Occurrence and fate of contaminants of emerging concern and their transformation products after uptake by pak choi (*Brassica rapa* subsp. *chinensis*)☆

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ARTICLE INFO

ABSTRACT

Recovery and reuse of nutrients is a major challenge in agriculture. A new process contributing to a circular economy is the anaerobic digestion of food waste, which is a sustainable way of recycling nutrients as the digestate can be used as fertiliser in agriculture and horticulture. However, the digestate may be polluted with contaminants of emerging concern (CECs) that can be circulated back into the food chain, posing a risk to the environment and human health. In this work, the nutrient solution was spiked with 18 selected CECs frequently detected in food waste biogas facilities, and subsequent uptake and fate of these CECs were evaluated in pak choi grown in two different nutrient solutions (mineral and organic). All spiked compounds except two (propylparaben, fenbendazole) were taken up by pak choi plants, with perfluorobutanoic acid (PFBA) and sertraline displaying the highest concentrations (270 and 190 μg/kg fresh weight, respectively). There were no statistically significant differences in uptake between mineral and organic nutrient solutions. Uptake of per- and polyfluoroalkyl substances (PFAS) was negatively correlated with perfluorocarbon chain length and dependent on the functional group (r = −0.73). Sixteen transformation products (TPs) were tentatively identified using suspect screening, most of which were Phase II or even Phase III metabolites. Six of these TPs were identified for the first time in plant metabolism and their metabolic pathways were considered.

1. Introduction

Huge quantities of food are lost or wasted in Europe (~15% of the total) and even greater quantities in Asia (~20%) and the United States (~35%) (United Nations Environment Programme, 2021). This is a pertinent issue as the global population increases, so new ways are needed to recover and reuse nutrients in a circular economy. Anaerobic digestion is an eco-friendly solution to closing the nutrient loop as it allows the reuse of food waste (Balagurusamy and Chandel, 2020). Apart from biogas, large amounts of organic residue (digestate) containing useful nutritional components are produced and can be used as crop fertiliser (Bergstrand et al., 2020). However, undesirable

components can also be present in the digestate, such as metals or contaminants of emerging concern (CECs) (Golovko et al., 2022a).

Thousands of chemicals can be categorised as CECs, but most are mainly unmonitored compounds with the potential to reach environmental compartments and cause known or suspected adverse ecological or human health effects (Rosenfeld and Feng, 2011). These include pharmaceuticals, personal care products, per- and polyfluoroalkyl substances (PFAS), pesticides, industrial chemicals, flame retardants, hormones, etc. Some CECs are persistent and can potentially enter the environment with wastewater treatment plant (WWTP) effluent or with anaerobically digested sewage sludge used as fertiliser. WWTP effluent makes a great contribution to CEC occurrence in surface water bodies,

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☆ This paper has been recommended for acceptance by Dr Jiayin Dai.
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where CECs are frequently detected at concentrations between ng/L and µg/L (Archer et al., 2017). The side-effects of using wastewater for irrigation in agriculture have been evaluated (Mañas et al., 2009; Sunyer-Caldú et al., 2022), but research is urgently needed on the relevance of anaerobic digestate for CEC concentrations in crops and ultimately in the environment and humans.

The presence of CECs in edible crops may have many undesirable effects on humans, e.g. low doses of antibiotics (clarithromycin, clindamycin, etc.) can result in the development of antibiotic resistance in bacteria, which is an emerging concern for human health (Golovko et al., 2022b; Nazaret and Aminov, 2014). Other CECs, such as PFAS, can have adverse effects on the environment (Ahrens and Bundschuh, 2014) and immunotoxicity (NTP, 2016), reproductive or carcinogenic effects (ATSDR, 2020) in humans. Parabens have known endocrine-disrupting capacity and estrogenic activity, with increasing potency with perfluorocarbon chain length (Boberg et al., 2010).

During anaerobic digestion, plant uptake, and translocation within plants, CECs may be partly or completely metabolised into new compounds, some unknown, with different physicochemical properties and in some cases more toxic effects than the parent compounds (Menger et al., 2021). Identification and monitoring of these transformation products (TPs) is critical to gain an overall picture of the contaminants present in crops fertilised with food waste digestate. Recent advances in high-resolution mass spectrometry (HRMS) and associated data treatment workflows have facilitated the identification of TPs (Menger et al., 2020).

Pak choi (*Brassica rapa* subsp. *chinensis*, also known as Chinese cabbage) was selected as a model crop in this study because of three relevant characteristics: (i) it is a commonly consumed crop in Sweden; (ii) it is a fast-maturing crop that can be harvested in 30 days; and (iii) the whole plant is edible and can be consumed raw or cooked. Despite it being a widely consumed crop in Asia, America, and Northern Europe, little information is available regarding CEC uptake in pak choi and whether this poses a potential risk to the environment and human health.

This study aimed to assess the uptake and fate of CECs by pak choi, using well-established target methodologies, and to identify TPs of any CECs present using HRMS-based suspect screening. Specific objectives were to i) evaluate the influence of nutrient solution on CEC uptake in pak choi; ii) identify TPs formed following uptake, and iii) investigate the fate of CECs and TPs in the plants.

2. Materials and methods

2.1. Chemicals and reference standards

All analytical standards used for analysis were of high purity grade (>95%). Propylparaben (PrPB), fenbendazole (FBZ), clarithromycin (CLA), clindamycin (CLI), sertraline (SER), perfluorobutanoic acid (PFBA), perfluoroundecanoic acid (PFUnDA), perfluoroheptanoic acid (PFHpA), perfluorotetradecanoic acid (PFTeDA), perfluorohexanoic acid (PFHxA), perfluorododecanoic acid (PFDoDA), perfluorooctanoic acid (PFOA), perfluorodecanoic acid (PFDA), perfluorononanoic acid (PFNA), perfluorooctanesulfonic acid (PFOS), perfluorooctanesulfonamide (FOSA), perfluorohexanesulfonic acid (PFHxS) and perfluorobutanesulfonic acid (PFBS) were purchased from Sigma-Aldrich (USA). Isotopically labelled standards (IS) (D_5-oxazepam-, D_5-diazepam, D_7-propylparaben, $^{13}C_2$-PFHxA, $^{13}C_2$-PFDA, $^{13}C_2$-PFDoDA, $^{13}C_4$-PFOA, PFHxS-18O2, $^{13}C_5$-PFNA, $^{13}C_4$-PFOS, $^{13}C_2$-PFUnDA, $^{13}C_2$-PFBA, $^{13}C_8$-FOSA) were obtained from Wellington Laboratories (Guelph, Canada), Teknolab AB (Kungsbacka, Sweden), Sigma-Aldrich (St. Louis, Missouri, USA) and Toronto Research Chemicals (Toronto, Canada).

