Water reuse: the risks of Contaminants of Emerging Concern (CECs) transfer from reclaimed wastewater to agricultural products.

Adrià Sunyer-Caldú[1] and M. Silvia Díaz-Cruz[1]

[1]Water, Environmental and Food Chemistry Unit (ENFOCHEM). Institute of Environmental Assessment and Water Research, Spanish National Research Council (IDAEA-CSIC), Barcelona, Spain
*E-mail contact: ascqam@cid.csic.es and sdcqam@cid.csic.es

1. Introduction

Pharmaceuticals and personal care products (PPCPs) encompass a hetergoeneous group of chemicals that includes ultraviolet filters (UV filters), parabens, antibiotics, analgesics, stimulants, among others, most of which are considered compounds of emerging concern (CECs). Over the last 15 years, PPCPs consumption has notoriously increased in the European Union (EU) [1], with its consequent greater spill in the aquatic environment. The pseudopersistence, accumulation in sediments and bioaccumulation in living organisms of PPCPs, combined with its generally poor removal in wastewater treatment plants (WWTPs), make them ubiquitous in the environment.

The global good quality water scarcity, that is only expected to increase, and the growing need of feed for a growing world population make the reuse of water in agriculture a suitable strategy to face the lack of fresh water. As agriculture is one of the main sources of food for humans, this constitutes a direct entry pathway of PPCPs in our organisms, putting human's health at risk. Many studies have been focused on environmental monitoring of PPCPs, mostly in waters. However, only limited information is available on their transfer from the environment (the transference vector being the water for irrigation) to crops. This could be due, in part, to the lack of simple, sensitive and roubust methods for the determination of PPCPs in these complex matrices.

The extraction method known as QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) developed to extract pesticides from vegetables [2, 3] has been optimized in the present work to extract PPCPs from different crops (lettuces, carrots and tomatoes) and its corresponding soils. All were cultivated in real conditions in gardens authorized in the area of the WWTP from where the two types of irrigation waters (secondary and tertiary treatment) were obtained. The irrigation waters (reclaimed wastewater) were also analyzed following an online methodology that can be found elsewhere [4]. Analysed samples comprised two different soils (clayly and sandy), two irrigation systems (drip and sprinkler) and two irrigation waters i.e (WWTP secondary treatment effluent and renaturalized water with a tertiary treatment consisting on infiltration through reactive barriers). A total of 55 PPCPs were analyzed by HPLC-ESI(QqLIT)-MS/MS.

2. Materials and methods

Sample pretreatment and extracion:

The crops and soils were lyophilized and shredded to particle size after sampling. For the analysis, ten grams of sample were weighted and ten mililiters of acetonitrile (ACN) were added along with the surrogate standard. After 4 min. of manual shaking, QuEChERS citrate salts were added and the shaking was done again. After adding the clean-up QuEChERS salts, the samples were centrifuged, acidified with formic acid, evaporated, transferred to a LC-vial, and reconstituted with the internal standards solution.

HPLC-MS/MS analysis:

These analyses were performed in a HPLC Symbiosis™ Pico from Spark Holland (The Netherlands) coupled to a mass spectrometer 4000 QTRAP™ MS/MS from Applied Biosystems-Sciex (California, USA). The chromatographic separation was performed with a Hilar Purosher STAR HR R-18 ec (50 mm × 2.0 mm, 5 µm) column with a precolumn of the same material. MS/MS detection was carried out under positive and negative electrospray ionisation and in selected reaction monitoring (SRM) mode.

3. Results and discussion

The methods for the solid matrices analysis (lettuces, carrots, tomatoes and soils) were validated separately. Validation was made in each case in terms of linearity, repeatability, reproducibility and sensitivity. Matrix effects were also evaluated. To this end, different experiments were performed:

- Validation: a small part of each original sample was mixed and, from this mix, five replicates at three different concentrations within the linear range were spiked before starting with the extraction of the samples, leaving one intact for analyze as a blank.
- Matrix effect: three samples of the mix were extracted following the same methodology and were spiked after all the process extraction, to check enhancements or suppressions of the signals in the presence of matrix.
- Samples analysis: a surrogate standard was added before the extraction to have an indicator of the quality of the extraction.

