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Evaluation of the impact of agricultural soil on the bioavailability of organic microcontaminants and heavy metals for uptake by crops

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ACRONYMS

ARGs	Antibiotic Resistance Genes
ARB	Antibiotic-Resistant Bacteria
CECs	Contaminants of Emerging Concern
CEC*	Cation Exchange Capacity
D_{OW}	pH adjusted octanol-water partitioning coefficient ($D_{OW}= K_{OW}/(1+10^{pH-pKa})$)
DOC	Dissolved Organic Carbon
EDC	Endocrine Disrupting Compound
K_{COC}	The organic carbon normalized K_p ($K_{COC}=K_p \times 1/f_{OC}$)
K_d	Soil-water partitioning or distribution coefficient
K_F	Freundlich partitioning or distribution coefficient
K_{oa}	Octanol-air partition coefficient
K_{oc}	The organic carbon normalized K_d ($K_{OC}=K_p \times 1/f_{OC}$)
K_{ow}	Octanol-water partitioning coefficient
K_p	Colloid partitioning coefficient ($K_p=[EC_{colloids}]/[EC_{free}][colloids]$)
NER	Non-Extractable Residue
PPCPs	Pharmaceuticals and Personal Care Products Compounds
SOM	Soil Organic Matter
TWW	Treated Wastewater
UWTPs	Urban Wastewater Treatment Plants

Bioaccessibility: The potential of a substance to interact with (and be absorbed by) an organism.

Bioavailability: The degree and rate at which a substance (as a drug) is absorbed into a living system or is made available at the site of physiological activity.

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Executive summary

Soils in the EU are exposed to numerous threats (e.g. erosion, floods and landslides, loss of soil organic matter, salinization, contamination, compaction, sealing and loss of soil biodiversity), which limit their ability to deliver ecosystem services (e.g. water and nutrient cycle regulation, food and fibber production) (Frelih-Larsen et al., 2017). Specifically, agricultural soil is receiving a variety of contaminants of emerging concern (CECs) (both chemical and biological) from different sources. Among them, irrigation with wastewater subjected to different treatment processes is one of the main pollution sources. CECs include pathogens, antibiotic-resistant bacteria and antibiotic resistance genes (ARB&ARGs) together with a large number of contaminants with different physical-chemical properties in neutral and/or in ionic forms (positive, negative and zwitterion). The chemical speciation depends also on the soil properties, which control their volatility, solubility, and mobility. Accordingly, the bioavailable / bioaccessible fraction of the CECs is the fraction dissolved in the soil pore water being accessible to microorganisms and plants. Because the pore water is in contact with mineral surface and soil organic matter (SOM), a fraction of CECs and extracellular DNA can be reversibly or irreversibly bound onto SOM or entrapped to mineral surfaces, such as clays decreasing the pore water concentration and consequently their bioaccessibility. On the other hand, the rhizosphere is microbiologically very active due to the root exudates leading to degradation of CECs in some extent and formation of degradation intermediates with different ability compared to the parent compound to be taken up by plants. The long-term disposal of reclaimed water and biosolids into the agricultural soil can affect the cation exchange capacity (CECs*) of soil, and the microbiological communities due to the accumulation of persistent CECs and trace elements.

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1. Introduction

According to a recent estimate (Mekonnen and Hoekstra, 2016), nearly 4 billion people worldwide are living under water scarcity conditions. Consequently, a potential solution for this problem is the recycling or reuse of the treated urban wastewater (TWW). This is an ancient practice, which has been applied since the dawn of human history, and is being contemporarily practiced in many parts of the world, which suffer from drought conditions (Sato et al., 2013).

Wastewater reuse offers a good opportunity for the conservation of the water resources, and furthermore provides an alternative method for the wastewater disposal in areas where the surface waters have limited capacity to assimilate nitrogen and phosphorus which remain in the treated wastewater (NRC, 1996).

In addition to the TWW, the biosolids, which are by-products of wastewater processing, constitute a source of organic matter and plant nutrients and micronutrients (N, P, K, Ca, Mg, Zn, Mn, Fe, Cu, B and Mo). The application of stabilized biosolids in agriculture is a common practice in the EU (Directive 86/278 EC) and in many parts of the world. The public scrutiny however, has increased significantly recently due to the potential environmental consequences that may accompany the reuse of these inputs in agriculture. The possible risk involved is related to the wastewater and biosolid heavy-metal and toxic-organic compounds content including pharmaceutical substances and other xenobiotic compounds (Fatta-Kassinos et al., 2011), which may have adverse effects on human and animal health, on plant and microbial diversity, and on microbial communities. As an example towards the opposite direction, Belgium, Switzerland and Romania ban the use of sludge as fertilizer (Milieu et al., 2013).

