.7
Metronidazole	64	<LOQ–4.6	1.4	–	–	–
Ofloxacin	100	5.6–130.7	33.5	–	–	–
Sulfamethoxazole	23	<LOQ–0.9	0.7	–	–	–
Trimethoprim	82	<LOQ–1.9	1.1	75	<LOQ–1.9	1.0
NSAIDs						
Diclofenac	18	6.7–15.0	9.5	–	–	–
Ketoprofen	100	<LOQ–21.3	10.0	–	–	–
Mefenamic acid	100	0.1–0.6	0.3	100	0.1–0.4	0.2
Naproxen	18	<LOQ–7.7	6.9	25	<LOQ–5.7	5.5
Analgesics						
Tramadol	73	15.6–81.0	44.1	75	<LOQ–24.5	14.6
Anesthetics						
Lidocaine	100	0.1–0.7	0.4	–	–	–
Anticonvulsants						
Carbamazepine	73	0.7–2.2	1.4	100	1.1–7.6	3.5
Lamotrigine	100	0.4–2.0	1.0	75	<LOQ–0.9	0.6
Antidepressants						
Citalopram	27	<LOQ–0.6	0.5	100	0.9–7.1	3.7
Venlafaxine	91	<LOQ–1.2	0.6	100	0.6–3.3	1.8
Antihistamines						
Cetirizine	100	2.5–29.7	11.1	75	<LOQ −20.0	13.2
Antipsychotic drugs						
Amisulpride	100	0.1–0.6	0.3	100	0.2–0.4	0.3
Sulpiride	100	0.9–5.8	3.1	100	0.2–2.4	1.2
Antiulcer agents						
Famotidine	27	<LOQ–0.9	0.5	–	–	–
UVA/UVB filters						
BP-3	14	1.6–1.9	1.7	–	–	–
Diuretics						
Furosemide	14	<LOQ–20.2	10.4	–	–	–
Hydrochlorothiazide	100	2.0–12.0	5.8	37	<LOQ-0.9	0.8
Stimulant						
Caffeine	73	<LOQ–66.5	14.6	100	0.8–4.9	2.1
Synthetic fragrances						
Galaxolide	95	<LOQ–3.0	1.2	100	0.3–7.4	2.8
Tonalide	50	6.9–27.7	18.9	–	–	–
Lipid regulators						
Bezafibrate	86	<LOQ–2.7	1.5	–	–	–
Fenofibric acid	50	0.7–3.8	2.0	–	–	–
Gemfibrozil	100	7.1–45.2	16.9	–	–	–
Beta-blockers						
Atenolol	95	5.9–23.8	15.0	–	–	–
Bisoprolol	27	<LOQ–0.9	0.7	–	–	–
Propanolol	100	0.2–1.5	0.6	37	<LOQ–0.9	0.7
Antihypertensives						
Irbesartan	100	0.6–3.5	2.0	75	<LOQ–1.0	0.5
Telmisartan	91	<LOQ–3.0	1.6	100	0.5–8.2	2.9
Valsartan	100	0.8–12.8	4.8	–	–	–
Total load of PPCPs			227.8			67.3
Pesticides						
Fungicides						
Azoxystrobin	50	<LOQ	<LOQ	75	<LOQ–1.2	0.9
Carbendazim	77	<LOQ–1.5	0.5	25	<LOQ–2.4	2.3
Propamocarb	32	<LOQ–0.9	0.5	100	0.2–0.4	0.3
Thiabendazole	23	0.3–0.4	0.3	100	0.1–0.2	0.1
Herbicides						
Diuron	23	<LOQ–1.7	1.5	100	0.2–0.3	0.2
Terbutryn	18	<LOQ–0.3	0.2	75	<LOQ–0.5	0.4
Insecticides						
Acetamiprid	91	0.1–35.7	2.9	–	–	–
DEET	59	0.3–0.7	0.4	–	–	–
Imidacloprid	100	0.2–9.2	1.8	–	–	–
Total load of pesticides			8.1			4.2

<LOQ: limits of quantification (μg/L).