For each sample, three replicates were performed, and quality controls were inserted randomly among samples, to ensure the quality of the analysis. The recovery rates obtained for all the matrices studied were between 80% and 120% for most compounds. As an example, Figure 1 shows the recovery rates determined for the analysis of lettuces. The limits of detection (LODs) and limits of quantification (LOQs) calculated were in the ranges 0.03-0.81 ppb and 0.1-2.69 ppb, with a correlation coefficient of $r^2 > 0.97$, indicating a quite good linear behavior.

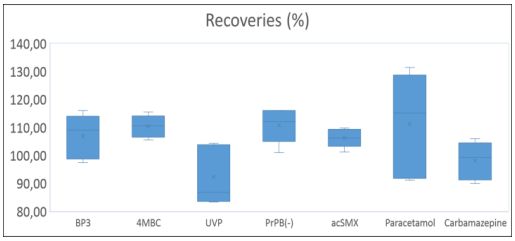

Figure 1: Recoveries (%) in lettuce samples of some of the compounds spiked with 1 00 ppb of standards (5 replicates)

Sample number	∑UVFs	∑PBs	∑Pharmaceuticals	∑Others	∑TOTAL
1	51,7	1,4	76,3	0,0	129,4
2	18,9	0,4	18,1	8,8	46,1
3	124,3	10,2	63,3	15,24	213,1
4	81,2	2,9	53,0	16,46	153,7
5	102,6	8,7	79,8	13,26	204,4
6	95,6	1,1	41,0	15,66	153,4
7	92,9	4,5	52,6	26,8	176,8
8	103,5	10,9	41,3	16,04	171,6
Units are in ppb; UVFs: Ultra violet filters; PBs: Parabens					

Table 1. Concentrations (ppb) of the target analytes grouped by family of compounds, i.e. UV filters, parabens, pharmaceuticals and other compounds

For the quality control, all of the retention time deviations were calculated, discarding the ones smaller than 2.5%. The ion ratio abundance was also evaluated discarding the results that showed differences above 5%. The summaries of the results obtained for the lettuce samples are shown in Table 1. Results indicated that the most frequently detected compounds were benzophenone-2 (BP2), 4-hydroxybenzophenone (4-HB), benzotriazol (BZT) and drometizole (UVP) (all UV filters), nalidixic acid (antibiotic), diclofenac (anti-inflammatory), carbamazepine-10,11-epoxy (anti-epileptic), N-desmethylvenlafaxine (N-desVFX, anti-depressant) and salicylic acid (anti-septic). All samples bioaccumulated more the UV filters type than the other groups of compounds. Higher values corresponded to 4-HB solar filter. Factors favouring lower accumulation were clayey soil and irrigation with renaturalized water by infiltration through reactive barriers by sprinkling system.

4. Conclusions

The validated method based on QuEChERS extraction and analysis by HPLC-ESI(QqLIT)-MS/MS proved to be suitable for the detection of PPCPs in vegetables and soils in the different conditions studied. According to the results obtained, the best combination, among the various tested to reduce the PPCPs transfer from the reclaimed wastewater to crops corresponded to the use of renaturalized water by infiltration through reactive barriers, irrigating by sprinkling in a clay soil.

5. References

[1] Lockwood S, Saïdi N, Ann Morgan V. 2019. Options for a strategic approach to pharmaceuticals in the environment (Final report), United Kingdom: Deloitte. 25-26 p.

[2] Anastassiades M, Lehotay SJ, Stajnbaher D. 2003. Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) approach for the determination of pesticide residues. J AOAC Int 86:412-431.

[3] Kmellár B, Fodor P, Pareja L, Ferrer C, Martínez-Uroz MA, Valverde A, Fernandez-Alba AR. 2008. Validation and uncertainty study of a comprehensive list of 160 pesticide residues in multi-class vegetables by liquid chromatography-tandem mass spectrometry. J Chromatogr A 1215:37-50.

[4] Gago-Ferrero P, Mastroianni N, Díaz-Cruz MS, Barceló D. 2013. Fully automated determination of nine ultraviolet filters and transformation products in natural waters and wastewaters by on-line solid phase extraction–liquid chromatography–tandem mass spectrometry. J Chromatogr A 1294:106-116

Acknowledgements - The authors thank the Project ROUSSEAU, CTM2017-89767-C3-1-R, supported by the Spanish Ministry of Science, Innovation and Universities, for the financial support and BEKOlut® QuEChERS Kits for the material provided.