

New Challenges for the Analytical Evaluation of Reclaimed Water and Reuse Applications

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Abstract Presence of unregulated and not assessed organic microcontaminants in wastewater effluents represents a significant challenge to wastewater reclamation, especially if intended for human consumption or irrigation practices. Problems associated to the repeated release of treated wastewater in the environment for reuse applications, such as infiltration into the underground including pollution of ground water or accumulation in soil and plants, are still scarcely investigated. Consequently, comprehensive and high-throughput analytical methods have to be developed and validated to provide a comprehensive evaluation of these microcontaminants in water, soils and crops. This chapter aims to give an overview of the analytical strategies currently used in this field, its requirements and limitations.

Keywords Mass spectrometry, Organic microcontaminants, Screening analysis, Transformation products, Wastewater

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D. Fatta-Kassinos et al. (eds.), *Wastewater Reuse and Current Challenges*,
Hdb Env Chem (2016) 44: 7–48, DOI 10.1007/698_2015_364,

© Springer International Publishing Switzerland 2015, Published online: 15 July 2015

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1 Introduction

Reuse of wastewater is nowadays accepted as a strategy that can contribute significantly to an efficient and sustainable water usage [1]. However, the inefficient removal of a large number of organic contaminants of emerging concern (CECs) during wastewater treatments can represent a limitation. Pharmaceuticals, perfluorinated compounds, artificial sweeteners, hormones, disinfection by-products, UV filters, brominated flame retardants, benzotriazoles, naphthenic acids, siloxanes, musk fragrances, etc. are among the long list of CECs reported, to which we must add the transformation products (TPs) generated during water treatment processes or by natural processes [2]. It is nowadays accepted that the removal of these compounds prior to discharge of treated water is essential to avoid damage of water resources. However, increasing reuse practices involve new exposure routes, such as soils and crops. Consequently, the accumulation of contaminants in soils after irrigation practices and the evaluation of the uptake by crop plants are new insights that demand research.

In the last decades, scientific community has made a great effort to provide analytical methods able to accurately determine CECs and their TPs in different environmental matrices, overcoming limitations associated to analytes (high polarity, instability, etc.) and matrix nature (matrix effects). This effort has been possible thanks to significant technological advances in analytical instrumentation. Chromatography–mass spectrometry coupled systems have emerged as the undisputed leaders in this field, due to their large separation and identification capacity for, in principle, an unlimited number of compounds. Multi-stage mass analysers like triple quadrupole (QqQ-MS) or quadrupole linear ion trap (QqLIT-MS) have dramatically enhanced the sensitivity, specificity and quantitative performance of target analyses. Likewise, the increasing availability and application of high-resolution mass spectrometry (HRMS) has contributed in the expansion of the scope of analyses, by implementing wide-scope screening methods for non-target analytes.

HRMS has also provided an excellent platform for identification studies of unknown TPs, although in many cases results are insufficient for a reliable identification and structure allocation.

This chapter intends to provide an overview of the main analytical methodologies currently applied for the evaluation of CECs and their TPs in wastewater, reclaimed water, soils and plants. Analytical methods are discussed considering new developments in sample preparation and determination. Finally, the current contamination status by different groups of organic contaminants in soils and crops is overviewed.

2 Determination of Organic Microcontaminants in Wastewater and Reclaimed Water

Trace analysis of organic contaminants in raw and treated wastewater is usually performed to assess the contaminants present in the effluents and identify the formation of possible TPs. Nonselective extraction/preconcentration steps are usually combined with extensive target analyses, non-target screening methods and/or with analytical strategies for the identification and structure elucidation of unknown compounds, by using different chromatography–mass spectrometry approaches.

2.1 Sample Extraction

Low concentrations of contaminants in wastewater make the sample enrichment a crucial step. However, the comprehensive evaluation of the samples entails great difficulty due to the large number of compounds involved and the differences in their properties. Some examples are included in Table 1.

Traditional liquid–liquid extraction (LLE) has been successfully applied for the extraction of less polar contaminants. However, new developments tend to focus on reducing solvent usage and improving extraction of more polar or ionic compounds.

Solid phase extraction (SPE) is the most comprehensive and widely used technique. To extend its applicability to more hydrophilic compounds, traditionally used sorbents have been replaced by new polymeric materials. Oasis HLB (hydrophilic–lipophilic balance) sorbent, containing lipophilic (divinylbenzene) and hydrophilic (*N*-vinyl-pyrrolidone) groups in its structure, and Strata-X material, based on a polydivinylbenzene resin containing piperidone, have been extensively used [3–6]. Both provide large capacity and high retention of a broad type of compounds. However, the lack of selectivity causes undesirable matrix effects when working with MS.

To improve selectivity and retention for ionic compounds, mixed-mode polymeric sorbents exhibiting both hydrophobic and ion-exchange properties have been developed. These materials base their structure on a polymeric skeleton chemically modified in its surface with strong and weak cationic or anionic functional groups. Commercially available sorbents, such Oasis MAX, Oasis MCX, Strata X-C, Strata

Table 1 Analysis of organic microcontaminants in wastewater

Analytes	Water matrix	Extraction	Separation	Analysis	Reference
Multi-class emerging organic pollutants (53)	Tap, surface and wastewater	SPE Oasis HLB	SymmetryShield RP18 (2.1 × 150 mm, 3.5 µm) in positive mode Luna Phenyl-Hexyl (150 × 2 mm, 3 µm) in negative mode	LC-(ESI+/-) TQ-MS/MS	[3]
Pharmaceuticals (38), metabolites (10), pesticides (6), disinfectants (2)	Wastewater	SPE Oasis HLB	Zorbax SB C18 (250 × 3.0 mm, 5 µm)	LC-(ESI) QqQLIT-MS/MS	[4]
Pharmaceuticals (50)	River water and wastewater	SPE Oasis HLB	Acquity UPLC HSS T3 (100 × 2.1 mm, 1.8 µm)	UPLC-(ESI) TQ-MS/MS	[5]
Pharmaceuticals (18)	Wastewater	SPE Strata X	Gemini C18 (150 × 2 mm, 3 µm) ESI + Synergi MAX-RP (100 × 2 mm, 2.5 µm) ESI-	LC-(ESI+/-) TQ-MS/MS	[6]
Multi-class emerging organic pollutants (pharmaceuticals, personal care products and illicit drugs) (50)	River water and wastewater	SPE Oasis MCX	Acquity UPLC BEH C18 column (100 × 1 mm, 1.7 µm)	UPLC-(ESI +/-)TQ-MS/ MS	[7]
Pharmaceuticals (48) and metabolites (6)	Surface water and wastewater	SPE Oasis MCX	BEH C18 column (100 × 1.0 mm, 1.7 µm)	UPLC-(ESI +/-)TQ-MS/ MS	[8]
Basic, neutral and acidic pharmaceuticals (15)	Wastewater	SPE in series Oasis MCX and Oasis MAX	Waters Acquity HSS T3 (100 mm × 2.1 mm, dp 1.8 µm)	LC-QTOF-MS	[9]

Amphetamine drugs	Wastewater	MISPE SupelMIP-Amphetamine	Halo C18 (100 × 2.1 mm, 2.7 μm)	LC-(ESI)TQ-MS/MS	[10]
Selected psychoactive pharmaceuticals (7)	River water and wastewater	MISPE SupelMIP-antidepressant	Acquity UPLC BEH C18 column (2.1 × 50 mm, 1.7 μm)	UPLC-(ESI)+TQ-MS/MS	[11]
Non-steroidal anti-inflammatory drugs (15)	Wastewater	MISPE Affinitube MIP-NSAIDs	Fused-Core™ Ascentis Express C18 (100 × 4.6 mm, 2.7 μm)	LC-UV LC-(ESI)TQ-MS/MS	[12]
β-blockers (8)	Wastewater	MISPE MIP4SPE™ β-blockers	Purospher Star RP-18 endcapped column (125 × 2.0 mm, 5 μm)	LC-QqLIT MS	[13]
Pharmaceuticals (56), metabolites (10) and corrosion inhibitors (2)	Hospital wastewater	On-line mixed-bed multilayer SPE Isolute ENV+ and Oasis HLB	Atlantis T3	LC-TQ-MS/MS	[14]
Polar organic micropollutants (88)	Ground, surface and wastewater	On-line mixed-bed multilayer SPE Oasis HLB, Strata XAW, Strata XCW and Isolute ENV+	Atlantis T3 (150 × 3.0 mm, 3 μm)	LC-(ESI)TQ-MS/MS	[15]
Cytostatics (13) and metabolites (4)	Groundwater, surface water, and raw and treated wastewater	On-line SPE PLRP-s (crosslinked styrene-divinylbenzene polymer)	Purospher STAR RP-18e (125 × 2 mm, 5 μm)	LC-(ESI) QqLIT-MS/MS	[16]
Estrogens (estrone, estradiol, estriol and ethinylestradiol) (4), perfluoroalkyl carboxylates (C4-C11) (8), and perfluoroalkyl sulphonates (5)	Wastewater	LVI (900 μL)	ZORBAX Eclipse Plus-C18 (75 × 3.5 mm, 3.5 μm)	LC-(ESI)TQ-MS/MS	[17]
Illicit and legal drugs and urinary indicators (cotinine, caffeine and creatinine)	Wastewater	LVI (1,800 μL)	Atlantis T3 C18 (150 × 4.6 mm, 5 μm)	LC-(ESI)TQ-MS/MS	[18]