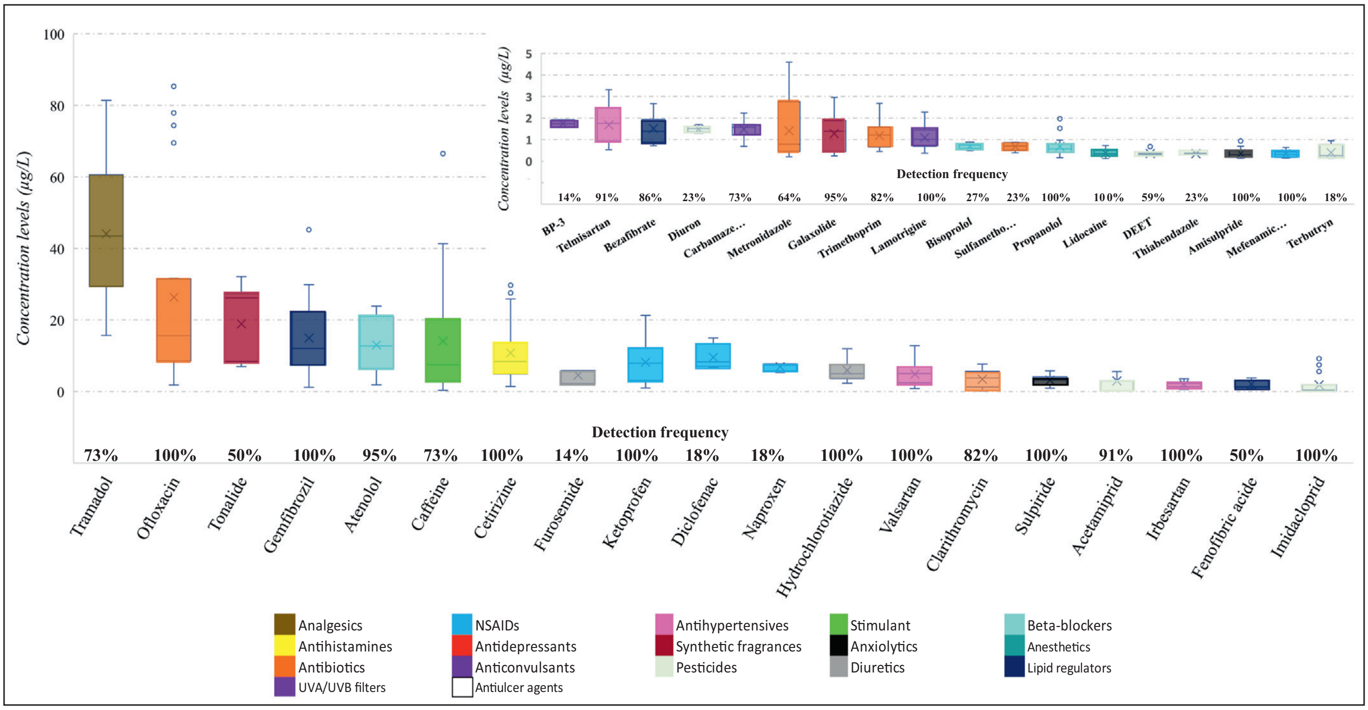

Fig. 1. CECs detected in the irrigation water samples analysed. Data <LOQ are not presented. The median is presented as boxplots. Detection frequencies are listed for each compound. The vertical lines represent the maximum and minimum concentrations detected for each compound in the samples analysed. Circles represent outlier measurements.

concentration was 44.1 μg/L in the irrigation water samples analysed. Ahmed et al. (2021) reported concentration levels of tramadol between 0.2 and 0.5 μg/L in different treated waters from Australia. Similar results were found by Nieto-Juárez et al. (2021) in treated wastewater from South America.

Fragrance substances have wide applications such as in cleaning, detergent and cosmetic products. In the EU alone, around 1000 tons per year are produced (Chen et al., 2007; Klaschka et al., 2013; Tasselli et al., 2021). The synthetic fragrances tonalide and galaxolide were detected in the irrigation water samples. Galaxolide was found in almost all the samples (95 %) at an average concentration of 1.2 μg/L, while tonalide was only detected in half of the analysed samples (50 %), although at higher concentrations (18.9 μg/L). These results are in line with the data reported by other authors. Chen et al. (2007) found similar concentration levels for tonalide in treated wastewater from a cosmetic plant (5.4 μg/L) whereas galaxolide was quantified at concentrations up to 32.1 μg/L.

Lipid regulators, such as gemfibrozil, fenofibric acid or bezafibrate, are used to treat abnormal lipid levels in the blood. Gemfibrozil was the lipid regulator detected at the highest average concentration (16.9 μg/L) in treated wastewater samples from Spain (Gros et al., 2012) and Costa Rica (Ramírez-Morales et al., 2020). These works reported gemfibrozil levels 20-times lower than in our results, while bezafibrate and fenofibric acid were detected at concentrations one order of magnitude lower (between 1.5 and 2.0 μg/L). To the best of our knowledge, this is the first time that fenofibric acid has been found in agricultural irrigation water.

