Influence of the spiking procedure on organic contaminants recovery from soil

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As world demands for water grow, effluent reuse becomes increasingly important as an indispensable component of the integral water resource management, and is widely regarded as a sustainable approach in agricultural irrigation. Effluent reuse in agriculture also contributes to nutrients recycling, as phosphorus, alleviating pressure on over-exploited resources (e.g. phosphate rock, included in the EU list of 27 Critical Raw Materials). However, it has been reported that pharmaceuticals and personal care products (PPCPs) are not completely removed from effluent in wastewater treatment plants (WWTPs). Thus, the use of reclaimed wastewater (RWW) for the irrigation of crops may result in the continuous exposure of the agricultural environment to pharmaceutical and personal care products (PPCPs). In recent years, certain evidence indicates that these organic contaminants may become disseminated in agricultural soils as a result of irrigation with RWW but also due to the amendment with manure and biosolids. The PPCPs, and other related compounds, may undergo sorption/desorption and transformation processes (both biotic and abiotic), and have the potential to affect the soil microbiota. PPCPs found in the soil pore water (bioavailable fraction) as a result of RWW irrigation may be taken up by crop plants, bioaccumulate within plant tissues and subsequently enter the food webs, representing an important alternative pathway for the exposure of humans to PPCPs, with potential health implications.

While investigating the fate and remediation strategies for organic contaminants in the environment, unavoidably, a number of chemical analyses must be performed regarding the amount or the concentration of the parent compounds and/or their transformation products and/or their metabolites in samples taken from the relevant environmental receptors.

One important aspect when conducting laboratory scale studies, with non-contaminated samples, is the way with which the spiking procedure is generally performed to determine the recovery of the analytical method. Spiking environmental samples, in particular solid samples, with standard solution followed by immediate extraction, can lead to an overestimation of the recovery. This is so, because no time is given to the system to establish possible equilibria between the solid matter inorganic and/or organic—and the contaminant. Therefore, the spiking procedure needs to be reconsidered by including a study of the extractable amount of the contaminant versus the time elapsed between spiking and the extraction of the sample, as well as the conditions to which the samples were exposed to (e.g. light/no light).

In this work, the spiking procedure was investigated using 3 PPCPs as target analytes, a non-steroidal anti-inflammatory, an antibiotic and an antibacterial and anti-fungal agent: Ibuprofen (IBU), sulfamethoxazole (SMX) and triclosan (TCS), respectively. The soil used was collected from an agricultural field used for organic tomato growth located in Santarém (39°12'42.6"N 8°42'41.5"W), Portugal.

Initially, an analytical methodology was developed enabling the determination of the 3 PPCPs in soil samples. The sample preparation procedure is based on the quick, easy, cheap, effective, rugged and safe (QuEChERS) principle based on a salting-out extraction with a solvent (acetonitrile) followed by filtration using PTFE syringe filters (Table 1). Analysis was performed by high-performance liquid chromatography (HPLC) with diode array (DAD) and fluorescence (FLD) detectors (Table 2).

Table 1. QuEChERS extraction recoveries and validation parameters.

Compound	Recovery SE (%)[a]	Matrix effect (%)	Recovery (%)[b]	Repeatability (CV %)	Intermediate Precision (CV %)	MDL (mg/kg d.w.)	MQL (mg/kg d.w.)
SMX	91	+ 19	72	8.5	5.5	0.4	1.1
TCS	95	+ 23	91	19	6.1	1.2	3.6
IBU	102	+ 24	112	5.1	7.3	0.3	0.9

Legend: [a] Recovery for the spiked extracts; [b] Recovery for the spiked matrix;

Table 2. HPLC-DAD-FL method validation parameters

Compound	LOD[a] (mg/L)	LOQ[b] (mg/L)	Working range (mg/L)	r^2
IBU	0.18	0.55	0.5-15.0	1.000
SMX	0.58	1.75	0.5-15.0	0.999
TCS	0.14	0.45	0.5-15.0	1.000

For the spiking experiments the following variables were studied:

i. spiking volume;
ii. mechanical shaking, enhance compounds contact with soil and homogenisation;
iii. sample drying, to allow water and solvent evaporation;
iv. storage at 4 oC, to simulate contamination ageing while decreasing biological activity.

All tests were carried out in duplicate.

The results showed that the drying process had the highest impact on PPCPs recovery. The obtained results also indicate that by using a spiking volume of 1:1 (w:v), allowed to obtain higher recoveries with lower standard deviations. As the water was not evaporated, most of the PPCPs were in a bioavailable form, being more easily extracted. The best recoveries and the lowest relative standard deviations (RSD) were achieved when the soil was spiked using volume of 1:1 (w:v), followed by 2h of mechanical shaking and 3 days at 4 oC (91±2%, 72±1%, 112±6% for IBU, SMX and TCS, respectively).

The results here obtained are of valuable knowledge for the study of PPCPs in soil samples where a spiking procedure is required as it allows the development of reliable spiking procedures prior conducting remediation or environmental fate studies.

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