(continued)

Table 1 (continued)

Analytes	Water matrix	Extraction	Separation	Analysis	Reference
Endogenous androgens (2) and synthetic androgens (9)	Wastewater	LVI (1,800 µL)	ZORBAX Eclipse Plus C18 (150 × 4.6 mm, 3.5 µm)	LC-(ESI)TQ-MS/MS	[19]
Drugs of abuse, along with some of their respective metabolites (22)	Wastewater and surface water	Direct injection (10 µL)	ZORBAX Eclipse XDB C8 (150 × 4.6 mm, 5 µm)	LC-(ESI)QqQLIT-MS/MS	[20]
Micropollutants (76)	Surface water, sea water and wastewater	HS-SPME (PDMS/DVB)	TRB-5MS (60 m × 0.32 mm, 1 µm)	GC-Q-MS	[21]
VOCs (20)	Surface water and wastewater	HS-SPME (CAR/PDMS)	BP624 (30 m × 0.25 mm, 1.4 µm)	GC-TQ-MS	[22]
Anti-inflammatory drugs (6)	Surface water and wastewater	HS-SPME (PDMS)	HP-5MS (30 m × 0.25 mm, 0.25 µm)	GC-Q-MS	[23]
Musk fragrances (9)	Wastewater	HS-SPME (PDMS/DVB)	ZB-50 (30 m × 0.25 mm; 0.25 µm)	GC-IT-MS	[24]
Endocrine-disrupting compounds (14)	Wastewater, solids and sludge	SBSE (PDMS)	DB-5MS (30 m × 0.25 mm; 0.5 µm)	GC-Q-MS	[27]
Insect repellents and synergists (8)	Surface water and wastewater	SBSE (PDMS)	HP-5MS (30 m × 250 µm, 0.25 µm)	GC-Q-MS	[38]
Chlorinated chemicals	River water and wastewater	SBSE (PDMS)	HP-5MS (30 m × 250 µm, 0.25 µm)	GC-TQ-MS	[39]
Pharmaceuticals and personal care products	Wastewater	SBSE (EG Silicone)	Kromasil 100 C18 (150 × 4.6 mm, 5 µm)	LC-(ESI)TQ-MS/MS	[28]

Pharmaceuticals and personal care products (16)	Wastewater	SBSE (poly-PEGMA-co-PETRA)	Kromasil 100 C18 (150 × 4.6 mm, 5 μm)	LC-(ESI)TQ-MS/MS	[29]
Nitro musks	Surface water and wastewater	DLLME	HP-5MS (30 m × 0.25 mm, 0.25 μm)	GC-Q-MS	[30]
Volatile siloxanes (8)	Wastewater	USA-DLLME	DB-624 (60 m × 0.25 mm, 1.40 μm)	GC-Q-MS	[31]

MISPE molecularly imprinted SPE, *SBSE* stir-bar sorptive extraction, *SPME* solid-phase microextraction, *MWCNTs* multi-walled carbon nanotubes, *LVI* large volume injection, *HS-SPME* headspace solid-phase microextraction, *CAR/PDMS* carboxen/polydimethylsiloxane, *PEGMA-co-PETRA* poly(ethylene glycol) methacrylate-co-pentaerythritol triacrylate, *DLLME* dispersive liquid-liquid microextraction, *USA* ultrasound-assisted

X-WA or Bond Elut Plexa PCX, have yielded good extraction for both charged and neutral compounds in wastewater [7, 8].

Although extraction in one single step is the most common approach, serial SPE separation using different sorbents also represent an interesting alternative. Relying on ion-exchange and reversed-phase mechanisms, different groups of compounds can be isolated in separate fractions by the application of different elution conditions. Thus, increasing recoveries for specific compounds and cleaner extracts can be simultaneously obtained. Lavén et al. [9] report simultaneous extraction of 15 basic, neutral and acidic pharmaceuticals in wastewater using mixed-mode cation- and anion-exchange SPE in series.

Another type of selective sorbents is based on molecularly imprinted polymers (MIPs). MIPs are synthetic polymeric materials with specific molecular-recognition properties that can specifically rebind a target molecule. The inherent specificity prevents their application to multiresidue extraction, but the high potential for single group analysis has contributed to their widespread use [10, 11]. As an example, a commercial MIP specific for non-steroidal anti-inflammatory drugs was successfully compared with three common sorbent (Oasis HLB, Oasis MAX and Oasis WAX), proving to be very effective in the reduction of matrix interferences and the selective extraction of 15 acidic pharmaceuticals from effluent wastewater samples [12]. Reduced matrix effects and higher sensitivity was also reported by molecularly imprinted solid phase extraction (MISPE) of 8 beta-blocker drugs, comparing with Oasis HLB [13].

An advantageous alternative to classical SPE, in terms of labour and time-consuming are on-line SPE methods. They usually involve a two-step procedure including automated sample loading in an extraction cartridge and subsequent elution directly onto the analytical column. This procedure provides similar or better detection limits than off-line methods using smaller sample and organic solvents volumes, in a shorter analysis time, with minimal interferences and good performance, largely due to easier handling and higher automation [14]. A recent application of online SPE-LC-MS/MS has been reported by Huntscha et al. [15] for the simultaneous enrichment and analysis of 88 neutral, cationic and anionic microcontaminants in wastewater. In this study a single mixed-bed multilayer cartridge was used, containing four different extraction materials: Oasis HLB, Strata XAW, Strata XCW and Isolute ENV+ in order to cover the different physical-chemical properties of the analytes. The majority of compounds was quantified with high precision and relative recoveries between 80% and 120%, using a sample volume of only 20 mL. The effort for manual sample handling was limited to filtration, reducing the whole analysis time to only 36 min. Other on-line SPE configurations use robotic systems working in parallel mode [32]. This means that one sample is loaded in one cartridge while another one is eluted into the HPLC system [16]. These sample preparation units use single-use cartridges, avoiding problems associated to the reusability of the pre-columns, such as changes in selectivity and capacity, or cross-contamination.

In contrast to SPE, large volume injection methods combined with liquid chromatography-mass spectrometry (LVI-LC-MS) are rapidly gaining acceptance,

because of their simplicity and good performance [33]. The method basically consists of injecting up to a few millilitres of a filtrated or centrifuged sample directly into a chromatographic column. This method presents clear advantages over SPE: (1) it reduces material and solvent consumption; (2) it increases sample throughput; and (3) it eliminates analytes losses associated with the extraction procedures. Despite its apparent simplicity, LVI also requires adequate optimization of the operating conditions to avoid effects related with overloading of the analytical column (poor peak shapes), lack of retention of more polar analytes or matrix effects associated to the absence of pre-treatment. Although the application of LVI-based methods to complex matrices such as wastewater is still limited, recent studies have demonstrated to produce analytical signals of similar quality to SPE-based methods [17–19].

To overcome limitations of LVI and to take advantage of the increasing mass spectrometers' sensitivity, direct injections of smaller volumes have been assayed. An example has been reported by Martinez Bueno et al. [20] for the simultaneous identification/quantification of 22 drugs of abuse and their major metabolites, in sewage and river water. The absence of pre-concentration and the use of 10 μ L injection volumes resulted in a reduction of matrix effects, with LODs ranging from 1 to 700 ng/L in wastewater.

Another group of extraction techniques includes sorptive extraction methods, which are based on a partitioning equilibrium of analytes between the aqueous sample and a solid sorbent supported in different devices. They mainly include solid-phase microextraction (SPME) and stir-bar sorptive extraction (SBSE) [34]. Both are based on the same principles and their merits yield on their simplicity of operation, solvent-free nature of the process, possibility of full automation and easy coupling with gas chromatography (GC).

In SPME a fine fused silica fibre coated with a polymeric stationary phase is used to extract and concentrate analytes directly from a sample. The choice of commercial fibre coatings is limited to poly(dimethylsiloxane) (PDMS), divinylbenzene (DVB), polyacrylate (PA), Carboxen (CAR) and poly(ethylene glycol) (PEG), while combinations of polar/nonpolar sorbents such as PDMS/DVB, PDMS/CAR, or CW/DVB have been designed for extracting more polar compounds [21, 22, 35]. However, increasing the polarity of the sorbent also increases the affinity for the matrix, leading eventually to the leaching of the analytes. Another choice to expand the applicability of SPME-GC is to decrease the polarity of analytes previously or simultaneously to the microextraction process by in situ [23] or on-fibre derivatization [36].