Atenolol, propranolol and bisoprolol are β-blockers that are usually used to treat hypertension or cardiac arrhythmias. Nowadays, they are found in treated water because of their persistence (Biel-Maeso et al., 2018; Gabet-Giraud et al., 2010; Gros et al., 2012; Marothu et al., 2019; Martínez-Piernas et al., 2019; Martínez Bueno et al., 2012; Picó et al., 2019). Picó et al. (2019) detected atenolol in treated wastewater used for crop irrigation in an area of Saudi Arabia at concentrations ranging from 0.1 to 0.9 μg/L. In another study carried out in southern Spain, atenolol and propranolol were found in irrigation water samples at mean concentrations of 1.1 μg/L and 0.1 μg/L, respectively (Biel-Maeso et al., 2018). In our study, atenolol was detected at higher levels than those found in the literature, at concentrations ranging from 5.9 to 23.8 μg/L.

Caffeine is the main stimulant used by humans due to the consumption of coffee and carbonated drinks. As indicated in the previous work by Martínez Bueno et al. (2012), caffeine is a drug that is removed very efficiency in WWTPs but its high consumption still leads to significant detection rates in the treated water. In this study, caffeine was detected at a detection frequency of 73 % and an average concentration level of 14.6 μg/L. Numerous studies have reported the presence of caffeine in treated water. Kosma et al. (2014) detected caffeine at concentrations between 0.05 and 4.1 μg/L. In another recent study carried out in Israel, Ben Mordechay et al. (2021) found caffeine in 71 % of the irrigation water samples analysed at concentration levels up to 3.9 μg/L.

Additionally, the irrigation water samples were subjected to chemical analysis where the metals, anions, physicochemical and agronomic parameters were evaluated. The physicochemical parameters evaluated were conductivity, water hardness, phosphorus, the degree of acidity or basicity and the dissolved solids, the values of which were 2510 μS/cm, 25.4 °F, 2.4 mg/L, 7.5 U. pH, and 1547 mg/L, respectively. In terms of anions, the chlorides, nitrates, and sulphates were analysed. The concentration values measured were 491.0 mg/L, <0.5 mg/L and 145.5 mg/L, respectively. A total of 9 metals were detected at levels above their respective LOQs in the irrigation water samples analysed. The mean concentrations were 93.4 mg/L for calcium, 5.0 mg/L for magnesium, 32.2 mg/L for potassium, 1.4 μg/L for arsenic, 1.3 μg/L for copper, 123.1 μg/L for iron, 25.2 μg/L for manganese, 19.3 μg/L for nickel, and 15.4 μg/L for zinc. Regarding the agronomic parameters, residual sodium carbonate, bicarbonates, carbonates, the sodium percentage, and the sodium and calcium ratio were analysed, the values of which were 4.4 meq/L, 579.4 mg/L, < 2.0 μg/L, 73.9 %, 313.9 mg/L and 0.25, respectively. The COD (chemical oxygen demand) and BOD (biochemical oxygen demand) were also evaluated. The COD is the amount of oxygen needed to oxidize organic matter by chemical means and convert it into carbon dioxide and water. The BOD is the amount of oxygen that microorganisms, especially bacteria, fungi, and plankton, consume during the degradation of organic substances. The COD and

BOD obtained from the samples were 32.4 mg O_2/L and 5.4 mg O_2/L, respectively.

3.3. Irrigated soil analysis

None of the agricultural soil samples analysed were free of CECs. A total of 24 CECs out of 293 were detected at concentrations above their LOQs in the samples from the soil irrigated with reclaimed water over a long period. All of them presented detection frequencies between 75 % and 100 %, except for the β-blocker propranolol and the diuretic hydrochlorothiazide (both 37 %), the pesticide carbendazim and the anti-inflammatory naproxen (both 25 %). Table 1 shows the detection frequencies, the average, and the ranges of concentration, as well as the average total load detected in the agricultural soil samples analysed. As one can see, the CEC concentrations in the reclaimed wastewater/irrigated soils ranged from the low μg/kg range to tens of μg/kg. Overall, 75 % of the CECs detected in the irrigated soil samples were pharmaceutical and personal care products (PPCPs) while the remaining 25 % were pesticides.