Ultrapure water was produced by a Milli-Q Advantage Ultrapure water purification system and filtered through a 0.22 µm Millipak Express membrane and LC-Pak polishing unit (Merk Millipore, Billerica, MA). Methanol, acetonitrile, ammonium acetate, formic acid, ammonia and ethyl acetate, all of high analytical grade, were obtained from Sigma-Aldrich.

2.2. Plant material

Seeds of pak choi (var. 'Joi Choi', Impecta Förhandel, Julita, Sweden) were sown in rock wool plugs (ø 20 mm, Grodan, Roermond, the Netherlands) in a greenhouse chamber (temperature set-points: heating at 19 °C during night, 22 °C during the day). Artificial light (high-pressure sodium lamps) was used for 16 h/day. Shading screens closed when outside radiation exceeded 700 W m^{-2}. The seedlings were fed with a standard hydroponic mineral nutrient solution consisting of YaraTera Kristalon Purple + Calcinit (Yara, Oslo, Norway) at electric conductivity (EC) of 1.2 mS/cm. Fourteen days after sowing (DAS), the plants were transferred to experimental vessels as described below.

2.3. Hydroponic cultivation system and nutrition solution

The experiment was performed in a 50 m^2 greenhouse chamber in Alnarp, Sweden, during March–April 2021. The greenhouse climate set-points were as described above. The plants were cultivated under hydroponic conditions in plastic vessels containing 1.5 L of constantly aerated nutrient solution. The experiment consisted of in total 24 vessels. One plant was grown in each vessel representing one replicate. Each treatment had three independent replicates. The vessels were totally randomized and placed on a greenhouse table of approximately 4 m^2. Two different nutrient solutions were used, an organic solution produced from liquid biogas digestate (for details, see Table S1 in the Supplementary Information (SI) and Bergstrand et al., 2020) and a mineral solution containing mineral salts with similar nutrient content to the digestate solution.

2.4. Experimental set-up

Plants growing on each nutrition solution were subjected to three treatments with increasing exposure (nominal concentration of 1, 10, and 100 µg/L) to 18 CECs (four pharmaceuticals, 13 PFAS, one paraben preservative) selected based on the frequency of detection in food waste facilities in Sweden (Golovko et al., 2022a). A control treatment without the addition of CECs was also included (experimental blank). Nutrient solution was exchanged once a week and sampling (50 mL) was performed to determine the initial and final concentration of CECs in each experimental vessel (Table S2 in SI). The plant material was harvested at 42 DAS and the fresh weight (fw) of shoots was recorded. The roots were washed three times in distilled water and left to drain for 2 min before fresh weight determination. The full plants were lyophilised before analysis, to minimise degradation during storage.

2.5. Analysis

2.5.1. Sample preparation for micropollutant (MP) analysis

Samples of pak choi shoots were extracted using a validated in-house method described elsewhere (Kodešová et al., 2019a, 2019b). In brief, 0.2 g dry weight (dw) of shoot sample was weighed into a 7-mL tissue homogenisation tube (Precellys, Bertin Technologies, France), followed by the addition of IS mixture (20 ng absolute per compound) and 2 mL of extraction solvent mixture (acetonitrile and 2-propanol (3:1, v/v) + 0.1% of formic acid). After 45 min, the samples were homogenised for two 40-s rounds at 5000 rpm, with a 20-s break in between. The tubes were then centrifuged at 3900 rpm for 15 min at 20 °C. The supernatant was collected and filtered through 0.2 µm regenerated cellulose filters into a 2 mL Eppendorf tube, which was stored at −20 °C for 24 h. Around 30 min before analysis, the supernatant samples were removed from the freezer and kept at room temperature, after which they were centrifuged at 10,000 rpm for 3 min at 4 °C. A 200 µL aliquot was used for analysis.

Further information about the blanks and quality controls is included in **section S**1 in SI.

2.5.2. Instrumental analysis of CECs

2.5.2.1. Target analysis.
Extracts were analysed for the presence of the 18 CECs using a DIONEX UltiMate 3000 ultra-high-performance liquid chromatography (UHPLC) system (Thermo Scientific, Waltham, MA, USA) coupled to a triple quadrupole (TSQ) mass spectrometer (TSQ QUANTIVA, Thermo Scientific, Waltham, MA, USA). An Acquity UPLC BEH-C18 column (2.1 × 50 mm, 1.7 μm particle size; Waters Corporation, Manchester, UK) was used as an analytical column for chromatographic separation. The temperature of the column oven was set at 40 ± 2 °C. The system was equipped with a heated electrospray ion source (ESI) with static spray voltage set at 3500 V positive mode and 2500 V negative mode. The temperature of the ion transfer tube and the vaporiser was set at 325 °C and 400 °C, respectively. Data acquisition was performed under multiple reaction monitoring (MRM) using Xcalibur software (Thermo Fisher Scientific, San Jose, CA, USA) and the data were evaluated using TraceFinder™ 4.1. software (Thermo Fisher Scientific).

The mobile phase consisted of Milli-Q water with the addition of 5 mM ammonium acetate (phase A) and acetonitrile (phase B). The same linear gradient was used in both ionisation modes, with a flow rate of 0.5 mL/min. The gradient started at 2% of phase B and increased to 99% from 0.5 min to 10.0 min. This composition of the mobile phase was maintained for 3 min, until 13.0 min, after which it returned to initial conditions at 13.1 min and remained there until the end of the analytical run, which took 15 min.

2.5.3. Suspect screening

The highest nominal concentration extracts (100 μg/L), controls (0 μg/L) and blanks were analysed for identification of TPs using a Vanquish Binary Pump H with TriPlus autosampler UHPLC system coupled to a Q-Exactive Focus Orbitrap mass spectrometer. An Acquity UPLC BEH-C18 (2.1 × 50 mm, 1.7 μm particle size) was used as an analytical column for chromatographic separation. The temperature of the column oven was set at 40 ± 2 °C. The mobile phases for the positive ionisation (PI) mode (ESI$^+$) consisted of Milli-Q water (phase A) and MeOH (phase B) with the addition of 0.1% of formic acid in both phases. In negative ionisation (NI) mode (ESI$^-$), the same mobile phases were used, but with 5 mM ammonium acetate instead of formic acid as a modifier. The same linear gradient was used in both ionisation modes, with a flow rate of 0.3 mL/min. The gradient started at 5% of phase B and increased to 95% from 1 min to 10.0 min. This composition of the mobile phase was maintained for 3 min, until 13.0 min, after which it returned to initial conditions at 13.1 min and remained there until the end of the analytical run, which took 15 min. The acquisition modes used were data-dependent (DDA), selecting the five most intense ions, and data-independent (DIA) at 35 eV of collision energy (CE), with a 53–800 m/z range with 70,000/70,000 and 70,000/35,000 resolving power, respectively.