Although SPME is a widespread technique, most of the studies are devoted to natural water samples and only a little percentage of them deals with complex wastewater samples. Applications are frequently focused to determination of specific groups of compounds [37]. Headspace mode coupled to GC is the preferred configuration to minimize matrix interferences. Musk fragrances [24], benzotriazole UV stabilizers [25], nonylphenol ethoxylates [26], anti-inflammatory drugs [23] and parabens [36] are among the groups of compounds analysed.

SBSE is expected to provide higher sample capacity and extraction efficiency than SPME derived from the larger volumes of extraction phase contained in the SBSE device, consisting of a magnetic stir bar covered with a polymeric coating. SBSE can be used in combination with thermal desorption and GC analysis or, in a more simple and versatile way, by liquid desorption using a small volume of an organic solvent, eliminating the need for specific devices and permitting GC or LC analysis [27, 38, 39]. Until recently, the only commercially available coating was based on PDMS, thus limiting the application of the technique to the extraction of apolar or moderately polar analytes (generally with $\log K_{o/w} > 3$). Very recently, novel polar coatings like poly(ethyleneglycol) (PEG)-modified silicone (EG Silicone Twister) and polyacrylate (PA) with a proportion of PEG (Acrylate Twister) have been marketed and applied to the analysis of pharmaceuticals and personal-care products (PPCPs) in wastewaters [28]. However, commercial coatings are still limited in terms of the more polar analytes. Novel approaches applied on the development of in-house coatings such as sol-gel technology, the synthesis of monolithic materials and polyurethane foams (PUFs) have yield promising results in the analysis of CECs in wastewater [29, 40, 41], but new polar monomers and novel formats need to be explored to improve extraction of polar compounds from complex matrices [42].

Finally, another group of miniaturized methodologies, included under the term liquid-phase microextraction (LPME) has emerged. They are based on the use of negligible volumes of a water-immiscible solvent (μL or sub- μL) and an aqueous phase containing the analytes of interest [43]. Simplicity of operation, speed, low cost and high enrichment factors are the main strengths of these techniques. Developments have led to different approaches of LPME, namely, single-drop microextraction (SDME), hollow-fibre LPME (HF-LPME), dispersive liquid-liquid microextraction (DLLME) and solidified floating organic drop microextraction (SFODME). Some applications of these techniques have been reported in the analysis of CECs in wastewater, being HF-LPME and DLLME the approaches most widely used [30, 31].

2.2 Chromatographic Separation and Determination

Liquid and gas chromatography coupled to mass spectrometry are by far the analytical techniques most often used for the analysis of wastewater and reclaimed water. In most cases the choice between GC and LC is based on the physico-chemical properties of the selected analytes. LC is the preferred choice for polar and less volatile compounds (e.g. pharmaceuticals, transformation products), while GC allows the determination of less polar and volatile analytes (e.g. fragrances, UV filters, fire retardants and antioxidants). The definition of the objective of the analysis is crucial for the choice of the most appropriate instrumentation and/or analysis strategy. Three approaches can be considered: (1) analysis of target

compounds, (2) comprehensive analysis of target and non-target analytes by screening methods and (3) identification of unknown TPs.

2.2.1 Analysis of Target Compounds

The analysis of CECs in wastewater often focuses on quantitative assessment of a selected group of compounds [44, 45]. In the last few years, there is a trend to expand the number of compounds included in the methods, with the aim to provide a more comprehensive assessment.

GC approaches typically use quadrupole, ion trap or triple quadrupole analysers working in selective ion monitoring (SIM) or tandem-mass-spectrometry (MS/MS) modes to enhance sensitivity and selectivity. These methods rely on only a few ions and are not designed to find compounds unless they are on the target list. Full-scan analyses improve confirmation and allow analysis of non-target compounds but the methods are less sensitive and prone to matrix interferences.

Recent progress in instrumentation has increased the use of time-of-flight (TOF) mass analysers coupled to GC [142]. The main advantage of TOF-MS relies on the full spectrum acquisition, with better sensitivity than conventional instruments. The high acquisition speed (100–500 spectra/s) provided by some instruments, make them suitable for coupling to ultra-fast GC or comprehensive two-dimensional gas chromatography (GC \times GC). GC \times GC-TOF-MS has emerged as a good alternative to analyse complex samples because it offers increased peak capacity, improved resolution and enhanced mass sensitivity. Sample preparation procedures can be minimized or eliminated due to the superior separating power, although at the expense of a more frequent maintenance and cleaning. In addition, the ability of GC \times GC to produce structured two-dimensional (2-D) chromatograms or “fingerprint” of a sample opens up the opportunity for sample comparison protocols. These advantages make GC \times GC-TOF-MS a very interesting tool in the evaluation of wastewater treatments. However, its application to this type of studies is still limited. Examples recently published include the application of a sensitive multiresidue method to assess the removal of a group of 55 contaminants (PCPs, PAHs and pesticides) in wastewater using ozonation, UV and visible light irradiation and TiO₂ photocatalysis [143]. Due to the enhanced separation capacity, GC \times GC-EI-TOF-MS has been also successfully applied to the identification of enantiomeric species (R) and (S) of HHCB-lactone and other relevant TPs of the synthetic musk HHCB during its degradation by various oxidative and irradiation processes [144].

The application of LC-MS to the quantitative evaluation of degradation processes usually is based on the use of hybrid triple quadrupole (QqQ) or quadrupole linear ion trap (QqLIT) analysers, which exhibit excellent performance working in the multiple reaction monitoring (MRM) mode. New generations of instruments allow ultrafast MRM acquisition speeds and ion polarity switching, which ensures compatibility with UHPLC analyses and get maximum response simultaneously for higher number of analytes.

In QqLIT analysers the third quadrupole (Q3) can be operated in the linear ion trap mode, leading to a unique tandem mass spectrometer capable of functioning as either a triple quadrupole for quantitative workflows or as a highly sensitive linear ion trap for qualitative workflows. Both capabilities can be combined in one analysis by operating under the Information Dependent Acquisition (IDA) mode. In this case, the MRM mode is used to screen for target compounds and whenever the MRM signal is above a specified threshold automatically enhanced product ion (EPI) spectra are acquired. These spectra can then be searched against a mass spectral library thus improving qualitative capabilities [4, 145]. In this way accurate quantitative and reliable qualitative information can be simultaneously acquired. LC-QqLIT-MS/MS based methods have been applied to monitor degradation of selected CECs after different wastewater treatments [44, 45].

As a consequence of the increasing interest of using accurate mass high resolution mass spectrometers (HRMS), e.g. Orbitrap and time-of-flight (TOF) instruments, in environmental analysis, recent studies have explored the quantitative potential of these instruments. Compared with first-generation instruments, the latest TOF instruments provide increased sensitivity and resolving power, and a wider linear dynamic range, which provides adequate quantitative skills [46, 47]. In addition, HRMS overcomes limitations of using MRM methods, such as the limited number of transitions that can be registered without damage in accuracy or sensitivity, the non-specificity of the MRM transitions or the absence of a second MRM confirmatory. Virtually all compounds present in a sample can be determined simultaneously operating in full-scan mode, making no pre-selection of compounds and associated MRM transitions necessary. Hybrid instruments, like quadrupole/time-of-flight (QTOF) or linear ion trap (LTQ) Orbitrap, have improved the capacities as screening tools for target compounds with respect to single ones, due to the combination of mass accuracy, for both precursor and product ions, and improved sensitivity. Furthermore, their high mass resolving power enhances the identification of isobaric compounds since they can distinguish between compounds of identical nominal masses. These instruments also offer the possibility of information dependent MS/MS acquisition, i.e. an MS/MS analysis is triggered if a target compound is detected in the full scan. As an example, Fig. 1 shows the identification of nicotine from a river water sample [46] in a QTOF system, based on (1) the measured mass of nicotine at m/z 163.1229, which matches the calculated mass 163.1222 with an error of -4.5 ppm, and (2) mass spectral library searching of the MS/MS spectrum (purity score = 68.5).

But, despite the reported improvements of modern instruments applied to target analysis, the matrix effects remain the main pitfall in target quantitative analysis of complex samples [48]. The suppression or, less frequently, the enhancement of the analytes signal is frequently observed. Standard addition is the most suitable method for compensating matrix effects in quantitative analysis, but it is time-consuming and laborious. Matrix-matched calibration has been widely used [146], but the absence of blanks and the variability of the matrix throughout the set of samples analysed, represents a drawback.



Fig. 1 Example of identification of the targeted compound nicotine in a river water sample based on accurate mass MS and MS/MS information (from Panditi et al. [46])

The use of internal standards (IS) also reduces matrix effects since the analyte-to-internal standard response ratio compensates for any ion suppression/enhancement that may be present. Use of isotopically labelled internal standards (ILIS) is the most recognized technique. Panditi et al. [49] report signal suppression/enhancement values lower than 20% in most cases in the LC-MS/MS analysis of 31 antibiotics in reclaimed water. Ibañez et al. [50] also report the use of ILIS to evaluate the efficiency of ozone treatment in the removal of a set of pharmaceuticals and drugs of abuse. A detailed study of matrix effects in wastewater samples [5] also highlight the use of ILIS, demonstrating that the selection of an analogue eluting at close retention time did not always ensure adequate correction.