As can be observed in Fig. 2, analgesics, antibiotics, and antihistamines were again the groups quantified at the highest average total load in the samples under study (14.6, 13.7, 13.2 μg/kg, respectively). This finding highlights the stability of these organic contaminants in the irrigation water-soil continuum. Similar to the reclaimed water samples, the analgesic tramadol was the pharmaceutical detected at the highest concentrations. Its average total load was 14.6 μg/kg. Garduño-Jiménez et al. (2022) reported that tramadol can be retained in soils that have a high organic content and/or are acidic (pH < 6.5). The antihistamine cetirizine was the pharmaceutical product detected at the second highest average concentration level (13.2 μg/kg). Only two of the seven antibiotics studied were detected in the agricultural soil samples. Clarithromycin was found at an average total load of 12.7 μg/kg while trimethoprim was detected at 1.0 μg/kg. According to the scientific literature, data on clarithromycin, trimethoprim and cetirizine have not yet been reported in soils irrigated with treated water. The stimulant caffeine was also detected at high concentrations ranging from 0.8 to 4.9 μg/kg (an average of 2.1 μg/kg). The levels of caffeine found by Biel-Maeso et al. (2018) in soil irrigated with treated water were of the same order of magnitude as those found in this study (1.3 μg/kg). With regard to NSAIDs, naproxen was detected at a higher average concentration level than mefenamic, 5.5 μg/kg and 0.2 μg/kg, respectively. Nevertheless, naproxen was only detected in two samples at levels above its LOQ while mefenamic was found in all the samples analysed. Other relevant pharmaceuticals that also exhibited high detection frequencies and relatively high mean concentrations (above 1 μg/kg) were the antidepressant citalopram (3.7 μg/kg), the anticonvulsant carbamazepine (3.5 μg/kg), the antihypertensive telmisartan (2.9 μg/kg), the synthetic fragrance galaxolide (2.8 μg/kg), the anxiolytic venlafaxine (1.8 μg/kg), and the anxiolytic sulpiride (1.2 μg/kg). The anticonvulsants carbamazepine and lamotrigine, and the antidepressant agent venlafaxine were previously reported in a similar concentration range in soils irrigated with reclaimed wastewater (Ben Mordechay et al., 2021). Furthermore, the antidepressant citalopram was detected in 27 % of the irrigation water samples and in 100 % of the irrigated soil samples analysed. These results, along with those reported in previous scientific works, emphasize the persistency of these compounds in the agricultural environment (Martínez Bueno et al., 2022; Paz et al., 2016; Picó et al., 2019). Thus, the compounds presenting the highest accumulation rates were citalopram (86 %), clarithromycin (73 %), venlafaxine (66 %), carbamazepine (59 %) and galaxolide (55 %). This fact is related to the physicochemical properties of the molecules and the high sorption capacity of hydrophobic and non-ionic pharmaceuticals. All of them presented Log K_{ow} values > 3, except for carbamazepine, which presented a Log K_{ow} value of 2.4; this is in agreement with previous results published by our group (Martínez Bueno et al., 2021, 2022). Other compounds, such as the antibiotic ofloxacin, the anti-inflammatory ketoprofen and the β-blocker gemfibrozil were not detected in the irrigated soil samples analysed even though they were found at high concentrations (>10 μg/L) in all the irrigation water samples. This finding has been supported by other authors and is due to the relatively low stability of these types of compounds in the water distribution system (Ben Mordechay et al., 2021) or because of the low recovery percentage from the soil matrix (<25 % in the case of ofloxacin).

Regarding the pesticides, four fungicides (azoxystrobin, carbendazim, penconazole and thiabendazole) and two insecticides (imidacloprid and