2.5.4. Suspect screening workflow

Data processing was performed using Compound Discover software (v 3.3.0.550) (for parameters and workflow used, see **section S2** and Fig. S1 in SI). From the features obtained, those present in the blanks were removed and the remaining features were verified or discarded manually in DDA data with Thermo Xcalibur software v. 3.1.66.7.

2.5.5. Quality assurance and quality control in CEC analysis

Method performance in terms of linearity in calibration, blanks, limit of quantification (LOQ), absolute recovery, precision, and matrix effect was assessed. Overall, LOQ ranged between 0.2 and 25 ng/g fw and all recovery rates were above 100%. Specific data on each parameter are provided in **section S1** in SI and recovery rates, LOQs, and matrix effect values are in Table S3 in SI.

2.5.6. Plant characterisation

Plant photosynthetic performance was measured by i) chlorophyll fluorescence and ii) gas exchange (leaf photosynthesis). Chlorophyll fluorescence parameters (basic fluorescence F_0, maximum fluorescence F_m and variable fluorescence F_v/F_m) were determined at 30 DAS using a Walz PAM-2500 instrument (Heinz Walz GmbH, Effeltrich, Germany). Leaf photosynthesis was measured at 30 DAS using a leaf-chamber photosynthesis instrument (LCPro, ADC Bioscientific, Hoddesdon, UK). Maximum photosynthesis was measured at a light intensity of 1000 μmol/s·m^2 and ambient CO_2 concentration. Leaf chlorophyll concentration was measured at the end of the experiment using a chlorophyll meter (Apogee MC-100, Apogee Instruments, Logan, UT USA). Fresh and dry weights (after lyophilisation) of shoots and roots were determined. Content of vitamin C, glucosinolates, and carotenoids in leafy plant parts was analysed using a high-performance liquid chromatograph coupled to a UV–vis detector (Esteve et al., 1997; Humphries and Khachik, 2003; Maldini et al., 2012; Panfili et al., 2004).

2.6. Uptake factor

Measured concentrations of the CECs in shoots and nutrient solution were used to calculate the uptake factor (UF) for each compound (Equation (1)). For the solution concentrations, an average value for weeks 1–3 (pak choi cultivation period) was calculated. The average plant CEC content for the three different spiking (exposure) levels tested was used to calculate UFs (Table S4 in SI).

$$UF = \frac{C_{PLANT}\left(\frac{\mu g}{kg}\right)}{C_{SOLUTION}\left(\frac{\mu g}{L}\right)} \tag{1}$$

where UF is uptake factor, C_{PLANT} is CEC concentration in shoots and $C_{SOLUTION}$ is CEC concentration in the nutrient solution.

2.7. Statistical analyses

The experiment was performed with three replicates and mean values and standard deviation are reported. Statistical analyses were carried out using Minitab (v.19) and data were tested for individual correlations with Pearson's tests and significant differences (p < 0.05) using ANOVA and Fisher's LSD method (Minitab). Values below LOQ were considered as LOQ/2 in all statistical analyses.

3. Results

3.1. Plant parameters

The different parameters related to plant development (plant photosynthetic performance, leaf photosynthesis, leaf chlorophyll concentration, content of vitamin C, glucosinolates and carotenoids, and fresh and dry weight) were measured to obtain more information about processes that can occur during plant uptake of CECs. The results are summarised in Table S5 in SI. Overall, no statistically significant correlations (Pearson correlation coefficient (r) < 0.8, confidence interval (p) > 0.05) were observed between detected levels of the target CECs and any plant parameter measured. However, for both nutrition solutions (mineral, digestate), a similar pattern of decreasing the fresh weight of shoots when exposed to CECs was observed and plants exposed to the highest concentration of CECs (100 μg/L) had significantly lower shoot fresh weight compared with the controls. This suggests that CEC uptake can affect certain processes and mechanisms in pak choi development, indicating a need for monitoring.

3.2. Uptake of CECs by pak choi shoots

Total CEC content in shoots of plants exposed to 1 and 10 µg/L of CECs ranged from 14 to 39 µg/kg fw in both nutrient solutions and no significant differences were observed between the solutions ($p > 0.05$) (Table S6 in SI). In plants exposed to the highest concentration of CECs (nominal concentration 100 µg/L) the total content in shoots was considerably higher (680 ± 41 and 620 ± 130 µg/kg fw for the mineral and digestate nutrient solution, respectively).

The concentrations observed for each treatment and compound are shown in Fig. 1. Among the pharmaceuticals, very different behaviours were observed. For example, FBZ was not detected at any exposure level, whereas shoot CLA concentration increased with the spiking level. CLI was only detected at the highest spiking level in the digestate substrate, suggesting that substrate characteristics were important for CLI uptake. SER showed the second highest shoot concentrations among the target compounds, while PrPB was not detected in any treatment. All PFAS showed a similar pattern at the 1 and 10 µg/L spiking levels in that they were mostly detected in shoots of plants grown in the digestate solution, but were not detected in the mineral solution. At 100 µg/L, all PFAS were found at notable levels in shoots of plants grown in both solutions.

Overall, the CEC concentrations differed significantly between shoots exposed to 100 µg/L and the other exposure levels (1 and 10 µg/L), suggesting that higher concentrations in the nutrient solution resulted in significantly different uptake by the crop ($p < 0.05$). However, no significant differences were observed about the use of mineral or digestate nutrient solution ($p > 0.05$). Thus, the type of nutrient solution used appears to be less important for CEC uptake in plants exposed to high concentrations of CECs. The compound present in the highest concentration in shoots was PFBA (272 µg/kg fw), followed by SER (190 µg/kg fw) and PFHxA (70 µg/kg fw). The compound families tested (PFAS, pharmaceuticals, paraben) showed similar average levels of bioaccumulation.