The focus of this report is on the impact of soil properties on the bioavailability and bioaccessibility of CECs by crops and the effects of reclaimed water and biosolids on the microbiota communities. Long-term disposal of reclaimed water and biosolids on the soil quality is also addressed from an agronomical perspective.

2. Key parameters affecting the bioavailability and fate of CECs

The irrigation of soil with treated wastewater can result in the accumulation of organic microcontaminants (Calderón-Preciado et al., 2011). Once introduced into soil, microcontaminants are subjected to sorption/desorption and transformation processes, which influence the concentrations available for biodegradation and plant uptake. The

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main factors affecting the bioavailability of CECs towards plants or soil microorganisms include the chemical form of the compound, which occurs on the soil in close contact with the plant roots and, the soil properties.

2.1 Contaminants of Emerging Concern (CECs)

CECs include a large number of compounds belonging to different chemical classes with physicochemical properties spanning from highly hydrophilic (log Kow<1; e.g. sweetener sucralose) up to hydrophobic compounds such as polycyclic musk fragrances (log Kow>4; e.g. galaxolide). In addition, they can occur as neutral or ionic forms (e.g. cationic, anionic and zwitterionic). As a consequence, their behaviour in a specific soil is compound-dependant.

The chemical speciation of ionisable CECs depends on the pKa of the compound and the soil pH (see next section). In this regard, the neutral fraction of one compound can be estimated from the soil pH and the compound's pKa (Trapp, 2009). At a soil pH higher than that of the compound pKa, the anionic form of acidic compounds ($HA \rightarrow A^- + H^+$; pKa<4; i.e. ibuprofen, diclofenac, ketoprofen, naproxen, gemfibrozil, atorvastatin) is predominant. Strong basic compounds ($HB^+ \rightarrow B + H^+$; pKa>7; fluoxetine, atenolol, primidone, meprobamate) occur mostly in the cationic form (soil pH<6). For very weak acids (pKa>8; triclosan, acetaminophen or triclorcarban) or weak bases (pKa<6; *N,N*-diethyl-meta-toluamide, sulfamethoxazole, carbamazepine, diazepam), the neutral form predominates (Wu et al., 2013). Complex molecules containing several functional groups have both ionisable acid and basic functional groups and consequently, positively and negatively charged functional groups may coexist in a single form (zwitterionic form). Most of the fluoroquinolones (e.g. ciprofloxacin) can appear in both anionic and cationic forms and depending on the soil pH, both forms can coexist as i.e. in zwitterionic form (Chen et al., 2011).

Anionic CECs can interact with soil cations such as metals or alkaline cations (e.g. Fe, Cu, Al, Ca) forming complexes or chelates, which usually decreases their water solubility. Limited information exists on the stability of these complexes except for few compounds such as fluoroquinolones (Chen et al., 2013). It has been shown that in the saturated sand media, the mobility of ciprofloxacin depends on the occurrence of the Cu/Ca and Al/Fe oxides in soil (Chen et al., 2013; Graouer-Bacart et al., 2016). The latter, have been shown to impede the ciprofloxacin transport due to its strong complexation, but Cu and Ca were found able to promote the ciprofloxacin mobility by

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90% and 30%, respectively. Relevant information for CECs, is currently missing from the literature.

A fraction of the CECs occurring in soil can interact with the soil colloids in the pore water or the dissolved organic carbon (DOC) from the irrigation water. The distribution coefficient concentration in the colloidal phase versus the dissolved phase (K_p) is used to describe their partitioning behaviour with respect to the truly dissolved fraction.

2.2. Soil characteristics and management

Agricultural soil is heterogeneous in nature, where organic (e.g. humic acids, polysaccharides) and mineral fractions (e.g. oxides and hydrous oxides of iron, aluminium and silicon, carbonates, sulphates, phosphates and sulphides) are very variable leading to different chemical properties such as pH, electrical conductivity, CECs* and soil organic matter (SOM). Moreover, water-holding capacity and porosity may affect the CECs leaching to deeper soil profile layers, thus also affecting their uptake by plants. Aeration of soil is also a key factor affecting CECs uptake by plants, as aerobic or anaerobic conditions in soil may affect CECs redox reactions, as well as the performance and ability of microorganisms to degrade them (Engelhardt et al., 2015; Pan and Chu, 2016).

The main mechanisms affecting the CECs transport in soils are the following:

a) **Partitioning**. It occurs as a result of interactions between dissolved contaminants in the pore water and soil solids (SOM and mineral reactive surfaces) resulting in chemical mass transfer from aqueous to solid surfaces.

b) **Soil architecture**. Physical hindrance is related to the availability of voids and channels for flow of solutes and contaminants.

Once introduced in soils, CECs are subjected to sorption/desorption and transformation processes, which influence the concentrations available for plant uptake. The extent and degree of sorption is dependent on both the nature of contaminant and the nature of the soil. The distribution coefficient (K_d) is usually used to determine the fraction of the contaminant sorbed to soil. While octanol-water coefficient is considered as a good descriptor for the hydrophobicity of the compounds, it fails to describe K_d for most of the CECs since many different types of interaction may occur between soil and the compound.