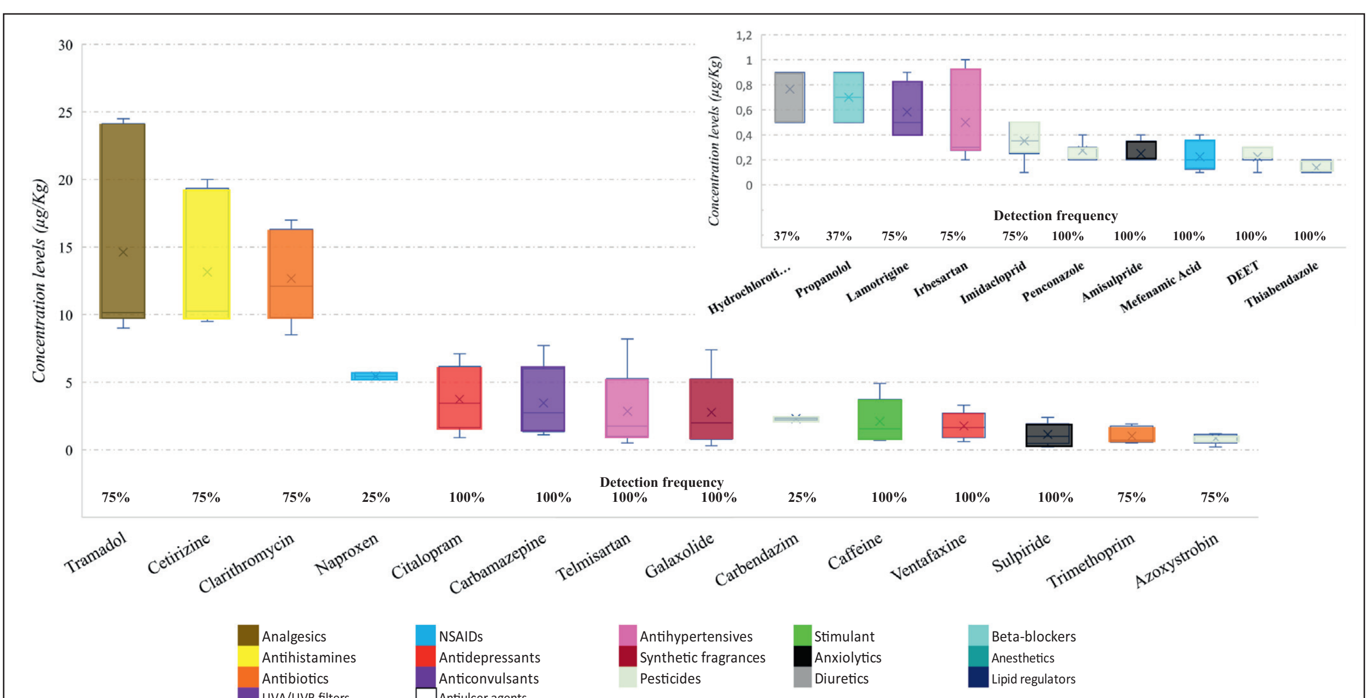

Fig. 2. CECs detected in the irrigated soil analysed. Data <LOQ are not presented. The median is presented as boxplots. Detection frequencies are listed for each compound. The vertical lines represent the maximum and minimum concentrations detected for each compound in the samples analysed.

DEET) were detected in the agricultural soil samples analysed. The average concentrations of the fungicides were 0.8, 2.2, 0.3 and 0.1 μg/kg, respectively. In contrast, the average total concentrations of the insecticides were 0.4 and 0.3 μg/kg, respectively. Picó et al. (2019) evaluated the accumulation of CECs in agricultural soil samples irrigated with treated water. The work reported levels of imidacloprid that were 250-times higher than our results (108 μg/kg) in cabbage soil samples. The fungicides penconazole and thiabendazole, and the insecticide DEET, were found in all the samples while carbendazim was only detected in one sample but at a higher concentration (2.2 μg/kg).

In summary, the concentration and fate of CECs in agricultural soils permanently irrigated with reclaimed water vary depending on the physicochemical properties of the CECs and the soil characteristics (Christou et al., 2019). In the Supplementary Material section (Table S4), additional information is given on the CEC concentration levels found in each soil sample irrigated with reclaimed water (μg/kg) according to the kind of crop. As can be observed, no significant differences were found in the CEC concentration levels detected in the analysed soil samples within the same crop. However, due to the differences in the soil characteristics, some small variations were found in the CEC concentrations between different crops. The highest average total load of CECs was detected in the cherry tomato soil samples (a mean of 101.2 μg/kg), followed by pepper (a mean of 47.6 μg/kg), cocktail tomato (a mean of 47.3 μg/kg), and cucumber soils (a mean of 43 μg/kg). The zucchini soil samples presented the lowest total load of CECs (a mean of 23.4 μg/kg).