3.2.1. Uptake factor

At high CEC concentrations in the nutrient solution, UFs did not differ significantly between shoots of pak choi plants grown in the mineral and digestate solutions ($p > 0.05$), confirming that type of nutrient solution did not influence the concentrations of CECs n shoots. The compound that showed the highest tendency to accumulate in shoots was SER, in plants grown both in the mineral and digestate solution (UF = 33 and 2.4 L/kg, respectively). The next highest UF with both solutions was obtained for PFBA, the PFAS with the shortest perfluorocarbon chain (n = 3) in this study, with UF of 1.8 L/kg (mineral solution) and 1.6 L/kg (digestate). All other compounds had UF < 1 L/kg, indicating low uptake by pak choi.

In a previous study on sewage sludge by Kodešová et al. (2019a), SER was the compound with the highest UF, with similar values (1–37.9) for spinach (*Spinacia oleracea*) as found here for pak choi. A high tendency for the short-chain PFBA to bioaccumulate from soil/sludge has been reported previously (Blaine et al., 2013; Krippner et al., 2015; Lesmeister et al., 2021).
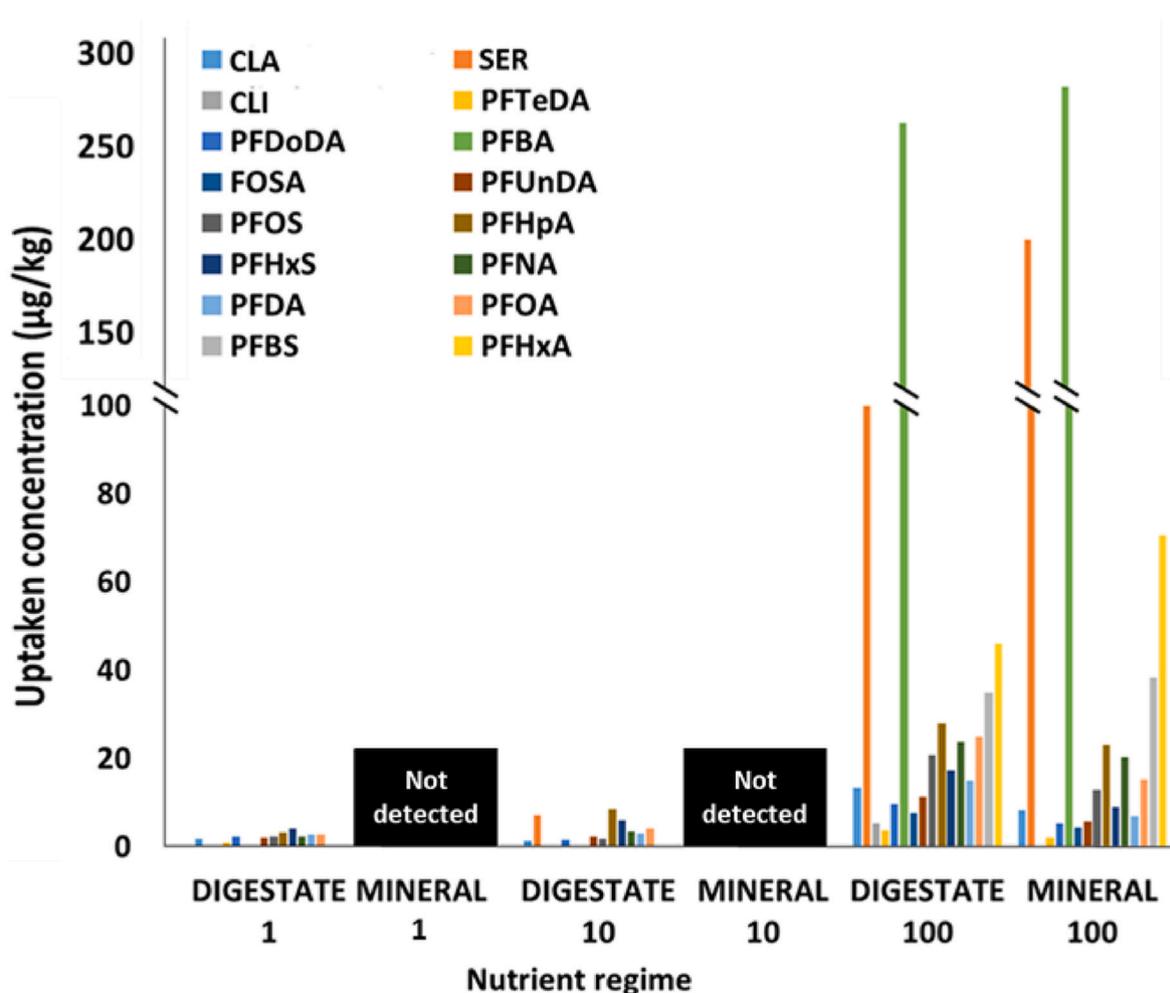
Fig. 1. Concentration (µg/kg fresh weight (fw)) of different target compounds detected in pak choi shoots grown on the nutrient solution (digestate or mineral) spiked with 1, 10 or 100 µg/L of contaminants of emerging concern (CECs).

3.3. Identification of transformation products

In data processing for the identification of TPs using Compound Discoverer, 340 features in PI and 224 in NI were obtained. The number of features of interest was reduced by (i) filtering out features present in the blanks; (ii) discarding features without MS/MS data; (iii) checking plausible retention time and fragments; and (iv) manual inspection. Only 16 features remained as tentatively identified compounds (14 in PI and two in NI). All TPs were found in plants grown on both nutrient solutions (digestate, mineral). Only four reference standards (oxfenbendazole (oxFBZ), FBZ sulfone, CLI sulfoxide, CLA N-oxide) are commercially available for these 16 compounds. This is consistent with previous findings that the greatest limitation in the identification of TPs is the lack of reference standards (Menger et al., 2021). The 16 tentatively identified TPs, along with their retention time, the parent compound, level of confidence (Schymanski et al., 2014) and evidence supporting their identification, are summarised in Table 1.

Most of the 16 TPs were generated from pharmaceuticals (six TPs of SER, five TPs of FBZ, two TPs of CLI, and one TP of CLA), while one PFAS generated two TPs. No TPs from the paraben preservative were identified. Glucoside conjugation and hydroxylation were the most common transformation pathways, but other transformations such as acetylation, (des)methylation and acid lactic conjugation were also observed. Most of the TPs identified corresponded to one-step transformation (Phase I

Table 1
Compounds tentatively identified and/or confirmed and their parent compound, level of confidence, and supporting evidence.