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Ploughing can affect the soil structure enhancing channelling effects and thus the hydraulic conductivity. On the other hand, the root system can also enhance the preferential transport of contaminants from irrigation to saturated zone due to preferential transport (Domínguez et al., 2014).

Fertilization management used in agriculture enhances the microbiological activity, which is very active in the rhizosphere where its microbiome is different from the surrounding zone (Lundberg et al., 2012). The role of rhizosphere in the phytoremediation of heavy metals and persistent organic contaminants is well documented but limited information exists concerning CECs (Hurtado et al., 2016). Moreover, the root exudates, which may contain organic acids (e.g. citric, oxalic, malonic) can reduce the pH up to 2 units in a distance of 2-3 mm from the root surface (Hinsinger et al., 2003). In the case of the ionisable CECs it can affect their speciation and therefore its bioavailability.

The impact of soil properties on the CECs sorption has been evaluated in several studies. Vasudevan et al. (2009) conducted a study with 30 soils from the eastern United States and found that the soil pH has statistical significance on the K_d values of CIP. In addition, the CECs* was the key soil factor influencing the extent of sorption at all pH values (3-8) with eletrostatic interaction being the predominant mechanism.

Usually the colloid bonded fraction of CECs is less bioaccessible/bioavailable to soil microbiota and plants. Metronidazole, which practically does not sorb to soil colloids, has been found to cause detrimental effects to plants even in quantities as low as 0.5 mg g^{-1} soil (Jjemba, 2002).

However, limited information exists on the K_d values to assess the fate of CEC in agricultural soil. Zhou et al. (2007) found that the organic carbon normalized partition coefficient for colloids K_{COC} for endocrine disrupting compounds (EDC) varied by a factor of 6-12. It was attributed to the properties of colloids leading to interactions such as H-bonding, van der Waals forces and charge transfer to the polar functional groups of different strength. Although no data are available regarding the role of colloids in the transport of CECs along the vadose zone, it is expected to be remarkable due to the high DOC.

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2.3 Processes taking place in soil

Sorption-desorption. Factors which influence the sorption of organic xenobiotic compounds to soil particles include the amount of organic matter, pH, mineral concentration, clay composition and soil temperature. Sorption behaviour is described by adsorption isotherms, which may be either linear in nature (giving rise to a distribution coefficient [K_d]) or non-linear as represented by the Freundlich isotherm and adsorption coefficient [K_F]. The adsorption coefficients are influenced by the soil composition, texture, and natural organic matter (Thiele-Bruhn et al., 2004). The K_d value is often normalised to the percentage organic carbon present in the soil to derive the K_{oc} value. Generally, compounds with log K_{oc} values < 2 are considered to be capable of only weak sorption. The application of biochar as a soil amendment leads to an increase in the K_d and then a decrease in the CECs bioavailability leading to a decrease in CECs concentrations in root and plant leaves (Hurtado et al., 2017).

For compounds possessing widely different structures, functionalities and molecular weights, it is important to experimentally determine their sorption properties in specific soils to derive an accurate understanding of their subsequent behaviour. Batch sorption experiments have been used to study the affinities of different soils for five pharmaceuticals and personal care products compounds (PPCP) (bezafibrate, carbamazepine, chloramphenicol, diclofenac and triclosan) (Revitt et al., 2015) and three sulfonamide antibiotics (sulfamethoxazole, sulfadimethoxine and sulfamethazine) (Park and Huwe, 2016).

The adsorption isotherms support the determination of K_d and K_F values and are particularly accurate when the *n* value from the Freundlich isotherm is close to unity and strong regression coefficients exist. *n* values close to unity indicate that the marginal sorption energy of the sorbates decreases with increasing surface concentration (Weber et al., 1991). This was consistently the case for bezafibrate, chloramphenicol and sulfonamides, indicating that the Freundlich-type isotherm was attributed to varying sorption energy, indicating that adsorption was presumably based on site-specific mechanisms. This has been shown to be the case for both hydrophobic and hydrophilic sorbates (McGinley et al., 1996; Gunasekara and Xing, 2003).

The sorption characteristics of CECs, as defined by K_d and K_F values, have not been extensively tested in soil matrices, and therefore, it is often necessary to rely on estimated K_{oc} values such as those derived from octanol-water coefficients (K_{ow}). However, considerable variations have been observed between predicted and

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experimental values leading to both under- and over-predictions of soil mobilities. There is clear evidence that SOM is an important factor influencing the sorption of pharmaceuticals and thus, their ultimate fate in the environment (Park and Huwe, 2016; Revitt et al., 2015; Xu et al., 2009; Chefetz et al., 2008).