2.2.2 Screening Methods

The target approach involves the purchase and measurement of hundreds of compounds, coming along with increase in time, effort and money. In addition, wastewater effluents contain a multitude of organic contaminants and TPs, which escape the target analysis alone. Thus, a good choice is combining extensive target analysis for the most relevant analytes and screening analysis, to identifying other potentially relevant compounds. In this sense, capabilities of HRMS are gaining in relevance together with novel data processing approaches to complement an extensive target analysis.

Krauss et al. [51] differentiate between “suspect screening”, looking for compounds that are expected to be in the samples, and “non-target screening” when no prior information about the identity of the compounds is available. Suspect

compounds can be screened using databases containing the exact mass of expected ions, calculated from the molecular formula. However, limitations rely on the limited availability of databases for LC-MS/MS and the lack of reproducibility between spectra obtained with different instruments. Some authors propose the creation of home-made suspect lists to occur in water samples [52]. A general weakness of the approach is the peak detection, which provides an extensive list of suspected peaks, which in many cases derived from matrix background. Thus, an extensive compound filtering has to be applied to discard false positive detections based on retention time prediction, the evaluation of isotope patterns, ionization behaviour, and HRMS/MS spectra.

“Non-target screening” involves masses that are detected in the samples, but where no a priori information on the underlying compound is available. Identification of masses of interest is possible when the MS is operated in a data-dependent acquisition (DDA) mode in which both MS and MSⁿ spectra are acquired without the need to specify parent masses. In this mode, the instrument is initially set to operate in full-scan (“survey”) and the acquisition software looks for the MS spectra in real-time on a scan-by-scan basis to select the most intense parent ions for MSⁿ analysis. This technique is capable of finding true unknowns, as long as they are ionized and behave accordingly in the chromatographic process, since the method does not require any pre-selection of masses. From the measured exact mass, the elemental compositions of non-target ions are calculated with a high degree of certainty (maximum deviation of 5 ppm is generally admitted). This elemental composition can be used to search electronic databases (NIST Library, Chemfinder or Chemspider) in order to provide a reliable structure assignment if the compounds are present there. Finally, the structures found in the libraries are evaluated based on the fragmentation patterns observed in the simultaneously acquired product-ion spectra [53].

2.2.3 Identification of Unknown Transformation Products

Currently it is becoming evident that the absence of parent contaminants in the analysis of wastewater does not guarantee the quality of treated or reclaimed water and the absence of an impact in the environment. During wastewater treatment, many organic microcontaminants undergo transformation reactions resulting in the appearance TPs [54]. Despite efforts in the identification, only a small portion of possible TPs that can be generated during treatments have been investigated, mainly because of labour-intensive and time consuming experimental and analytical steps and the frequent absence of analytical standards for an unequivocal confirmation.

HRMS represents an interesting choice for this kind of analysis because of the ability of providing accurate mass and elemental composition of both molecular and MS/MS product ions [55], although structural isomers cannot be distinguished. Figure 2 shows an example of identification of the TP thiazole-4-carboxamide generated by Fenton oxidation treatment of the pesticide thiabendazole in water

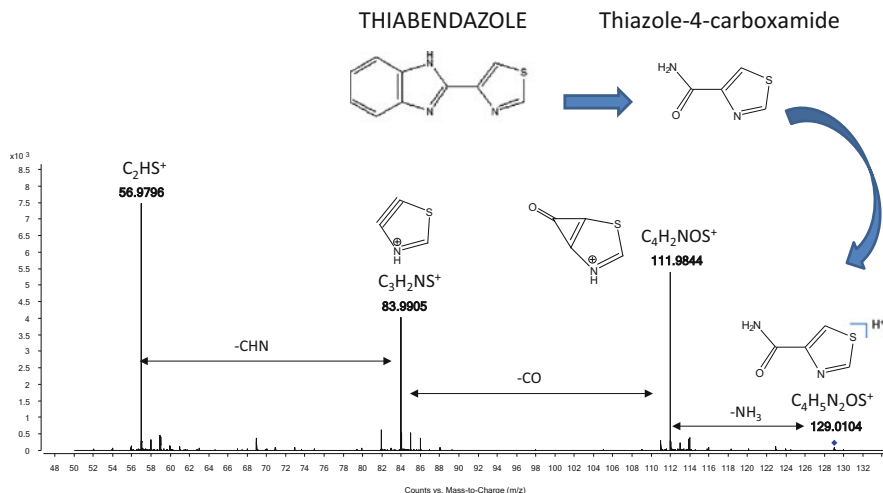


Fig. 2 Identification of the TP thiazole-4-carboxamide generated by Fenton treatment of the pesticide thiabendazole in water solution based on the accurate mass spectrum obtained by LC-QTOF-MS/MS

solution. Structural elucidation was based on the accurate mass spectrum obtained by LC-QTOF-MS/MS and then confirmed by analysis of the analytic standard.

Most published studies dealing with the identification of TPs are performed with individual compounds and under laboratory conditions (distilled water and high initial concentration of the contaminant studied). However, the “ideal” conditions applied hardly are comparable to those that occur in real processes. Methods are needed allowing high-throughput elucidation of TP structures in real waters. With this objective in mind, a systematic approach has been proposed [154]. This approach is based on the use of characteristic fragmentation undergone by organic contaminants during MS/MS fragmentation events, and its relationship with the transformations experimented by these chemicals in the environment or during water treatment processes [56]. Thus, a database containing accurate-mass information of 147 compounds and their main fragments generated by CID MS/MS fragmentation experiments was created using an LC-QTOF-MS/MS system. This database was applied to the identification of tentative TPs and related unexpected compounds in wastewater effluent samples. The approach comprises the automatic extraction of compounds using the “Molecular Feature Extraction (MFE)” algorithm to search and create a list of all the peaks that represent real molecules. This list is compared to the database to identify possible matches. Once the potential TPs have been tentatively identified, confirmation of their identity is obtained by MS/MS fragmentation.

Another strategy has been proposed by Helbling et al. [147]. In this case, candidate TPs were preliminarily identified with an innovative post-acquisition data processing method based on target and non-target screenings of the full-scan MS data obtained by an LTQ Orbitrap system. For the target analysis, single ion

chromatograms were extracted at the exact masses of plausible TPs predicted by the University of Minnesota Pathway Prediction System (UM-PPS) [57]. In addition, non-target screening was based on full-scan MS data obtained from two samples obtained at $t=0$ and $t>0$ to identify compound masses that formed during the biotransformation experiment. A series of mass filters (mass and retention time domain constraint, a background subtraction algorithm, a constrained molecular formula fit, presence of ^{13}C monoisotopic masses) was applied to reduce the number of extracted masses. The list of candidate TPs must be further analysed through manual inspection of the XICs, MS spectra and MS/MS spectra. This procedure yielded the identification of 26 TPs but the extent of TP formation remains unknown. Additional TPs may have formed but remained undetected because of different causes, such as low concentration levels, limited ionization efficiency, and poor separation in the LC system.

3 Determination of Organic Microcontaminants in Soils Associated with Reclaimed Wastewater Reuse

3.1 Analytical Methods/Sample Preparation in Soil Samples

Solid–liquid extraction (SLE) is the oldest sample preparation technique for extracting organic microcontaminants from soil and other solid matrices. It is still used mainly because of its easy use and procedural simplicity. However, two main disadvantages, the lengthy time and low extraction efficiency, have been pointed out for this technique. To this purpose, ultrasound treatment is often used to accelerate and favour the extraction process. Ultrasound-assisted solvent extraction (USE) is considered a good option for organic-compound extraction from soil matrices, as it provides more efficient contact between sample and solvent due to an increase of pressure (which favours penetration and transport) and temperature (which improves solubility and diffusivity). Thus, USE is one of the most widely used techniques due to its distinct advantages, such as low cost, easiness of use, wide-ranging applicability and availability. The extraction solvents employed are usually mixtures of buffer solutions and organic solvents such as acetonitrile, methanol, acetone and ethyl acetate. Ethylenediaminetetraacetic acid (EDTA) and McIlvaine buffer solutions (mixture of citric acid and Na_2HPO_4 , (e.g. 0.1 M Na_2EDTA –pH 7 McIlvaine buffer, 50:50, v/v) a) are used as chelating agents in order to improve the isolation of some antibiotic compounds from solid samples, like tetracyclines (TCs) (e.g. tetracycline, chlortetracycline and oxytetracycline) which tend to form chelate complexes with metal ions and are strongly sorbed to soil [63–65]. In most cases, extraction conditions such as pH must be controlled in order to enhance analyte extraction. Thus, for pharmaceutical compounds with acidic (e.g. inflammatory drugs) or zwitterionic characteristics (fluoroquinolones—FQs), the extraction is usually carried out at acidic pH. For

example, Chen et al. [66] reported the acidification of ethyl acetate with formic acid for the extraction of 19 pharmaceuticals from soils. Golet et al. [67] demonstrated that the adjustment of pH at 2 is necessary for simultaneous determination and high extraction yields of FQ analytes from soils. At low pHs, FQs present a higher water solubility as they are then mainly present as cations that enhances the extraction efficiency. Moreover, both FQs and soil surface are protonated and, therefore, electrostatically repulsed favouring the extraction [63]. On the other hand, for basic or neutral compounds higher pHs are required to improve the extraction efficiency [68]. Overall, pH should be chosen according to pK_a value, since for some antibiotics like β -lactams, hydrolysis may occur below or above neutral pH.

