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Determination of organic microcontaminants in agricultural soils irrigated with reclaimed wastewater: Target and suspect approaches

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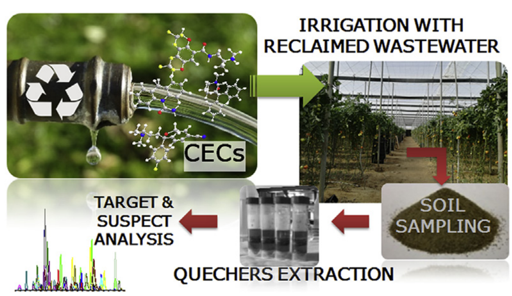
HIGHLIGHTS

- Wide-scope target/suspect analysis to determine organic micro-contaminants (OMCs).
- Modified and validated QuEChERS method for the target analysis of 73 OMCs in soil.
- Development of a suspect workflow for the screening of >1300 analytes in soil.
- Monitoring of OMCs in real agricultural soils irrigated with reclaimed wastewater.
- Reporting of 11 compounds in real samples monitored with the proposed methods.

GRAPHICAL ABSTRACT



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ABSTRACT

Water scarcity is a problem worldwide, affecting specially countries with desert/semi-desert areas and low/irregular rainfall. In this context, reuse of reclaimed wastewater (RWW) for agricultural irrigation is undoubtedly a key strategy to reduce fresh water consumption. It is well-known that current wastewater treatments do not effectively remove organic microcontaminants (OMCs), and research in water analysis of OMCs is extensive. However, the focus on agricultural soils irrigated with RWW as potential recipients of OMCs and potential sources of OMCs to crops is still in their beginnings. This study aims to apply a target and a suspect approach for the multi-residue monitoring of OMCs in agricultural soils and a soilless subtract, both irrigated with RWW for more than ten years. The study involved, firstly, the development and validation of an extraction method for target analysis of 73 OMCs using a QuEChERS-based method and liquid chromatography coupled to quadrupole-linear ion trap mass spectrometry (LC-QqLIT-MS/MS); and secondly, the application of a suspect workflow for the screening of a list of 1300 potential contaminants using LC coupled to quadrupole-time-of-flight MS (LC-QTOF-MS). The results demonstrated the occurrence of 11 OMCs in the agricultural soil samples and 26 in the soilless subtract (0.1–100 ng g^{-1}, dry weight, d.w.). The suspect analysis leaded to the confirmation of 28 OMCs analytes from the list of candidates. The subsequent combination of both strategies (suspect and target) revealed the presence of 11 new OMCs which were not previously reported. Furthermore, this study presents the first application of a OMCs suspect screening to agricultural soils irrigated with RWW for a long period.

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These results highlight the importance of monitoring soils with RWW-based irrigation and the application of wide-scope approaches for environmental analysis.

1. Introduction

Nowadays, water scarcity for agriculture purposes has become one of the main problems worldwide due to the climate change and raising population. In Mediterranean countries, where low rainfall is unevenly distributed over the year and water resources are limited, reuse of reclaimed wastewater (RWW) for crop irrigation is essential to deal with water shortages. This practice reduces fresh water withdrawals and contributes to an efficient water usage [1].

Nevertheless, the inefficient removal of organic microcontaminants (OMCs) in wastewater treatment plants (WWTPs) leads to unpredictable long-term consequences for the environment. In particular, these OMCs are released in agricultural fields after repeated RWW irrigation occurrences, being able to accumulate in soils [2,3] and translocate to crops intended for human consumption [4–6]. Their behavior and persistence depend on their different physical-chemical properties, adsorption, conjugation form and charge in the soil-compound system, but also on soil characteristics and agricultural practices [7]. Data about the occurrence/accumulation of OMCs in agricultural soils and their possible translocation to the final product are needed to ensure a safe use of RWW and subsequent consumer acceptance.