Therefore, hydrophobicity-independent mechanisms, such as cation exchange, cation bridging at clay surfaces, surface complexation and hydrogen bonding may contribute to reduced mobility (Yamamoto et al., 2009). Soils with high organic content are not able to retain compounds with high water solubility, such as chloramphenicol due to potentially reduced active surface sorption sites. In a series of controlled experiments, Shimizu et al. (1992) showed that the sorption of pentachlorophenol to a range of natural solids was more dependent on the expansive clay content and the CECs* than the organic carbon content. Polyfunctional CECs are unique in that they sorb onto environmental solids at multiple receptor sites via multiple interaction mechanisms (MacKay and Vasudevan, 2012). The authors proposed a mechanism-based framework for conceptualizing the equilibrium solid-water sorption coefficient, K_d with particular emphasis on the mechanisms of cation exchange and surface complexation /cation bringing (Fig 1).

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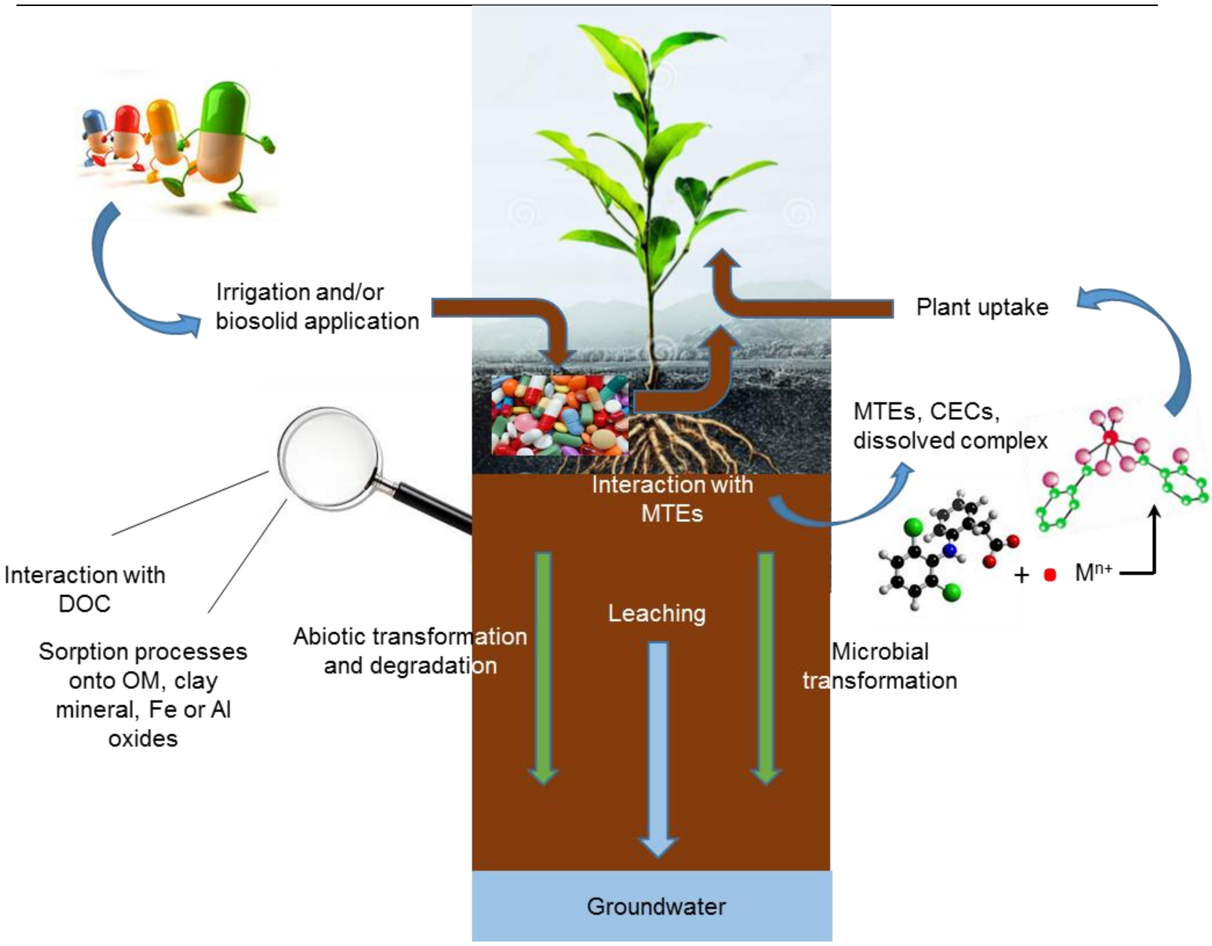

Figure 1 - Fate of CECs in the soil-root system (MTEs: metals, CECs: contaminants of emerging concern). Credits Dr. E Guillon and Dr. S. Sayen (Reims University)