In addition to conventional SLE, instrumental methods such as pressurized liquid extraction (PLE), also known as accelerated solvent extraction (ASE), and microwave-assisted extraction (MAE) have attracted growing interest in CEC analysis of soil samples (Table 2). They have the advantages of easier automation and higher extraction throughput, whereas they require smaller volumes of solvent and provide better extraction efficiencies (in terms of extraction yield and/or recovery) when compared to conventional SLE. PLE has been successfully employed for the determination of different groups of ECs [79]. A very interesting feature of this technique is the possibility of full automation and many samples can be extracted sequentially. The amount of time spent for method development can therefore be significantly reduced compared to other techniques. In general, the extraction is carried out with methanol [86, 99], mixtures of methanol (MeOH) and hexane/acetone [85], dichloromethane (DCM) and acetone [92], water [69], or mixtures of water with organic solvents, such as acetonitrile [100], isopropanol [101], acetone/hexane [95] or MeOH [102, 103]. When water is used as extraction solvent, pH is also controlled in the case of analytes with acid–base properties, as in the case of macrolide, sulphonamide and β -lactam antibiotics (MeOH–citric acid (0.2 M, pH 4.7) [102]).

The extraction efficiency of PLE is dramatically influenced by extraction pressure and temperature, and therefore, both parameters must be carefully optimized. Extraction pressure is usually kept in the range of 500–1,500 psi. The extraction is commonly carried out at temperatures ranging from 60 to 100°C because at higher temperatures thermal degradation of analytes can occur and more matrix components can be co-extracted affecting the extraction efficiency and leading to interfering signals in MS chromatographic systems. Other particular variables of PLE that are usually studied are the number of cycles and/or extraction time. Usually, one to five cycles are carried out, although two cycles are mostly used [94]. Extraction time of 5 min is commonly used [103], whereas longer extraction is employed in dynamic mode as in the case of static extraction process.

Another interesting and environmental friendly instrumental approach which nowadays attracts considerable attention for the determination of CECs in solid matrices is MAE. MAE simply involves placing the sample with the solvent in specialized containers and heating the solvent using microwave energy. Hence, extraction solvents available for MAE are limited to those solvents that absorb microwaves (solvents with a permanent dipole). The use of solvent mixtures with

Table 2 Analysis of ECs in soil and crops samples

Analytes	Matrix	Sample preparation	Instrumentation	Rec.	LOD/LOQ (ng/g)	Reference
<i>Pharmaceuticals</i>						
Pharmaceuticals (19)	Soil	USE: 10 mL EtAc–formic acid) (50:1, v/v) ($\times 3$) Clean-up: Silica gel	LC-ESI-MS/MS	43–245	0.02–4.20	[66]
Pharmaceuticals (6) and metabolites (2)	Soil	PLE: acetone–hexane–HAc (50:50:2, v/v/v), 100°C Clean-up: Oasis HLB	GC-MS (MTBSTFA)	62–118	0.5–2	[148]
Pharmaceuticals (32)	Soil	PLE: 0.1 M ammonium–MeOH (1:1 v/v), 80°C Clean-up: MAX-HLB in tandem	LC-ESI-MS/MS	66–114	0.1–1.5	[149]
Pharmaceuticals (19)	Soil	PLE: ACN–water (7:3, v/v), 130°C	LC-ESI-MS	63–113	0.76–5.46	[100]
Pharmaceuticals (20)	Crops (pepper collard, lettuce, radish, tomato)	USE: two-step extraction; 20 mL MTBE; 20 mL ACN Clean-up: OASIS HLB	LC-ESI-MS/MS	56.3–129.6	0.04–3.0	[96, 140]
Pharmaceuticals (17)	Soil	PLE: water, 90°C Clean-up: SAX + HLB in tandem	LC-ESI-MS/MS	34–105	0.1–6.8	[69]
Pharmaceuticals (18)	Soil	MAE: 10 mL MeOH–water (3:2, v/v) Clean-up: SPE (Oasis HLB)	GC-MS (BSTFA + 1% TMCS)	91–101	0.8–4.7 ng/kg	[75]
Anti-inflammatory drugs (4), Clofibrac acid	Soil	USE: 9 mL acetone + 9 mL EtAc Clean-up: C18	GC-MS (MTBSTFA)	52–11	70.2–0.4	[77, 105]
Anti-inflammatory drugs (3), Diphenhydramine hydrochloride	Soil	MAE: 10 mL DCM–MeOH (2:1, v/v) ($\times 3$), 115°C Clean-up: Silica microcolumns	GC-MS (pyridine–BSTFA (2:1))	<40		[72]

PPCPs (118)	Biosolids	USE: buffered ACN + ACN Clean-up: SPE	LC/ESI-MS/ MS	0.03–5.080	[150]
PPCPs (118)	Crops (tomatoes, carrots, potatoes and sweet corn)	USE: buffered ACN + ACN Clean-up: SPE	LC/ESI-MS/ MS	0.24–54.15	[150]
Ibuprofen, Ciprofloxacin	Soil	Shaking: ACN USE: 50 mL Na ₂ -EDTA phosphate buffer pH 3–ACN (1:1, v/v) Clean-up: Oasis HLB	LC-UV GC-MS (MSTFA)	28–97 0.27–25.56	[131]
Diclofenac sodium, Naproxen	Crops (lettuce (Lactuca sativa) and collards (Brassica oleracea)	USE: two-step extraction; 20 mL MTBE; 20 mL ACN Clean-up: OASIS HLB	HPLC-UV	74–85.8	[76]
Carbamazepine	Crops (cucumber)	USE: 12 mL Methanol	LC/ESI-MS/ MS	70 and 40 ng/L	[151]
Carbamazepine	Soil	USE: 15 mL isopropanol–water (8:2, v/v) (×2) Clean-up: Oasis HLB – Florisil in tandem	GC-MS	67–96 110	[107]
<i>Antibiotics</i>					
Antibiotics (15)	Soil	USE: 10 mL citric acid buffer (0.2 M, pH 4.4) + 10 mL ACN (×3) Clean-up: Oasis HLB	LC-ESI-MS/ MS	64–245 0.08–4.20	[66]
Antibiotics (7)	Soil	USE: 90 mL MeOH + 45 mL acetone + 45 mL EtAc Clean-up: LiChrolut C18	LC-ESI-MS/ MS	38–121 3–20 ^a	[78]

(continued)

Table 2 (continued)

Analytes	Matrix	Sample preparation	Instrumentation	Rec.	LOD/LOQ (ng/g)	Reference	
Antibiotics (13)	Soil	SAs + TCs	SAs + TCs	61–94	0.8–23	[64]	
		USE: 10 mL EDTA-McIlvaine buffer–MeOH (1:1, v/v)	LC-UV				
		Clean-up: C18 + SAX in tandem	QNs				
		QNs	LC-FL				
Antibiotics (11)	Soil	USE: 5 mL 50% MgNO ₃ aqueous solution containing 4% aqueous ammonia	TCs + SAs	61–105	100 ^a	[63]	
		Clean-up: C18 + SAX in tandem					LC-ESI-MS/MS
		TCs + SAs					MS
		USE: 30 mL MeOH–EDTA–MacIlvaine buffer pH 6 (9:1, v/v) (×3)					FQs
		Clean-up: C18					LC-ESI-MS
		FQs					
Antibiotics (14)	Soil	USE: 30 mL ACN acidified with formic acid 2% + 0.5 g organic substratum (×3)	LC-ESI-MS/MS	48–160	0.08–4.2	[152]	
		Clean-up: LLE (n-hexane)					
		USE: 10 mL citric buffer (0.2 M, pH 4)–ACN (1:1, v/v) (×3)					
		Clean-up: Oasis HLB					