3.4. Irrigated vegetable analysis

Of the 293 CECs selected in this study, only three pharmaceutical products were detected in the irrigated vegetable samples analysed over the study period at concentration levels above their LOQ (no pesticide was detected in those samples). These compounds were carbamazepine, lidocaine, and caffeine, with a detection frequency of 100 %. All were found in the irrigation water samples, whereas only carbamazepine and caffeine were detected in the irrigated soils. The carbamazepine and caffeine concentration levels quantified in the vegetable samples were as much as 5-times lower than in the soil samples. Table 2 shows the CEC concentration levels detected in each vegetable. The average CEC concentrations found in the fruits were 0.9 μg/kg for caffeine, 0.6 μg/kg for carbamazepine and 0.2 μg/kg for lidocaine. Two factors might explain the uptake of these compounds into the plant — the Log Kow and pKa. Compounds with Log Kow values lower than 2.5 have lower hydrophobicity and higher solubility in water. Therefore, these types of CECs can be taken up by the plant instead of accumulating in the soil (Christou et al., 2019; Martínez Bueno et al., 2022). Such was the case for the anaesthetic lidocaine, which was detected in 100 % of the irrigation water and vegetable samples analysed but not in the irrigated soil samples, thus indicating its translocation from the roots to the fruit. Furthermore, the plant uptake of carbamazepine and caffeine might be explained by the pKa of these compounds. Carbamazepine (pKa 3.8) and caffeine (pKa 10.4) are neutral compounds in the irrigation water (at pH 7.8). Therefore, they can cross the cell membranes, enter through the roots, and translocate to different parts of the plant by transpiration. Previous publications have reported that caffeine and carbamazepine are taken up in the edible parts of the plant (Beltrán et al., 2020; Ben Mordechay et al., 2022; González García et al., 2019; Gworek et al., 2021; Hyland et al., 2015; Martínez Bueno et al., 2022; Picó et al., 2019; Wu et al., 2014). As can be seen in Table 2, caffeine was detected at higher concentration levels than carbamazepine and lidocaine in all the commercial produce, except in the case of zucchini. In this crop, the anticonvulsant carbamazepine was the compound detected at the highest concentrations (a mean of 1.6 μg/kg). As in the irrigated soil samples, no significant differences were found in the CEC concentration levels detected within the same crop over the study period. Only small variations were found between vegetable types due to the differences in the matrix and the soil characteristics. The highest average total load of CECs was found in the zucchini samples (a mean of 2.9 μg/kg), followed by cherry tomato (a mean of 2.0 μg/kg) and cucumber (a mean of 1.9 μg/kg). The pepper and cocktail tomato samples presented the lowest total CEC load (a mean of 0.9 μg/kg). Our results are in line with previously reported works in the literature. For example, Martínez-Piernas et al. (2019) quantified caffeine and carbamazepine in tomato fruit at average concentrations of 0.3–1.0 μg/kg and 0.01–0.2 μg/kg, respectively, at concentrations similar to our results. On the other hand, Picó et al. (2019) reported caffeine at concentrations ranging from 48 to 125 μg/kg in crops irrigated with treated water under real-world environmental conditions. However, Picó et al. (2019) did not detect carbamazepine in the fruit even though it was found in the irrigation water and the soil. Regarding the anaesthetic lidocaine, this was found in all the vegetable samples analysed at concentrations ranging from 0.1 to 0.6 μg/kg. To the best of our knowledge, this is the first time that lidocaine has been detected in crops irrigated with treated water under real agricultural conditions.

Finally, Fig. 3 summarizes the average total load of CECs detected in the irrigation water samples (μg/L), the irrigated soil samples and the vegetable samples analysed (μg/L) as well as the accumulation rates in the soil and crops. The accumulation rates were calculated from the average total concentrations of CECs measured in the irrigation water samples against the concentrations found in the irrigated soils and vegetables. The results reveal that the accumulation rates were 31 % in the soils and only 1 % in the vegetables that were permanently irrigated with reclaimed water.

3.5. Human exposure

The different plants irrigated with reclaimed water took up contaminants into their edible parts (zucchini, cucumber, tomato and pepper). Table 3 presents the bioconcentration factor (BCF) values and the per capita daily exposure data on the three CECs detected in the irrigated vegetables. Using the average concentration of CECs in the edible part of the plant (μg/kg) and the average concentration in the irrigation water samples (μg/L), the BCF values were calculated for the three CECs detected in each vegetable. The BCF values ranged from 0.1 to 1.4 L/kg. The average BCF values found in this study were 0.1 L/kg for caffeine, 0.4 L/kg for carbamazepine and 0.6 L/kg for lidocaine. Of all the CECs detected, the anaesthetic lidocaine had the greatest tendency to accumulate in the edible part of the plant in all the crops studied. In all cases, the BCF values were below 1 L/kg, except for carbamazepine and lidocaine in the zucchini samples.

Table 2
Detection frequency (%), concentration range (μg/kg), average concentration (μg/kg), and total load (μg/kg) of the CECs detected in the analysed vegetable samples.