Sorption characteristics can be strongly influenced by the pK_a of the investigated compound relative to the pH of the soil. Where the soil pH is higher than the pK_a value, the prospective sorbate (i.e. molecule prone to be adsorbed or absorbed on or in a sorbent respectively) will tend to exist in the dissociated form as negatively charged species, sorbing less strongly than their neutral counterparts. This is reinforced by the presence of a negative net surface charge on most subsurface soil particles. However, for strong bases at low pH values (see section 2.1), the existence of positively charged species will facilitate increased adsorption to negatively charged soil particles. This is the case when performing batch sorption experiments under different pH conditions. Park and Huwe (2016) were able to show that sulphonamides exhibited increasing sorption potential with decreasing pH as positive species became more predominant.

Binding to the soil. Formation of non-extractable residues (NER) is central to the fate and persistence of pesticides. The formation of active intermediates or the reconversion to

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parent compounds from the metabolite pool has been heavily underestimated (Loos et al., 2012) and this behaviour is expected, as well for pharmaceuticals. Under similar conditions, spiking experiments have shown that acetaminophen was rapidly converted to bound residue (73.4-93.3% of the initially spiked amount), whereas carbamazepine was retained at < 4.2% in the same soil (Li et al., 2013; Li et al., 2014). Sulfadiazine exhibited also a very fast irreversible formation of NER described by a first-order rate process (Müller et al., 2013). Revitt et al. (2015) showed similar differences in behaviour between triclosan (strongly bound) and chloramphenicol (weakly bound). It is the latter (also known as the exchangeable or reversibly sorbed fractions) together with the dissolved species, which are readily available for migration, microbial utilization and plant uptake (Semple et al., 2004).

Vertical transport. The poorly sorbed contaminants are also the most likely to migrate downwards leading to their presence in groundwater or drainage water (Bondarenko et al., 2012). The mobility of many organic microcontaminants in soils generally decreases as soil organic matter increases, as occurs during the application of biosolids, due to enhanced sorption. However, in the case of PPCP, this needs to be balanced against the role of dissolved organic matter, which may either assist or retard movement depending on chemical and environmental properties (Navon et al., 2011; Haham et al., 2012). It is not only the quantity of SOM, which affects the extent of sorption but also its quality of interaction with phenolic compounds, lignin monomers and dimers, as well as lipids and alkylaromatics being particularly influential. A variety of models exist that are able to predict the soil mobility of organic contaminants but a few of them take into account the impact of plants. In this regard, the root zone water quality model is one widely used for simulating agricultural management effects on crop production and soil and water quality (Ma et al., 2012; Fang et al., 2017).

Biodegradation. In natural and non-sterile soils, PPCP may be degraded or transformed as a result of biodegradation (Yu et al., 2013). The role played by microorganisms in biodegrading diclofenac has been demonstrated by comparing its behaviour in non-sterile and sterilized agricultural soils. Xu et al. (2009) showed that after a 45-day incubation period, 57% of the amount of diclofenac was biodegraded whereas for the same compound, Balogh (2012) has determined a rate of biodegradation of 0.44 d^{-1} with the concentration of a specific biodegradation product peaking after 6 days. This rapid conversion to metabolites in soils is similar to that reported by Li et al. (2014) for acetaminophen and is in contrast to the slow and limited transformation observed for carbamazepine (Li et al., 2013). Using ^{14}C-labelled compounds, naproxen

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and diclofenac were found to be mineralised (50-80%) to $^{14}CO_2$ in different soils (Dodgen et al., 2014) compared to only a small part of ^{14}C-carbamazepine (< 1.2%) and ^{14}C-acetaminophen (17%). Usually, the DT50 parameter is used to evaluate the stability of chemicals in soils. It is defined as the time needed (h) to degrade the 50% of the initial concentration. These values are estimated taking into account a first order decay kinetics but other order kinetics can give a better fit to the experimental data.

Table 1 - Experimental values of dissipation times (DT_{50}) to reduce the initial concentration to halve values in cropped soils

EOC	Experiment Type	Plant	DT_{50} (d)	References
Bisphenol A	Hydroponics	Dracaena	0.5 – 24	Cousins et al. (2002), Dodgen et al. (2013), Hurtado et al (2016), Saiyood et al. (2010), Xu et al. (2009), Ying et al. (2005)
		Lettuce, collard		
Caffeine	Soil	Cucumber, tomato, sweet potato, carrot	1.5 – 3	Goldstein et al. (2014), Hendel et al. (2006), Hurtado et al., 2016, Lin et al. (2010), Malchi et al. (2014)
		Cucumber, tomato		
		Sweet potato, carrot		
Carbamazepine	Soil	Soybean, radish, cucumber, tomato, sweet potato	6.4 – 693	Carter et al. (2014), Goldstein et al. (2014), Hurtado et al (2016), Malchi et al. (2014), Monteiro et al. (2009), Walters et al. (2010), Wu et al. (2010)
		Soybean, radish, sweet potato, carrot		
		Cucumber, tomato		
Propranolol	Soil	Radish, ryegrass	7.9- 40	Carter et al. (2014), Hurtado et al (2016)