Antibiotics (6)	Soil	PLE: MeOH-citric acid (0.2 M, pH 4.7) (1:1, v/v), RT Clean-up: SAX + HLB in tandem	LC-MS/MS	50-100	0.6-5.6	[102]
Quinolones (10)	Soil	USE: 8 mL MgNO ₃ aqueous solution (50%, w/v) + 4% ammonia	LC-UV	82-104	40-80	[74]
Fluoroquinolones (5)	Soil	USE: 8 mL MgNO ₃ aqueous solution (50%, w/v) + 4% ammonia Clean-up: MISPE Ciproflaxin	LC-UV	75-85	40-70	[153]
Tetracyclines (3), Tylosin	Soil	Shaking: 1.2 mL citrate buffer (1 M, pH 4.7) + 6 mL EtAc	LC-ESI-MS/MS	33-127	1-2	[70]
Enrofloxacin, Ciprofloxacin	Soil	Shaking and USE: 15 mL phosphate buffer (pH 3)-ACN (1:1, v/v) Clean-up: SAX + Oasis HLB in tandem	LC-FL	61-100		[71]
Oxytetracycline Norfloxacin Chlortetracycline	Soil	USE: 25 mL MeOH-EDTA-MacIlvaine buffer pH 6 (9:1, v/v) (×3)	HPLC-DAD	65-78	0.08-0.50 mg/ Kg	[65]
Oxytetracycline	Crops	USE: 25 mL MeOH-EDTA-MacIlvaine buffer pH 6 (9:1, v/v) (×3) Clean-up: (Strata-X)	HPLC-DAD	65-78	0.08-0.50 mg/ Kg	[65]
Norfloxacin Chlortetracycline						
Sulphonamide antibiotics and their metabolites	Soil	PLE: MeOH-water (90:10, v/v), (×3), 100°C; Clean-up: OASIS HLB	LC-MS/MS	60-130	0.01-4.19 ng/g	[103]
Estrone 17-Estradiol, 17-ethynylestradiol estriol	Soil	PLE: DCM-acetone (3:1, v/v), 60°C; Clean-up: Strata X	GC-MS (BSTFA)	71-118	0.02-0.19 ng/g	[92]

(continued)

Table 2 (continued)

Analytes	Matrix	Sample preparation	Instrumentation	Rec.	LOD/LOQ (ng/g)	Reference
Bisphenol A (BPA)	Soil	PLE: DCM-acetone (3:1, v/v), 60°C; Clean-up: Strata X	GC-MS (BSTFA)	90–128	0.37	[92]
<i>Ionophores</i>						
Salinomycin A	Soil	PLE: 30 g sample with MeOH (1% NH ₄ OH) Clean-up: UCT Diol SPE 2 g Elution with 0.1 M NH ₄ Ac–MeCN (2:3)	APCI(+) Triple quad (QqQ) SRM mode	76 ± 32	5.3 ^a	[79]
Monensin A	Soil	SLE: 1 g sample LLE with EtOAc (NH ₄ -citrate, NH ₄ OH, pH 5.8)	ESI(+) Triple quad (QqQ) SRM mode	75	2,000	[82]
Lasaloid, Monensin, Salinomycin and Narasin	Soil	PLE: MeOH–water (1:1, v/v), 50°C; Clean-up: OASIS HLB	LC-MS/MS	71–123	0.64–0.98 µg/kg	[94]
<i>EDCs</i>						
Bisphenol A	Biosolids	USE: buffered ACN + ACN Clean-up: SPE	LC/ESI-MS/MS		5,080	[150]
Bisphenol A	Crops (tomatoes, carrots, potatoes and sweet corn)	USE: buffered ACN + ACN Clean-up: SPE	LC/ESI-MS/MS		396	[150]
Bisphenol A	Crops (lettuce (Lactuca sativa) and collards (Brassica oleracea)	USE: two-step extraction; 20 mL MTBE; 20 mL ACN Clean-up: OASIS HLB	HPLC-UV	81.5		[76]

<i>UV filters and parabens</i>						
BP (5)	Soil	USE-clean-up: 16 mL EtAc-MeOH (90:10, v/v), C18 Shaking: 20 mL MeOH + 20 mL EtAc	GC-MS-EI-SIM (BSTFA)	89-105	0.07-0.28	[87]
BP (7)	Soil		GC-MS (MSTFA)	60-125	0.1	[88]
Parabens (6)	Soil	SAESC: 4 mL ACN (x3)	LC-MS/MS	83-110	0.04-0.14	[89]
Parabens (7)	Soil	SAESC: 4 mL ACN (x3) Clean-up: MISPE	HP LC-UV LC-MS/MS	80-90	1	[90]
Triclosan, Triclocarban	Soil	PLE: 70% MeOH, 100°C Clean-up: pH 4 cartridge ABN	LC-ESI-MS/MS	80-142	0.1-5.1	[99]
Parabens (6)	Biosolids	USE: buffered ACN + ACN Clean-up: SPE	LC/ESI-MS/MS		3.5-14.3	[150]
Triclosan, Triclocarban						
Parabens (6)	Crops (tomatoes, carrots, potatoes and sweet corn)	USE: buffered ACN + ACN Clean-up: SPE	LC/ESI-MS/MS		3-175	[150]
Triclosan	Crops (Bean)	SLE: 10 mL ACN-water, 1:1 (v/v) Clean-up: SPE C ₁₈	HPLC-UV	76.5	0.12 mg/g dw	[131]
Triclosan	Soil	SLE: 50 mL ACN	HPLC-UV	93	1.04 ng/g dw	[131]
Triclosan	Soil	PLE: water-isopropanol (80:20, v/v), 100°C Clean-up: Oasis HLB cartridge	LC-ESI-MS/MS	87	2 ^a	[101]
Triclosan	Soil	MAE: 10 mL MeOH-water (3:2, v/v) Clean-up: SPE (Oasis HLB)	GC-MS (BSTFA + 1% TMCS)	92	3 ng/kg	[75]
<i>Musk fragrances</i>						
Nitro musk	Soil	MAE: 30 mL DCM-MeOH (2:1, v/v), 160°C Clean-up: Silica gel	GC-MS (BSTFA)	90		[72]

(continued)

Table 2 (continued)

Analytes	Matrix	Sample preparation	Instrumentation	Rec.	LOD/LOQ (ng/g)	Reference
Polycyclic musk	Soil	PLE-clean-up: DCM, silica gel + hydromatrix, 60°C	GC-MS	>80	1	[91]
<i>Estrogenic compounds</i>						
Estrone	Soil	USE: 10 mL EtAc-acetone (1:1, v/v) Clean-up: C18	GC-MS (MTBSTFA)	63–110	1.2	[105]
Estrone	Soil	MAE: 10 mL MeOH-water (3:2, v/v) Clean-up: SPE (Oasis HLB)	GC-MS (BSTFA + 1% TMCS)	92–96	4.7–5.1 ng/kg	[75]
17 β -Estradiol						
17 α -Ethinylestradiol						
Hormones (17)	Biosolids	USE: buffered ACN + ACN Clean-up: SPE	LC/ESI-MS/MS		–	[150]
Hormones (17)	Crops (tomatoes, carrots, potatoes and sweet corn)	USE: buffered ACN + ACN Clean-up: SPE	LC/ESI-MS/MS		19.0–44.8	[150]
17 α -ethynylestradiol	Crops (Bean)	SLE: 10 mL ACN-water, 1:1(v/v) Clean-up: SPE C ₁₈	HPLC-UV	71.9	0.10 mg/g dw	[131]
17 α -ethynylestradiol	Soil	SLE: 50 mL ACN	HPLC-UV	99.8	0.96 ng/g dw	[131]
<i>Alkylphenols</i>						
AEOs, ANEOs	Soil	PLE: (A) MeOH and (B) hexane-acetone (1:1, v/v), HAc (75 mmol/L) and TEA (100 mmol/L), 150°C Clean-up: Porapak RDX	LC-APCI-MS	27–109	7–43	[85]
APs (3), APEOs (7)	Soil	PLE: MeOH, 70°C Clean-up: Isolute ENV+ cartridges	GC-MS (BSTFA-TMCS, 1:1,v/v) LC-FL	97–104 96–104	3–38 6–60	[86]

APs, APEOs, AEOs,	Soil	PLE: acetone-hexane (1:1, v/v), 60°C Clean-up: C18	LC-APCI-MS	89-102	0.3-30	[85]
4-Nonylphenol	Crops (lettuce (<i>Lactuca sativa</i>) and collards (<i>Brassica</i> <i>oleracea</i>)	SLE: 50 mL Hexane	HPLC-UV	66.8	-	[76]

MTBE methyl *tert*-butyl ether)

^aLOQ

and without dipoles opens up a variety of potential solvent mixtures. As in the case of PLE, to develop a successful MAE, several parameters (i.e. solvent volume and composition, extraction time and temperature, pressure, water content, matrix characteristics, etc.) that influence the extraction yield of MAE has to be studied and optimized.

In the case of solvent mixtures, the most popular is the MeOH–H₂O mixture, which has been applied to the extraction of pharmaceuticals, triclosan and estrogenic compounds [75]. DCM–MeOH has also been applied for extracting nitromusks and anti-inflammatory drugs [72] from soils. According to the literature, the extraction times used in MAE for CECs in soil and plant samples are within 6 and 15 min. Concerning extracting volumes, they range from 10 to 60 mL, whereas extraction temperature and pressure ranged between 110 and 130°C and <10 mPa, respectively. In the case of microwave treatment, values in the 150–1,600 W were applied for closed systems, while 500 W is most common used.