P: Transformation product; RT: Retention time; PI: Positive ionisation; NI: Negative ionisation

TP	RT (min)	Parent compound	Level of confidence	Evidences
Norsertraline (norSER)	8.46	Sertraline	2a	Characteristic fragments m/z: 91.0542 [C7 H7]; 129.0694 [C10 H9]; 158.9758 [C7 H5 Cl2]; Plausible RT in PI and in accordance with sertraline (8.35) Similarity with mzCloud [Creference3373#T5606#c#650869]
Acetyl sertraline (Acetyl SER)	9.78	Sertraline	3	Characteristic fragments m/z: 91.0542 [C7 H7]; 129.0694 [C10 H9]; 158.9758 [C7 H5 Cl2]; 275.0389 [C16 H13 Cl2] Plausible RT in PI and in accordance with sertraline (8.35) and isotopic profile match
4-hydroxy sertraline (4-hydroxy SER) (two isomers)	7.52/ 7.96	Sertraline	2 b (both isomers)	Characteristic fragments m/z: 273.0223 [C16 H11 Cl2] (https://doi.org/10.1002/elps.201700482); 238.0536 [C16 H11 Cl] Plausible RT in PI and in accordance with fenbendazole (8.35)
SER ketone	9.84	Sertraline	4	Plausible RT in PI according to the QSRR model and in accordance with sertraline (8.35)
SER oxime	9.91	Sertraline	4	Plausible RT in PI according to the QSRR model and in accordance with sertraline (8.35)
Acetyl hydroxysertraline (Acetyl hydroxySER)	9.02	Sertraline	3	Characteristic fragments m/z: 273.0225 [C16 H11 Cl2]; 238.0536 [C16 H11 Cl] Plausible RT in PI and in accordance with sertraline (8.35) and acetyl sertraline (9.78)
N-methylsertraline (N-methylSER)	8.22	Sertraline	3	Presence of characteristic fragments m/z: 129.0694 [C10 H9]; 158.9758 [C7 H5 Cl2]; 275.0389 [C16 H13 Cl2] Plausible RT in PI and in accordance with sertraline (8.35)
Oxfendazole (OxFBZ)	7.08	Fenbendazole	1	Characteristic fragments m/z: 159.0422 [C8 H5 N3]; 191.0320 [C8 H5 N3 O3]; 223.05811 [C15 H11 S]; 267.0452 [C14 H9 N3 O S]; 284.0478 [C14 H10 N3 O2 S] Similarity with mzCloud [Creference1614#T2472#c#276359] Confirmed with reference standard
Fenbendazole sulfone (FBZ sulfone)	7.25	Fenbendazole	1	Characteristic fragments m/z: 159.0421 [C8 H5 N3]; 191.0319 [C8 H5 N3 O3]; 300.0428 [C14 H10 N3 O3 S] Similarity with mzCloud [Creference4902#T8036#c#1386225] Confirmed with reference standard
Fenbendazole glucoside (FBZ glucoside)	7.8	Fenbendazole	2a	Characteristic fragments m/z: 159.0421 [C8 H5 N3]; 191.0319 [C8 H5 N3 O3]; 300.0428 [C14 H10 N3 O3 S] Plausible RT in PI and in accordance with fenbendazole (8.57). Neutral loss of 162 (glucoside) Similarity with bibliographic spectra (Fig. 3, E, from https://doi.org/10.1016/j.ijpddr.2019.09.001)
Oxfenbendazole + hexose (OxFBZ hexose)	6.25	Fenbendazole	2a	Characteristic fragments m/z of oxfenbendazole: 159.0422 [C8 H5 N3]; 191.0320 [C8 H5 N3 O3]; 223.05811 [C15 H11 S]; 267.0452 [C14 H9 N3 O S]; 284.0478 [C14 H10 N3 O2 S]; 299.0713 [C15 H13 N3 O2 S]; 316.0140 [C15 H14 N3 O3 S] Plausible RT in PI and in accordance with oxfenbendazole (7.08) Similarity with mzCloud [Creference1614#T2472#c#276359]
Fenbendazole sulfone + hexose (FBZ sulfone hexose)	6.38	Fenbendazole	2a	Characteristic fragments m/z of fenbendazole: 159.0421 [C8 H5 N3]; 191.0319 [C8 H5 N3 O3]; 300.0428 [C14 H10 N3 O3 S]; 332.0700 [C15 H14 N3 O4 S] Plausible RT in PI and in accordance with oxfenbendazole (7.25) Similarity with mzCloud [Creference4902#T8036#c#1386225]
Clindamycin glucoside (CLI glucoside)	7.08	Clindamycin	3	Plausible RT in PI and in accordance with clindamycin (7.25) Match of 0.999 score with Metfrag, being the only TP that contains clindamycin original structure
Clindamycin sulfoxide (CLI sulfoxide)	6.42	Clindamycin	1	Characteristic fragments m/z: 126.1273 [C8 H11 N]; 377.1826 [C18 H32 Cl N O3 S]; Similarity with MassBank of North America [CCMSLIB00005716876] Confirmed with reference standard
Clarithromycin N-oxide (CLA N-oxide)	8.52	Clarithromycin	1	Characteristic fragments m/z: 83.0494 [C5 H7 O]; 113.0596 [C6 H9 O2]; 123.0802 [C8 H11 O]; 137.0958 [C9 H13 O]. Similarity with mzCloud [Creference3138#T5031#c#600039] Confirmed with reference standard
FOSA hexose	9.2	FOSA	3	Characteristic fragments m/z of PFOSA: 77.9655 [NO2S]; 118.9925 [C2F5]; 168.9894 [C3F7]; 218.9863 [C4F9]; 268.9829 [C5F11]; 497.94568 [C8 H N O2 S F17] Neutral losses of 120.0421 [sulfo-hexoside] and 162.0546 [hexose] Plausible RT in NI and in accordance with PFOSA (9.63)
Lactic acid conjugation of FOSA (FOSA lactate)	9.55	FOSA	3	Characteristic fragments m/z of FOSA: 77.9655 [NO2S]; 497.94568 [C8 H N O2 S F17] Plausible RT in NI and in accordance with FOSA (9.63) Similarity with mzCloud [Creference3204#T5238#c#618600]

metabolites, e.g. CLA), but some TPs were formed through two or even three transformation steps, mostly from FBZ or SER as parent compounds. Fig. 2 shows the metabolic pathways from each parent compound to all TPs identified.

The different TPs identified and their occurrence was considered based on the parent origin (Table 1) and findings in previous works.