Considering the large number of OMCs commonly found in RWW and their various properties, it is necessary to apply wide-scope extraction methodologies to provide a thorough evaluation and, therefore, a better understanding of their behavior and effects. The most frequently extraction methods applied to soil samples are ultrasound-assisted extraction (USE), pressurized-liquid extraction (PLE) and microwave-assisted extraction (MAE) [8]. However, the QuEChERS (acronym of quick, easy, cheap, effective, rugged and safe) method, which was primary developed for the determination of pesticides in crops [9], has been successfully applied to the extraction of OMCs (including pesticides, pharmaceuticals, veterinary drugs among others) in different environmental commodities such as sewage sludge [10,11], water, soil, sediments [12–14], agricultural fields which were amended with manure or sludge [15], agricultural soil [16] and vegetables [4,17]. However, in most cases, the scope of the methods is limited and focused on the monitoring of selected groups of compounds, very often in studies conducted under controlled conditions. Nevertheless, a comprehensive evaluation of the occurrence of OMCs in real soils, often exposed to long periods of irrigation with RWW and subject to the influence of a large number of pollutants, requires multi-analyte methods able to identify a larger number of compounds, as well as their transformation products (TPs), whose relevance has been previously highlighted [5].

In addition to the need for multi-residue extraction procedures, the analysis of OMCs at trace level in complex environmental commodities is necessarily accomplished by liquid chromatography-tandem mass spectrometry (LC-MS/MS) for target analysis in search of sensitivity and selectivity [4]. Likewise, screening methodologies carried out by high-resolution mass spectrometry (HRMS) using quadrupole time-of-flight (QTOF-MS) and Orbitrap analyzers, have opened a new scenario making possible the identification of OMCs out of the scope by non-target and suspect screening strategies [18,19].

Although the number of studies investigating the presence and accumulation of OMCs in soils is increasing in the recent years, evidence in real agricultural fields is scarce, especially when irrigation based on RWW is applied [3,20]. Table S1 compiles some of the most recent studies conducted under field conditions. Although these studies provide valuable information for the understanding of the behavior of OMCs in real soils, it is still necessary to expand knowledge about the influence of factors as diverse as the type of soil, type of crop, type of irrigation or the influence of cultivation practices, such as intensive or soilless cultivation. Besides, it is important to notice that the application of a target and a suspect strategy to obtain wide scope occurrence data is very limited. Up to our knowledge, this is the first application of a combined target-suspect analysis for the monitoring of OMCs in agricultural soils irrigated with RWW.

Under this scenario, the main objectives of this work have been: i) the development and validation of a QuEChERS-based method for the multi-analyte analysis of OMCs (73 analytes) in agricultural soils and their analysis by LC-MS/MS; ii) the development of a suspect screening strategy able to identify new OMCs out of the target analysis by LC-QTOF-MS; and iii) the application of both, target and suspect approaches, to soils of intensive agriculture, which have been constantly irrigated with RWW for a long period.

2. Materials and methods

2.1. Chemicals and reagents

A total of 73 target compounds (priority substances, pharmaceuticals and TPs) have been selected based on their recurrent identification in WWTP effluents (Table S2). Reference standards (purity > 98%) were acquired from Sigma-Aldrich (Steinheim, Germany). Acetonitrile (ACN), methanol (MeOH), glacial acetic acid and formic acid (LC-MS grade) were purchased from Sigma-Aldrich. Ultrapure water was produced using a Milli-Q water purification system from Millipore (Darmstadt, Germany). For QuEChERS extraction, anhydrous magnesium sulfate ($MgSO_4$), sodium acetate (NaOAc), sodium chloride (NaCl), sodium citrate tribasic dihydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) and disodium hydrogen citrate sesquihydrate ($C_6H_6Na_2O_7 \cdot 1.5H_2O$) were purchased from Sigma Aldrich (all purity > 98%). Octadecyl silica (C18) and primary-secondary amine (PSA) were from Supelco (Bellefonte, PA, USA).

Stock standard solutions of each analyte were prepared at 1000–2000 mg L^{-1} in MeOH. The surrogate standards carbamazepine-d_{10} and cyclophosphamide-d_4 were used as internal quality standards for extractions. Multi-compound working solutions were prepared at a concentration of 10 mg L^{-1} in MeOH by proper dilution of the individual stock solutions. All standard solutions were stored in amber glass vials at −20 °C. Daily working solutions, prepared at appropriate concentrations in ACN:H_2O (10:90, *v/v*) or in matrix extract, were used for the preparation of the calibration standards and the validation study.

2.2. Sample collection and preparation

Soil samples from three greenhouses (intensive production, 13000–25000 m^2) in Almeria province (Spain) were selected to monitor the occurrence and accumulation of the target OMCs in