The MAE technique is more environmental friendly than the others as it uses substantially smaller amounts of solvents, reduces sample consumption, waste production and shortens extraction times, thereby reducing overall energy input and costs [98, 104]. However, similarly to PLE, additional clean-up is usually needed prior to chromatographic analysis. Moreover, special care with temperature and irradiation time is required to avoid degradation of analytes. For instance, accelerated decomposition of pharmaceuticals such as clofibrac acid, metoprolol and propranolol has been observed at high microwave powers, in combination with long extraction times [75].

3.1.1 Clean-Up Methodologies for Soil Samples

One of the problems with most methods used for extracting organic pollutants most prominent in solid samples is that large amounts of co-extracted compounds will add to the complexity of the chromatograms and interfere with detection of analytes. Thus, after the target compounds are extracted from the sample into the liquid phase, a further sample clean-up step is necessary to enable a robust analysis. Solid-phase extraction (SPE) is currently the most widely used choice to prepare extracts from solid samples for instrumental analysis. Before SPE, the organic-solvent content of the extract has to be reduced to less than 5% to prevent early breakthrough of analytes from the cartridges. The majority of studies performed SPE by using predominantly Oasis-HLB sorbent [66, 69, 76, 93, 96] that due to its hydrophilic–lipophilic balance allows the separation of compounds with a wide range of polarity. Other sorbents such as C18 [63, 78, 105], silica [66], Strata X [69], SAX and alumina [106] have also been used. Methanol is the main solvent used in the elution of these cartridges. Although the clean-up is, in general, carried out using one cartridge, some authors have performed two successive clean-up steps using SPE cartridges with different functionalities [102, 107]. For example, PLE extracts were further cleaned by a two-step SPE clean-up using SAX and HLB sorbents for the analysis of antibiotics [102].

3.2 Occurrence of Microcontaminants in Soils Associated with Reclaimed Wastewater Reuse

The use of reclaimed water may often provide a technically and economically feasible solution [73]. Nevertheless, its use in irrigation and/or aquifer recharge can introduce a range of CECs into the terrestrial environment, if these are not effectively removed during WWTPs. In addition to irrigation with reclaimed water, the application of sludge or manure to amend land and to fertilize agricultural soils can be another major pathway into the terrestrial and subsequently again in to the aquatic environment for these chemicals [61, 62, 64, 65].

The fate of CECs in soils is mainly dependant on their physico-chemical properties, which will influence their mobility, persistence and bioavailability in the soil matrix. The physico-chemical properties of CECs can vary widely; however, many of them contain a non-polar core with a polar functional moiety which complicated their fate patterns. Prevailing climatic conditions, soil types and a variety of other environmental factors are also critical for their fate and transport processes (e.g. volatilization, transformation and plant uptake).

In general, the CEC concentrations of reclaimed water are quite low (ng/L or $\mu\text{g/L}$) and their fate and transport in the receiving soils would be difficult to track and quantify [81]. Moreover, the water quality of reclaimed water fluctuates and thus the stability and reliability of reclaimed water quality are difficult to be ensured in the long run. Consequently, very little is known about the behaviour and occurrence of such contaminants in soils associated with reclaimed wastewater reuse. Only a few specialized reports are available on exposure of receiving soils to CECs by reclaimed wastewater irrigation. While only a few studies have explored the occurrence of CECs in the soil environment, available data indicate that a broad range of pharmaceuticals and personal care product (PPCPs) classes, including non-steroidal anti-inflammatory drugs, antidepressants, anticonvulsants, musk compounds, estrogens, UV filters and antibacterial agents does occur in soils in concentrations up to the low mg/kg level [81]. For example, Xu et al. [105], demonstrated the occurrence of six different PPCPs, endocrine-disrupting compounds (EDCs) and estrogenic compounds (clofibric acid, ibuprofen, naproxen, triclosan, bisphenol A and estrone) in soil samples collected from a golf course irrigated with reclaimed wastewater in southern California at concentration levels ranging from 0.55 to 9.08 ng/g dry weight soil. The findings of this study indicate that trace organic contaminants in the reclaimed wastewater may accumulate in the top soils during irrigation with reclaimed wastewater, consequently exposing the groundwater to a potential contamination. Another interesting study by the same research group [84] found that significant amounts of reclaimed water borne PPCP and EDC compounds, such as Ibuprofen, naproxen, triclosan, bisphenol A, clofibric acid and estrone, accumulated at the top (30 cm) of an irrigated turf grass field. However, no compound was detected in the leachate draining through the 89-cm profile of a loamy sand soil and a sandy loam soil turf grass field during 4 months of irrigation. Chen et al. [77] detected six PPCPs and ECDs, namely, bisphenol-A,

4-nonylphenol, triclosan, triclocarban, salicylic acid and clofibric acid in soil samples from four irrigated plots in Guangzhou. Finally, in a recent study, Fang et al. [108] reported that gemfibrozil in reclaimed water applied on land might reach the groundwater aquifer underneath.

Occurrence of synthetic musk fragrances (SMFs) (six polycyclic musk compounds (galaxolide, tonalide, celestolide, phantolide, traseolide, cashmeran) and two nitro musk compounds (musk xylene and musk ketone) was determined in soil cores from a land application site, groundwater below as well as in plants irrigated with treated effluent [109]. For most of the target SMFs, only traceable amounts were detected in soil samples (ND to <1 ng/g, (method detection limit, soil = 0.3 ng/g)), except for galaxolide and tonalide, the concentration of which ranged from trace levels to 5.69 and 6.24 ng/g in the top six inches (15,24 cm) of soil, respectively. The findings demonstrated that there was no difference in SMF occurrence whether samples were from inside or outside the pivot irrigation system. For cashmeran, celestolide, phantolide and musk ketone the concentrations ranged from ND (method detection limit, soil = 0.3 ng/g), to 1.57 ng/g, while traseolide and musk xylene were not detected in soil samples. The results of this study are in contrast to those for a similar land application site that had similar soil type, square metres and years applied [83]. However, it should be emphasized that the volume of water applied in a study of Ternes et al. [83], was much lower than in the first study. With concentrations in discharge already being lower, the absence of SMFs in groundwater it could have been expected. In addition, other environmental factors such as climate (e.g. arid versus humid) may play a role in the differences observed between the two sites with similar land application characteristics.

Finally, in a recent review study by Li et al. [81], it was demonstrated that the antibiotics (trimethoprim, sulfadiazine and triclosan), analgesics (ibuprofen and diclofenac) and antiepileptic (carbamazepine) were among the most common PPCPs found in soils with concentration levels up to 60.1 µg/kg. Considering the data of five studies [66, 110–113], it can be concluded that among the target compounds carbamazepine is the most frequently detected compound in soil. It is worth mentioning, however, that much of the environmental occurrence of this compound is likely associated with their selection as target compound in most comprehensive monitoring studies. It is resistant to degradation and can be discharged to the soil in various ways. However, according to the studies by Gibson et al. [111] and Chen et al. [66], the irrigation of reclaimed water is considered the major pathway introducing PPCPs into soils.

In addition to the aforementioned works, a number of field and laboratory-scale studies provided a snapshot of the PPCP mobility, persistence and bioavailability in soil matrix [97, 114–117]. For example, Drewes et al. [118] examined the fate of selected PPCPs during the ground water recharge at two reclaimed water reuse sites. They found that diclofenac, ibuprofen, ketoprofen and naproxen were not detectable, whereas carbamazepine and primidone were found in the recharged aquifer throughout 8 years of operation. Yao et al. [119] tested the ability of different types of biochar to sorb aqueous sulfamethoxazole (SMX) and determined the leaching and retention of SMX in simulated reclaimed water through soils

amended with selected biochar. The authors found that mobility and bioavailability of SMX in biochar-amended soils were lower than that of non-amended soils. Biochar soil amelioration, therefore, should be promoted in areas where reclaimed water or wastewater is used for irrigation.

Overall, various detailed field and screening studies have been performed during recent years, and preliminary data are available for a variety of CECs in soils including antibiotics, sulphonamides, fluoroquinolones, musks, etc. However, the fate and transport of CECs in the terrestrial pathway have not been well understood, and most emphasis should be laid on this issue.

4 Determination of Organic Microcontaminants in Crops

4.1 Extraction Methods/Sample Preparation in Crops

Similarly to analysis of PPCPs in soil, determination of trace levels of PPCPs in plants presents great challenges due to high contents of pigments, and fatty or waxy materials, which may induce severe matrix interferences. Therefore, sample preparation methods that eliminate potential interferences while permitting the improvement of isolation and extraction of these compounds are usually performed. Most of them are focused on commonly used techniques, including PLE [112, 120–122], SLE by using buffers or solvent mixtures [65, 123, 124] and QuEChERS (quick, easy, cheap, effective, rugged and safe) [125]. After extraction, purification is usually performed by using preferably SPE.