SER. Desmethylsertraline (norsertraline, norSER)) and N-hydroxysertraline (N-hydroxySER) are the most commonly reported TPs of SER and have been detected in activated sludge and the helminth *Haemonchus contortus* (Gornik et al., 2020; Zajíčková et al., 2021). These TPs were both tentatively identified in pak choi in the present study. Additional TPs potentially identified in pak choi included SER ketone (exact mass and retention time (R_T)), acetyl SER (characteristic fragments and

R_T), and acetyl hydroxysertraline (acetyl hydroxySER) (characteristic fragments and R_T). These three TPs have been reported previously in residues after biological degradation and human metabolism (Gornik et al., 2020; Zajíčková et al., 2021). An additional two SER TPs, SER oxime and N-methyl SER, were detected for the first time in this study, probably because SER oxime and SER are very similar in terms of mass (m/z 306.0447 and m/z 306.0811, respectively) and can only be differentiated with a very sensitive HRMS instrument. The same applies to N-methyl SER and dihydroxy SER (m/z 320.0967 and m/z 320.0603, respectively).

FBZ. FBZ sulfoxide (oxFBZ) and FBZ sulfone are the TPs from FBZ reported most commonly in the literature (Stuchlíková et al., 2016) and were confirmed with respective reference standards in the present study.
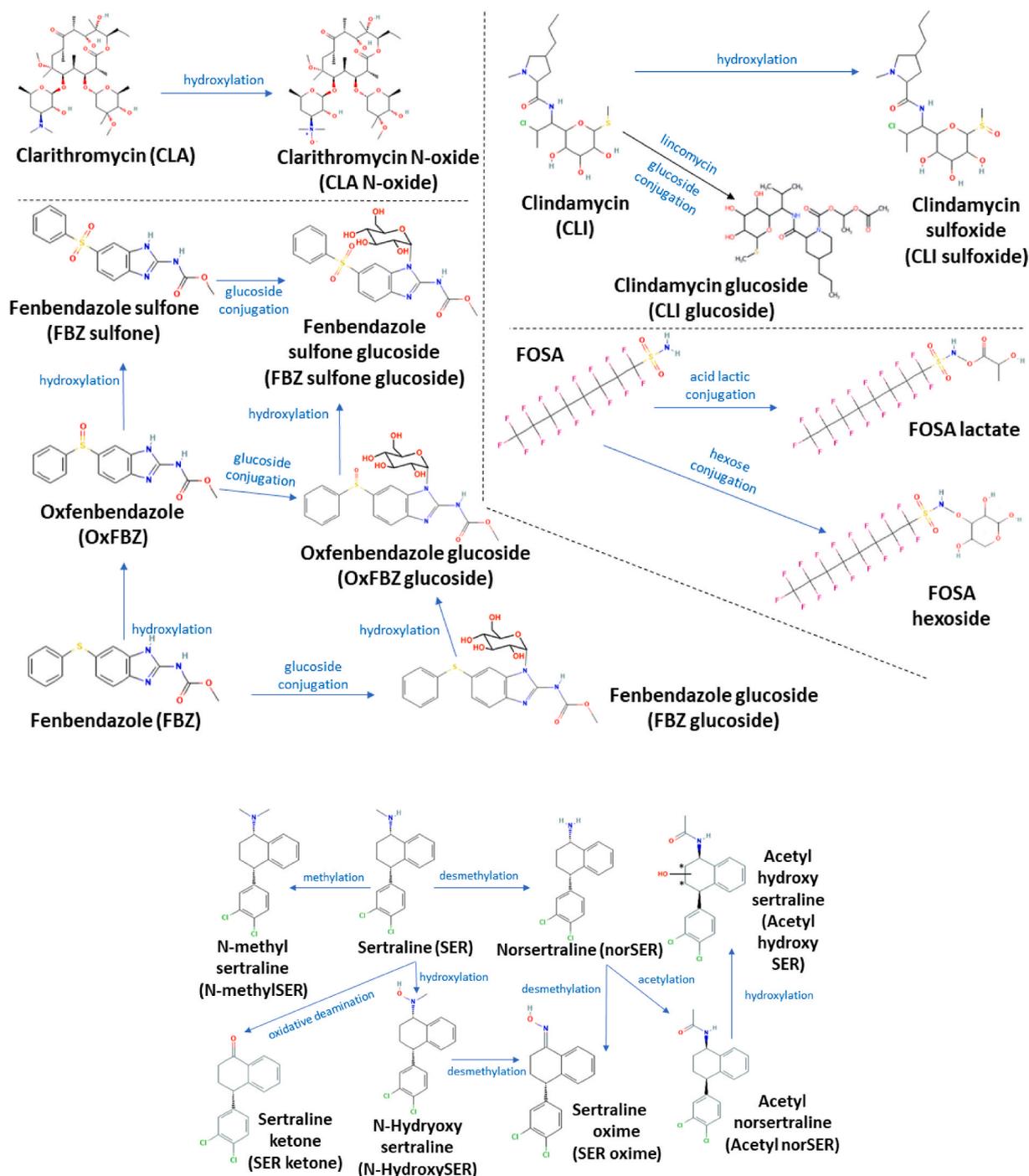
Fig. 2. Proposed metabolic pathways of the transformation products (TPs) tentatively identified in pak choi.

FBZ glucoside spectra displayed the common neutral losses (162 and 192) for glucosidation, and the same spectra have been reported recently in other plants (Stasiuk et al., 2019). These are the outcome of simple Phase I (hydroxylation) and Phase II transformations (double hydroxylation and glucosidation). All TPs from FBZ have been reported previously, without structure, in studies in vivo in harebell (*Campanula rotundifolia*) (Stuchlíková et al., 2016, 2018), but to our knowledge, the present study is the first to detect oxFBZ glucoside and FBZ sulfone glucoside in plants after degradation of FBZ. Both these TPs are formed through a combination of hydroxylation and glucosidation (Fig. 2). There is strong evidence to support these identifications, e.g. the spectral profile is practically identical to that of oxFBZ and FBZ sulfone, it has the two characteristic neutral losses (162 and 192) for glucoside addition and the retention times are plausible (Fig. 3). These two TPs are also reported here for the first time in plant metabolism.

CLI and CLA. The most commonly reported TPs for both CLI and CLA are their respective hydroxylated form (Calza et al., 2012; Ooi et al., 2017), and both were confirmed here with their respective reference standard. CLI glucoside was tentatively identified at level 3 because it was not clear which hexose structure was added in which position. However, the structure (see Fig. 2) showed a high match with Metfrag (0.999, representing CLI complete structure) as it is a lincomycin derivative and CLI differs from lincomycin only in the addition of chlorine on the parent molecule.