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Triclosan	Soil	Radish, ryegrass	18 – 693	Carter et al. (2014), Hurtado et al (2016), Ying et al. (2007), Walters et al. (2010), Chen et al. (2014)
Tonalide	Soil	Carrot	50 – 133	Chen et al. (2014), Hurtado et al (2016)
		Carrot, barley, meadow		

Acronyms used in this table: BPA: bisphenol A; CAF: caffeine; CBZ: carbamazepine; IBU: ibuprofen; PROP: propanolol; TCS: triclosan; TON: tonalide.

Soil properties, such as organic carbon content, can inhibit PPCP biodegradation by reducing their bioavailability and hence by inhibiting their availability to microbial populations (Xu et al., 2009). Therefore, biosolid amendment of soils reduces biodegradation (Li et al., 2013; Li et al., 2014) and prolongs PPCP persistence in soil due to increased sorption. In addition, biosolids may serve as a more readily available nutrient or carbon source for microorganisms compared to PPCP thus contributing to a reduced biodegradation. The role of biosolids is not mirrored by irrigated wastewater, which has been observed to have no discernable effect on the biodegradation of PPCP in soil (Grossberger et al., 2014).

Volatilization. Once the CECs are introduced in the soil, a variety of physical processes such as volatilization and photooxidation might occur on the topsoil but this depends on the compound volatility and soil organic matter. The octanol-air (K_{OA}) and air-water (K_{AW}) partitioning coefficients are usually used to estimate the compound volatilization from soil or from leaf surface (Undeman et al., 2009). However, a limited number of CECs, such as fragrances have sufficiently high K_{AW} to be volatilized, and are thus significantly removed from topsoil.

Photodegradation. Direct or indirect CECs photooxidation might occur for compounds with significantly high quantum yield or those reactive to sensitizers. Although photodegradation of pharmaceuticals dissolved in water is a significant removal pathway (Matamoros et al., 2009; Fatta-Kassinos et al., 2011; Kawabata et al., 2013), this process is believed to be very limited in the case of soils, especially to the few top soil millimetres. It is worth mentioning that the SOM and DOC can act as quenchers of UV irradiation decreasing the photodegradation kinetics compared to clean water.

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3. Soil microbiological processes

The soil microbiological processes are vital for the processing of chemicals into compounds that the plant can utilise as nutrients e.g. carbon, nitrogen as well as the metabolism of a wide range of compounds. Thus, the soil microbiome and plant interact on a molecular level. The soil bacteria, most associated with the plant are present in the rhizosphere (area directly surrounding the roots). The processes occurring in this region control a range of reactions regulating terrestrial carbon and other element cycles. Plant species and soil type have an enormous influence on plant and microbial community function and structure which greatly influence a variety of ecosystem-level processes (van der Heijden et al., 1998; Wardle et al., 2004; Berg and Smalla, 2009).

The soil microbiome is by itself a natural source of compounds, including antibiotics. During the evolution of the soil bacterial populations, bacteria have developed methods to avoid or resist the inhibitory effects of antibiotics. Thus, soil is a natural source of antibiotics, antibiotic resistance mechanisms (i.e. genes and antibiotic-resistant bacteria). The antibiotic resistance genes present in soil bacteria may be transferred via horizontal gene transfer to other bacteria, including pathogens.

The rhizopshere is a hotspot of horizontal gene transfer (van Elsas et al., 2003; Heuer and Smalla, 2012), which appears to be controlled by exudation and root growth affecting the cell density, distribution, and metabolic activity. The effects of adding animal manure and fertilisers on the abundance and variety of antibiotic resistance genes and bacteria present in soil have been investigated in order to identify the potential selection processes provided by the addition of bacteria, antibiotics and antibiotic resistance genes present in manure. The addition of manure also provides a large influx of nutrients to the soil. However, the effects of adding reclaimed water from UWTPs is unknown, but based on the concept of adding manure would increase the prevalence and diversity of antibiotic resistance genes in the soil and rhizosphere.

4. Long-term irrigation with reclaimed water and biosolids

4.1. Effect on cation exchange capacity (CECs*)

Application of biosolids can enrich the soil with organic matter, which obviously, results in cation exchange capacity (CECs*) increase. The organic matter is an amorphous substance consisting of a large number of organic molecules with variable chemical composition containing 40-60% C, 30-50% O, 3-7% H and 1-5% N. From the structural

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point of view, it contains complex series of carbon chains and ring structures with numerous chemical functional groups (ligands). That is why it has a high CECs*.