	Cucumber 12/21	Pepper 01/22	Tomato-cocktail 04/22	Tomato-cocktail 05/22	Tomato-cherry 04/22	Tomato-cherry 05/22	Zucchini 04/22	Zucchini 05/22	Detection frequency (%)	Concentration range (μg/kg)	Average concentration (μg/kg)
Anticonvulsants											
Carbamazepine	0.5	0.3	0.2	0.3	0.2	0.3	1.7	1.5	100	0.2–1.7	0.6
Anesthetics											
Lidocaine	0.1	0.2	0.1	0.1	0.1	0.1	0.6	0.5	100	0.1–0.6	0.2
Stimulant											
Caffeine	1.3	0.4	0.6	0.5	1.7	1.6	1.0	0.4	100	0.4–1.7	0.9
Total load (μg/kg)	1.9	1.0	0.9	0.9	2.0	2.0	3.3	2.4			

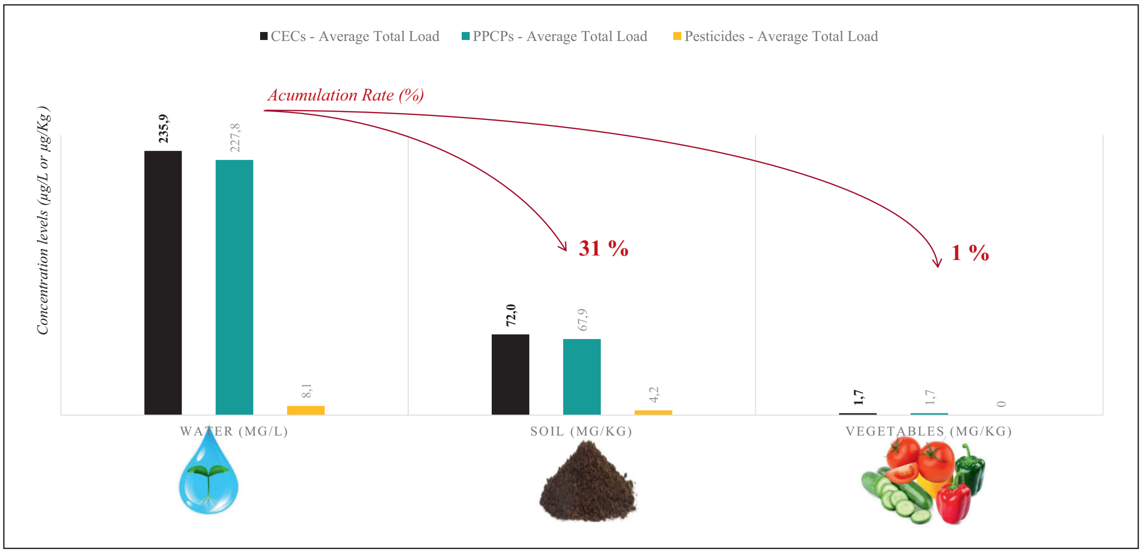

Fig. 3. Impact of reclaimed water reuse on an agroecosystem. Average total load of CECs detected in the irrigation water samples (μg/L), irrigated soil samples, and vegetable samples analysed (μg/L). Accumulation rate of CECs in the irrigated soils and vegetables.

These were found at levels of 1.1 L/kg and 1.4 L/kg, respectively, indicating that these CECs accumulate in the edible part of this plant.

According to various publications, consuming vegetables that contain contaminants, especially PPCPs, can pose a risk to human health. However, in all the previously published papers, the estimated levels were several orders of magnitude below the maximum permitted for daily human intake (Beltrán et al., 2020; González García et al., 2019; Hyland et al., 2015; Martínez Bueno et al., 2022; Wu et al., 2014). As can be seen in Table 3, in a conventional diet, the highest daily human exposure came from consuming irrigated cocktail tomatoes, which contained a total contaminant load of 0.073 μg/day (caffeine 0.06 μg/day, carbamazepine 0.009 μg/day, and lidocaine 0.004 μg/day). In contrast, cucumbers irrigated with reclaimed water were the commercial produce showing the lowest daily human exposure, with a total contaminant load of 0.011 μg/day. These values could be as much as 3-times higher in a vegetarian diet than in a conventional diet (0.219 μg/day for cocktail tomatoes and 0.032 μg/day for cucumbers). The total daily CEC exposure values ranged from 0.09 to 0.13 μg/day and from 0.26 to 0.38 μg/day in a conventional and vegetarian diet, respectively.

No regulation exists regarding the concentration levels of PPCPs in food. Regardless, all of them presented concentrations lower than the levels established by the latest regulation — (EC) No 155/2021, concerning the maximum residue limits (MRLs) for most of the pesticides found in food (10 μg/kg) (European Commission, 2021). In any case, the levels found in the commercial vegetables were as much as 3 orders of magnitude lower than the typical medical dose of these pharmaceutical products.