FOSA. This PFAS is a major intermediate usually transformed to PFOS but two TPs were tentatively identified, the only TPs from PFAS among the 13 investigated. The PFAS, in particular perfluoroalkyl acids (PFAA), are not expected to degrade during uptake or within plants, due to their high persistence (Ahrens, 2011). However, one TP was observed corresponding to conjugation with acid lactic, probably attached to the nitrogen of FOSA (Fig. 2), the most nucleophilic part. The reported confidence level was kept to 3 since no spectral evidence could be obtained, as only common PFAS fragments (m/z 77.9655 and m/z 497.94568) were present. More spectral information was available for the other TP, which had many fragments in common with FOSA (m/z 77.9655, 118.9925, 168.9894, 218.9863, 268.9829, and 497.94568 (FOSA)). Characteristic neutral losses of sulfo-hexoside (m/z of 120.0421) and hexose (m/z of 162.0546) were also detected (Fig. 2). FOSA has been reported previously in Swedish plants (leaves of birch trees) due to soil contamination (Gobelius et al., 2017), but the FOSA TPs were detected as plant metabolites for the first time in the present study.

PrPB. The most commonly detected TPs from the paraben family are their hydroxylated derivatives (Penrose and Cobb, 2022). However, no hydroxylation or any other TPs from PrPB were found in this study. Moreover, PrPB itself was not detected in pak choi plants, suggesting

extremely low or no uptake, although further rapid degradation of potential TPs could not be ruled out.

4. Discussion

4.1. Occurrence and fate of target CECs

Overall, pak choi plants cultivated on the two different nutrient solutions did not differ significantly in the uptake of CECs, although some differences were observed at low spiking levels (1 and 10 µg/L). At these spiking levels, more of the target compounds were detected when pak choi was cultivated on digestate solution compared with the mineral solution. Since CECs have a high affinity to accumulate in media with more organic content, the higher organic matter content in the digestate solution probably favoured a pre-concentration of CECs, and thus affecting their uptake by plant roots. This trend was not observed at the highest spiking concentration (100 µg/L), probably because the processes in the nutrient solution and in the plant that govern the uptake of the compounds were unable to cope with the high CEC concentrations in the solution. Considering that all TPs tentatively identified were detected in pak choi cultivated in both solutions, the type of nutrient solution provided does not seem to affect the degradation processes that most probably take place inside the crop.

PrPB. PrPB was the only target compound that was not detected, unaltered, or as TPs, in pak choi, indicating very different uptake capacity or high degradability. In previous studies, PrPB has been found in sewage sludge (Golovko et al., 2022a; Haman et al., 2014) and in lettuce (*Lactuca sativa*) (Sunyer-Caldú and Diaz-Cruz, 2021), oyster mushrooms (*Pleurotus ostreatus*) (Golovko et al., 2022b) and radish (*Raphanus sativus*) (Abril et al., 2021), although at very low levels. Other studies investigating paraben uptake have not found this compound (Margenat et al., 2019; Sabourin et al., 2012). These results agree with its octanol-water partition constant ($logk_{ow}$ of 3.04), which indicates moderate lipophilic behaviour. However, $logk_{ow}$ values alone have limited accuracy as bioconcentration predictors (Dowdy and Mckone, 1997), and it is preferable to use a combination of $logk_{ow}$ and other properties such as pKa, pH, ionic strength, biodegradation or sorption capacity (Jurado et al., 2014).

FBZ. This antiparasitic drug was not detected in pak choi, but up to five TPs from FBZ were tentatively identified. FBZ has been detected previously in sewage sludge (Golovko et al., 2022a) and at low levels in ribwort plantain (*Plantago lanceolata*) (Stuchlíková et al., 2018) and harebell (*Campanula rotundifolia*) (Stuchlíková et al., 2016). FBZ has a high $logk_{ow}$ (3.93) and can be expected to be taken up by pak choi, so its low occurrence in shoots can probably be explained by its tendency for biotransformation into new TPs. Little information is available about the toxicity of most FBZ
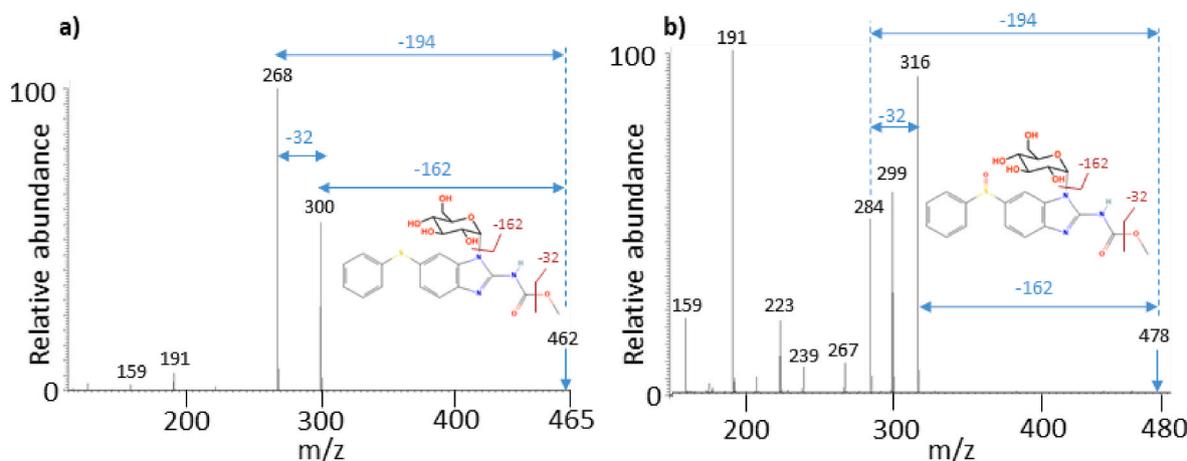
Fig. 3. Experimental mass spectra of (a) tentatively identified fenbendazole (FBZ) glucoside and (b) oxfenbendazole (oxFBZ) glucoside, with their neutral losses.

TPs.

SER. This antidepressant was the pharmaceutical that accumulated the most in pak choi and seven TPs were tentatively identified. Potential of SER to bioaccumulate in the environment has been reported previously (Boström et al., 2017; Grabicova et al., 2017). It has been detected in sewage sludge (Golovko et al., 2022a) and garden cress (*Lepidium sativum*) (Reichl et al., 2018) and spinach (Kodešová et al., 2019a). In both cases, SER was the compound that accumulated the most, reaching 190 μg/kg fw in spinach leaves exposed to 10 mg/L in water and 550 μg/kg fw in spinach roots exposed to 285–305 ng/g in the soil in the study by Kodešová et al. (2019a). Similar levels were found in pak choi shoots in the present study. Considering the high log k$_{ow}$ of SER (5.29), high accumulation in plants can be expected. However, only a few studies have examined the uptake of this common pharmaceutical in crops, and even fewer have investigated the formation of TPs from SER during plant metabolism.