Application of wastewater and biosolids may alter the CECs*, as well the levels of the exchangeable cations. Long-term irrigation with wastewater and biosolids can increase the organic matter content of the irrigated soils, as well as the concentration of heavy metals in the top layer of soil (Zhe et al., 2014). Upon decomposition of organic matter, heavy metals are being released (e.g. As, Co, Cd, Mn, Pb). Part of these metals may be involved in exchange reactions. Another part may form sparingly soluble salts. Since these salts cannot be taken up by the plants, they accumulate on the surface becoming part of the soil matrix (McGrath et al., 1984; Kalavrouziotis et al., 2012).

Long-term application of wastewater and biosolids results in the accumulation of heavy metals to toxic levels (Chang et al., 1992; Papaioannou et al., 2016), the accumulation varying with the soil pH. Thus, crops grown in acidic soils may be more sensitive to toxicity as more heavy metals can accumulate due to the fact that the release of these metals is favoured under acidic soil conditions (McBride, 1995).

The wastewater reuse seems to be directly related to CECs*. To this regard, Qian and Mecham (2005) found that long-term wastewater application for crop irrigation of a golf course for 4 years, increased the organic matter content of soil from 0.9% to 1.3%, and the CECs* increased from 48.1 to 55.5 meq 100 g^{-1} soil, Cu from 3.2 to 4.6, and Zn from 2.2 to 4.6 mg L^{-1}. After 5 years of wastewater application the changes of the above characteristics were as follows:

(i) Soil organic matter increased from 2.37% to 2.88%.
(ii) The CEC* increased from 17.6% to 23.9%, and Mn from 59% to 72%, Cu from 1.95 to 2.6 mg L^{-1}, and Zn from 15.5 to 19.4 mg L^{-1}.

Also, a remarkable increase in the mineral-associated organic carbon C from 6.9 (fertilizer control) to 26.6 g Kg^{-1} (biosolid amended) in mineral soils, and from 8.9 g Kg^{-1} (fertilizer control) to 23.1 g Kg^{-1} (biosolid amended) in non-mineral soil, was found.

Similarly, an increase of the amorphous Fe and Al, was found to cause a further improvement of SOM stability, which increased 2-7 fold by the long-term application of biosolids. Thus, it was shown that biosolids can modify the resistance of organic matter to decomposition more than the fertilizer treatments, and therefore long-term biosolid application was found to be able to increase significantly the organic matter stability (Tian et al., 2013).

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4.2. Accumulation of Contaminants of Emerging Concern (CECs)

Studies on the long-term effects of wastewater irrigation and/or biosolid application under field conditions on the uptake of PPCP by plants should also be considered as imperative, as such studies are scarce. Tang et al. (2015) reported that long-term manure application resulted in increased antibiotics' concentrations in paddy soils, as well as antibiotic resistance genes, and that their concentrations correlated with the antibiotic concentration and soil properties (pH, soil organic matter), as well with the extent of soil aeration. In addition, Dalkmann et al. (2012) evaluated the accumulation of pharmaceuticals in soils irrigated with wastewater for 0 to 100 years in central Mexico and concluded that pharmaceuticals reached an upper limit concentration in soil following 20 to 30 years of wastewater irrigation, reflecting a steady-state condition between pharmaceuticals input and dissipation. Thus, one cannot expect that the concentration of CECs in soils will linearly increase with the increase in duration of wastewater irrigation or biosolid application, because equilibrium will eventually be reached between CECs input and degradation due to the adaptation and bio-concentration of CECs degradation microorganisms in soil.

The CEC's physicochemical properties (pKa, logD_{OW}) and soil type (fine or coarse mechanical structure; clay, silt and sand content), as well as soil pH, organic matter content and electrical conductivity may affect the uptake of CECs by plants. A frequently neglected phenomenon is the existence of fungal mycelial networks in top soils which are acting as highways or pipelines allowing microbes to distribute in the soil, and on the other hand distribute bioavailable pollutants to remote bacteria, hence initiating their degradation or the formation of NER (Banitz et al., 2013). All the above affect the dissociation of CECs in the soil, their adsorption therein and their possible degradation by the CECs bacteria consortium and, consequently, their uptake by plants.

4.3. Effects on microbiota communities

Soil microorganisms include bacteria, actinomycetes, fungi and algae. The microbial activity and biomass production, the biological nitrogen fixation and the vesicular and arbuscular mycorrhizae are potentially affected by the accumulation of heavy metals after long-term application of wastewater and biosolids (McGrath et al., 1994; Smith, 1991). In fact, long-term field experiments have shown that microbial biomass levels in high biosolid treated soils, were about half those of the manure treated soils (McGrath et al., 1994). Similarly, increased levels of nitrogen in soil biomass were accumulated

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following eight years of biosolid application (NRC-1996). Nevertheless, similar information is not available for CECs associated with biosolids or TMWW.