4.2 Occurrence of Microcontaminants in Crops Associated with Reclaimed Wastewater Reuse

Since residual concentrations of CECs from both human and agricultural uses can be found in soils, many of these compounds have the potential to be taken up from the soil via plant roots. Once the CEC has entered the plant, a posterior translocation, driven by the transpiration process, can take place. The extent of distribution within the plant will depend on the compound's physico-chemical properties [126]. Octanol-water partition coefficient (K_{ow}) and dissociation constant are among the most useful chemical descriptors of for organic contaminants plant uptake and distribution. If a compound is too hydrophilic, it will be unable to enter and to cross hydrophobic lipid membranes. For compounds of high lipophilicity, adsorption or "solution" in the lipid material is usually happening which reduces its ability to cross the endodermis. Hence, in general, uptake is greatest for compounds with a $\log K_{ow}$ in the range of 1–4 [127] for non-ionizable compounds. If a compound dissociates in the physiologically relevant pH range,

this will influence both uptake velocity and level [128] and $\log D$ has to be considered instead $\log K_{ow}$.

In the last decades, most plant uptake studies were focused on pesticides or on legacy chemicals that are often less hydrophilic organic contaminants such as PCB, dioxins and PAHs. Little attention has been paid to the plant uptake of CECs and especially to ionized compounds and zwitterionic species. However, the presence of PPCPs and other CECs in the environment and the possible transfer to the animal and human food chain, calls for a better general understanding of uptake and translocation processes in plants. Thus, the number of studies dedicated to plant uptake of CECs is steadily increasing in recent years, proving that many of the CEC groups such as musks and pharmaceuticals (fluoroquinolones, sulphonamides, tetracyclines, anti-inflammatory and other drugs) are taken up by plants [123, 129–131]. For example, Eggen et al. [124] demonstrated the uptake of metformin, ciprofloxacin and narasin in carrot (*Daucus carota ssp. sativus cvs. Napoli*) and barley (*Hordeum vulgare*), with the root concentration factors (RCF) being higher than the corresponding leaf concentration factors (LCF) for all the target pharmaceuticals. The uptake of metformin was higher compared with the other two tested pharmaceuticals for all the target plant compartments, showing a generally higher bioaccumulation pattern in roots (RCF 2–10) and leaves (LCF 0.1–1.5). Negative effects on plant growth such as reduced biomass were observed for all three studied compounds, with narasin showing the most pronounced effect. Uptake of 17- α -ethynylestradiol (EE2) and triclosan in bean plants (*Phaseolus vulgaris*) grown in sand and soil was demonstrated by Karnjanapiboonwong et al. [131]. According to the authors, roots were the primary plant part in which EE2 and triclosan accumulated, and the accumulation of both test compounds was higher in plants grown in low organic carbon substrate. Antibiotics such as oxytetracycline, enrofloxacin, chlortetracycline and sulfamethazine were found to be taken up by alfalfa, corn, lettuce, potato, onion, cabbage and cucumber from manure-amended soil, agar medium or nutrient solutions [132–135]. Furthermore, bioaccumulation and phytotoxicity in algae, rice, cucumber and wetland plants have been reported by other authors [80, 136–138].

The majority of the aforementioned studies, however, is focused on the bioavailability and uptake of CECs by plants grown in soil-based mediums with artificial added contaminants [129, 139] or contaminated bio-solids used to fertilize agricultural soils [137]. Up to date only a handful of studies have considered plant uptake of CECs after application of reclaimed water for crop irrigation. For instance, the uptake of eleven, frequently detected PPCPs (diclofenac, carbamazepine, clofibric acid, caffeine, ibuprofen, naproxen, triclosan, methyl dihydrojasmonate (MDHJ), galaxolide, tonalide and hydrocinnamic acid) in apple (*Malus domestica*) and alfalfa (*Medicago sativa*) was evaluated by Calderón-Preciado et al. [121] under actual field conditions. Five of the 11 target contaminants were identified and quantified, namely, ibuprofen, naproxen, MDHJ, caffeine and tonalide. Caffeine and MDHJ were found in both crops in concentration levels between <0.011 and 0.016 and 0.041 and 0.532 mg/kg (fresh weight), respectively, whereas galaxolide, ibuprofen and naproxen were detected only in alfalfa with

levels from <0.011 to 0.061 mg/kg (fresh weight). Comparing the studied crops, it seems that the occurrence of the PPCPs in alfalfa is higher than those in apple. Besides the aforementioned field study, in vitro uptake of triclosan, hydrocinnamic acid, tonalide, ibuprofen, naproxen and clofibric acid by lettuce (*Lactuca sativa* L) and spath (*Spathiphyllum spp.*) was investigated by the same research group [139] in order to evaluate the reuse of treated wastewater for irrigation of agricultural crops. The authors conclude that compounds with a carboxylic group in their structure such as hydrocinnamic acid, naproxen and clofibric acid exhibited higher uptake rates. In relation to previous study, Wu et al. [140] examined a larger suite of PPCPs (20 frequently occurring compounds in irrigation) that had different K_{ow} or pK_a values and they compared their accumulation into four staple vegetables (lettuce, spinach, cucumber and pepper) grown in nutrient solutions containing PPCPs at 0.5 or 5 $\mu\text{g/L}$. Results showed significant disparities between the studied compounds regarding their potential for root uptake and subsequent translocation. Out of the 20 PPCPs considered in this study, triclocarban, fluoxetine, triclosan and diazepam accumulated in roots at levels relatively higher than the other PPCPs, while translocation to leaves/stems was more extensive for meprobamate, primidone, carbamazepine, dilantin and diuron. The authors suggested a positive correlation between root uptake and pH-adjusted $\log K_{ow}$ (i.e. $\log D_{ow}$) for non-ionic compounds and a negative correlation for translocation from roots and $\log D_{ow}$, indicating that compounds with strong hydrophobicity (i.e. high D_{ow}) tended to remain in the roots with limited in-plant redistribution. Consequently, and according to the study for the later compounds higher residues may be found in tuber vegetables (i.e. carrot and radish), while for PPCPs with high translocation potential, higher levels are expected in leafy vegetables such as lettuce, spinach and cabbage.

Finally, in the field study of Jones-Lepp et al. [141], greenhouse experiments were performed in which selected food crops were irrigated with three different water types (wastewater effluent known to contain CECs, CEC-free well water and Colorado River water containing trace-level CECs) spiked with three antibiotics. The results showed the potential for uptake of one or more of the antibiotics evaluated at very low levels only. The industrial flavouring agent, *N,N'*-dimethylphenethylamine (DMPEA), was consistently found in food crops irrigated with wastewater effluent, whereas none of the evaluated contaminants were found in crops irrigated with Colorado River water.

In summary, biosolids seem to be a more significant reservoir or sink for plant uptake of particular compounds than reclaimed water and therefore, much of the occurrence of some CECs is likely associated with biosolids. Meanwhile, although relatively few studies have specifically examined the role of reclaimed water usage in crop irrigation, detections of trace concentrations of selected CECs in different plant species have been documented. These plant uptake studies have provided a snapshot of the CECs in plant species, but many of them have been done at unrealistic exposure concentrations (in most cases higher than those detected in real samples), and therefore, more systematic investigation under real environmental conditions is required. The data generated must be supported by an appropriate

QA/QC system, which has not always been done and experiments should integrate phytotoxicity/ecotoxicity tests. In addition, further research is required to clarify the transport processes and bioavailability of CECs to plants and whether species-specific uptake patterns can occur from contaminated soil. Such information is also important for the identification and prediction of CECs with potentially high transfer to human and livestock food webs that could provide a scientific framework for establishing environmental regulations.

5 Conclusions

Over the past few years a vast amount of research has been conducted in sample preparation and instrumental analysis and a number of methods have been proposed for analysis of organic microcontaminants in reclaimed water as well as in soils and crops associated with wastewater reuse. Thus, in recent years more data and broader knowledge have become available on CECs detection and identification in these matrices. Despite, however, this effort, innovative methods combining efficient extraction and selective mass spectrometric detection have to be designed and applied to improve non-target screening and identification of unknown transformation products. Furthermore, there is an urgent need for laboratory trials and field-scale studies in order to explore the fate, distribution and uptake of a range of organic microcontaminants in soil–plant systems to provide essential data for modelling their environmental behaviour.

Acknowledgements This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program “Education and Lifelong Learning” of the National Strategic Reference Framework (NSRF) – Research Funding Program “Excellence II (Aristeia II)”, Research Grant, No 4199, which is gratefully appreciated. The authors would also like to thank the Cost Action “ES1403: New and emerging challenges and opportunities in wastewater reuse (NEREUS)” for support.

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Wastewater Reuse and Current Challenges

Fatta-Kassinos, D.; Dionysiou, D.D.; Kümmerer, K. (Eds.)

2016, XIV, 261 p. 25 illus., 12 illus. in color., Hardcover

ISBN: 978-3-319-23891-3