According to the World Health Organization (1987), the acceptable daily intake (ADI) is the maximum amount of a residue that can be ingested daily over a lifetime without posing an appreciable health risk. The ADI values for caffeine, carbamazepine, and lidocaine are 1.0×10^6, 1.2×10^6 and 1.4×10^6 μg/day, respectively (https://www.vademecum.es). In all cases, the daily human intake was as much as 5 orders of magnitude lower than the ADI, both in the conventional diet and the vegetarian diet, meaning that none of them pose a risk to human health. The obtained

Table 3
Estimated per capita daily exposure values to the three CECs detected (taken up) in the irrigated vegetables.

	Compound	Water	Vegetable		Daily human intake (μg/day)	
		Average concentration (μg/L)	Average concentration (μg/kg)	BCF (L/kg)	Conventional diet	Vegetarian diet
Cucumber	Caffeine	14.6	1.3	0.1	0.007	0.022
	CBZ	1.4	0.5	0.3	0.003	0.008
	Lidocaine	0.4	0.1	0.3	0.001	0.002
Pepper	Caffeine	14.6	0.4	0.1	0.006	0.018
	CBZ	1.4	0.3	0.2	0.004	0.012
	Lidocaine	0.4	0.2	0.5	0.003	0.008
Tomato-cocktail	Caffeine	14.6	0.6	0.1	0.020	0.060
	CBZ	1.4	0.3	0.2	0.009	0.027
	Lidocaine	0.4	0.1	0.3	0.004	0.011
Tomato-cherry	Caffeine	14.6	1.7	0.1	0.060	0.180
	CBZ	1.4	0.3	0.2	0.009	0.027
	Lidocaine	0.4	0.1	0.3	0.004	0.011
Zucchini	Caffeine	14.6	0.7	0.1	0.008	0.023
	CBZ	1.4	1.6	1.1	0.018	0.053
	Lidocaine	0.4	0.6	1.4	0.006	0.018
				Total	0.09[a]–0.13[b]	0.26[a]–0.38[b]

CBZ: carbamazepine; BCF: bioconcentration factor; Consumption data: 13.3 kg/person/year to tomato, 4.8 kg/person/year to pepper, 4 kg/person/year to zucchini and 2 kg/person/year to cucumber in a conventional diet (https://www.statista.com/statistics/745474/fresh-vegetables-consumption-per-person-in-spain-2015-by-product/#statisticContainer). Daily human exposure to a conventional diet (in the case of vegetarian diet it was established 3 times more).

[a] Total load (μg/day) considering the intake of zucchini, cucumber, pepper and cocktail tomato.

[b] Total load (μg/day) considering the intake of zucchini, cucumber, pepper and cherry tomato.

results suggest that an adult would have to consume around 100,000 kg of irrigated vegetables a day to reach the intake limit.

4. Conclusion

One of the three macrolide antibiotics included in the Commission Implementing Decision (EU) 2018/840 (clarithromycin) and two of the pesticides (diuron and terbutryn) included in the list of priority substances covered by the Water Framework Directive (Directive 2013/39/EU) were detected in the irrigation water samples and irrigated soil samples. However, none of them were detected in the vegetables permanently irrigated with that water. Carbamazepine and caffeine were the only compounds detected across the entire water-soil-plant continuum. The anaesthetic lidocaine was detected in all the irrigation water samples and vegetables samples analysed, but not in the irrigated soil samples. This finding emphasizes the great potential of this CEC to translocate through the plant.

The results obtained in this work support the reuse of water for agricultural irrigation since the concentration levels of the CECs detected in all the commercial produce analysed were very low compared to their therapeutic doses. Thus, their intake does not pose a risk to human health. This enables a circular economy to be established, improving confidence among consumers towards agricultural products grown with this type of water, and especially those produced in greenhouses, as these are very important to the EU market. Nonetheless, the study highlights the importance of carrying out a long-term control strategy on agricultural soil that is permanently irrigated with reclaimed water to avoid high accumulation rates among certain organic contaminants that could migrate over further crop seasons. The compounds that presented soil accumulation rates above 50 % were citalopram, clarithromycin, venlafaxine, carbamazepine and galaxolide. Undertaking specific soil cleaning treatments, such as washing and/or solarization processes, between crop rotations could be a useful agronomic strategy for improving and extending the reuse of the soil.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare no conflict of interest. This is an independent research. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Appendix A. Supplementary data

A detailed description of the physicochemical properties of all the pesticides selected in this study (Table S1) shows the optimal mass spectrometric parameters for each target compound using LC-MS/MS (Table S2). Detailed information on the validation data (Table S3) and on the CECs concentration levels in the irrigated soil samples for each crop (Table S4) are presented in this section. Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.160462.

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