CLA. CLA is an antibiotic prescribed to treat bacterial infections, such as pneumonia or bronchitis. It was found to be present at low levels in pak choi shoots (~10 μg/kg fw) and only its hydroxylate derivative was confirmed as a TP. CLA has been detected previously in lettuce (*Lactuca sativa*) (Tian et al., 2019) and oyster mushrooms (Golovko et al., 2022b). Tian et al. (2019) found extremely high concentrations of CLA, probably because they spiked it at 1 mg/L in the irrigation water, while Golovko et al. (2022b) found average levels similar to those reported here (~5 μg/kg fw). These results agree with the logk_{ow} value of CLA (3.16), which is lower than that of SER and FEN, indicating moderate hydrophilic behaviour. Considering that only one TP was found, it appears that CLA is not readily taken up by crops and also that it does not generate many TPs. An alternative explanation is the rapid elimination of any TPs back to the substrate, depending on their physicochemical properties.

CLI. This antibiotic was taken up at a low level (5.2 μg/kg fw) in pak choi plants grown on the organic nutrient solution, but two TPs from CLI were detected in both the digestate and mineral solution. Previous works have detected CLI in spinach, lettuce, and carrot (*Daucus carota*) (Jones-Lepp et al., 2010), but we found no further information on CLI detection in crops. In the study by Jones-Lepp et al. (2010), the level was below the limit of detection in lettuce and spinach and was 53 μg/kg fw in carrots, indicating a low tendency for translocation from soil to crop. The logk_{ow} of CLI was the lowest of all pharmaceuticals investigated here (2.16). Therefore, CLI showed very similar behaviour to CLA, i.e. it was present in low levels and had fewer than three TPs.

PFAS. PFAS uptake was negatively correlated with perfluorocarbon chain length (r = −0.73, p > 0.05; test performed only with carboxylic acids), as observed previously (Ghisi et al., 2019; Golovko et al., 2022b; Zhang et al., 2021). This was not unexpected, as perfluorocarbon chain length in PFAS is usually correlated with hydrophobic characteristics (Rostvall et al., 2018). Different uptake levels for PFAS with different functional groups were also observed, with sulphonamide and sulfonic acid PFAS showing lower uptake than carboxylic acid PFAS (Joerss, 2020). Both trends were apparent when the PFAS were arranged in order of perfluorocarbon chain length (Table S7 in SI). Many studies have reported PFAS uptake in crops such as carrots (Bizkarguenaga et al., 2016; Blaine et al., 2013; Lechner and Knapp, 2011), cucumber (*Cucumis sativus*) (Lechner and Knapp, 2011), potatoes (*Solanum tuberosum*) (Lechner and Knapp, 2011), radish (Blaine et al., 2013), spinach (Navarro et al., 2017), tomato (*Solanum lycopersicum*) (Blaine et al., 2013; Navarro et al., 2017) and oyster mushrooms (Golovko et al., 2022b), in levels very similar to those detected in this work. The two most relevant PFAS cases were PFBA and FOSA.

PFBA. This short-chain PFAS was taken up most, reaching a shoot concentration of 250 and 270 μg/kg fw in pak choi grown in the digestate and mineral solution, respectively. PFBA is also the PFAS with the highest plant concentrations or UF in most previous studies assessing plant uptake, e.g. in carrots, tomatoes, or radish (Bizkarguenaga et al., 2016; Blaine et al., 2014, 2013). Even though it showed high

bioaccumulation in plants, no TPs of PFBA were identified, indicating low degradation and a long lifetime once translocated in the crop.

FOSA. The levels of FOSA detected in pak choi shoots were low (7.6 and 4.4 μg/kg fw) compared with those of other PFAS, probably because the sulfamide at the end of the chain allows this compound to degrade more readily than other PFAS. This may explain why it was the only PFAS for which TPs were tentatively identified (two TPs, after conjugation with lactic acid and hexose).

5. Conclusions and outlook

The CEC concentrations in pak choi plants cultivated in different nutrient solutions (mineral and digestate) did not differ significantly, but there was a trend for higher levels of bioaccumulation in plants grown in the digestate solution. This could be due to higher organic matter content in the nutrient solution favouring pre-concentration in the substrate, leading to higher concentrations in plant material. Among the target CECs analysed, uptake of pharmaceuticals was found to be compound-dependant, e.g. PrPB was not taken up, while PFAS uptake was negatively correlated with perfluorocarbon chain length and functional group.

From the 18 selected CECs used for spiking, 16 TPs were tentatively identified (four confirmed with standard) regardless of the nutrient solution used. This indicates that transformation processes occur when the compounds are translocated by the plant and do not depend on the cultivation solution. For the TPs reported here for the first time, no toxicity information is available and further studies are needed to identify potential harmful effects on human health.

The levels of CECs detected demonstrated uptake and transformation in pak choi. Risk assessment based solely on monitoring the parent compound may lead to underestimation of TP concentrations (and their toxicity), which need special monitoring. Identification and quantification of CECs and their TPs in edible plants are necessary to clarify their effects on human health before digestate reuse as a crop fertiliser as part of food recovery and nutrient recycling in a circular economy.

Author statement

Adrià Sunyer-Caldú: Methodology, formal analysis, validation, investigation, data curation, writing-original draft, writing-review & editing, visualization. **Oksana Golovko**: Conceptualization, methodology, formal analysis, validation, investigation, resources, data curation, writing – Original Draft, writing-review & editing, visualization, supervision. **Michał Kaczmarek**: Validation, investigation, data curation. **Håkan Asp**: Methodology, investigation, writing-review & editing. **Karl-Johan Bergstrand**: Methodology, investigation. **Rubén Gil-Solsona**: Methodology, validation, formal analysis, data curation, writing-review & editing, supervision. **Pablo Gago-Ferrero**: Methodology, validation, formal analysis, data curation, writing-review & editing, supervision. **M. Silvia Diaz-Cruz**: Methodology, resources, writing-review & editing, supervision. **Lutz Ahrens**: Resources, writing-review & editing, supervision. **Malin Hultberg**: Conceptualization, methodology, resources, writing – Original Draft, writing-review & editing, project administration, funding acquisition.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2022.120958.

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