Accordingly, it has been concluded that long-term application of biosolids has been shown to reduce the levels of microbial biomass. Giller et al. (1998) reported that there is an increasing evidence suggesting that microorganisms are far more sensitive to metal stress than animals and plants. More recently, Sobolev and Begonia (2008) reported that both low (1 ppm) and high (500-2000 ppm) levels of heavy metals may shift dramatically the profile make up of microbial community diversity. They state that there is increased evidence, which suggests that microorganisms are far more sensitive to heavy metal stress. Some microorganisms such as the denitrification bacteria may be affected to a greater extent than the generalized microbial communities.

The various contaminants which accumulate in soils above certain threshold concentrations can not only exert toxic effects on the respective biota, but they will most probably also disturb the autochthonous microbial communities. They also contribute to the reduction of microbial biomass, which is impaired by the limitation of C and N mineralization, enzyme activity and of decomposition (Brookes, 1995). Indeed, the heavy metals may affect negatively the C biomass as shown by the statistically significant correlation with metal stress in areas closely to industrial sites. Also, in such areas, enzyme activity biomass is greatly depressed by the heavy metals (Wang et al., 2007). Increased concentrations of heavy metals resulted in changes of microbial activity as shown by the changes of their metabolic activity near the smelters. Also, according to the above research, the heavy metals may affect significantly the bacterial and actinomycetic community structure.

The microbial activity was also decreased by Cr and Pb, the latter affected the accumulation of soil organic C, and it posed greater stress on soil microbes than Cr (Shi et al., 2002). It must be underlined that both microbial biomass and its activity are very important in the role of microorganisms related to the degradation of organic matter. Thus, they concluded that heavy metals may have at high concentration adverse effects on soil biomass activity.

Regarding the toxicity of heavy metals on soil microorganisms, there seems to exist a difference between the various metals. Bååth (1992) ranked the toxicity of the heavy metals on soil microbes as follows, As>Cu>Cd>Zn>Pb. Also, Aoyama and Nagumo (1997) reported the following order of toxicity Cu>>Pb>As, the toxic effect of Cr of the microorganisms not having been so far documented (Kimbrough et al., 1999).

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Lu-Sheng et al. (2006) reported that application of Pb at a level < 300 mg Kg^{-1} in the form of lead acetate, caused a slight increase of microbial activity compared to the control, but at higher concentration (>500 mg kg^{-1}) caused an inhibitory effect. This concentration was considered as a possibly critical one, causing significant decline in soil microbial activity, but it was pointed out that the effect was related to clay and organic matter content of soils. Similarly, an initial increase of chlorophyll was observed at the beginning of Pb application, but later on it decreased with the increase of lead concentration (Lu-Sheng et al., 2006).. AbdouSalam (2010) stated that Co and Pb had the smallest effect on the decrease of CO_2 production, the strongest inhibition being exerted on CO_2 production, by Cd.

A symbiotic relationship between certain strains of rhizobia has been found to be adversely affected by the accumulation of heavy metals due to long-term application of biosolids (McGrath et al., 1994). Also, nitrogen biological fixation was decreased resulting in yield reduction of white clover due to the application for 20 years of biosolids. It was found that the nodules of the treated plants were smaller and ineffective for N fixation (McGrath et al., 1994).

5. Concluding remarks and outlook

Irrigation with reclaimed water and biosolids disposal have been recognized as a main source of CEC and heavy metals in soil. The information gathered allows predicting their soil sorption, mobility and bioavailability in different soils. However, their binding to soil and factors that might affect their release are largely unknown. Rhizosphere has been identified as a highly active area of microbiological processes, where the SOM and CECs can be biodegraded leading to the formation of a variety of CECs transformation products and it might induce horizontal gene transfer and then potentially lead to the evolution of antibiotic-resistant bacteria and resistance genes. We are just beginning to unravel the role of the plant in shaping the rhizosphere environment, and the crucial effects of plant endophytic bacteria for soil chemistry, and the fate of CECs or SOM. So far, effects of mixtures have not been investigated sufficiently. Long-term disposal of reclaimed water and biosolids does not seem to increase the concentration of most of the CECs in soil at an alarming level, but it can lead to an increase of metals and metalloids. In addition, it can affect the physical and chemical properties of soil (salinity, CECs) and some trace elements can affect the soil microbiota. The occurrence of nanoparticles in TMWW or biosolids can affect the fate of CECs in the soil-plant interface by increasing the soil

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mobility and as a consequence their bioavailability. On the other hand, the role of microplastics in biosolids as a carrier of organic microcontaminants appears to be limited to hydrophobic contaminants but their fate in the agricultural soil is largely unknown. Their high abundance though is a reason to assess their potential implications in this framework.

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