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Development of a qualitative approach to assessing risks associated with the use of treated wastewater in agricultural irrigation

Abstract
The European Commission's draft regulation for minimum water requirements for water reuse in agriculture addresses microbial and basic water quality parameters but does not consider the potential impacts of chemicals of emerging concern (CECs) on human and environmental health. Because insufficient data prevents the quantitative characterisation of risks posed by CECs in treated wastewater (TWW), this paper presents a framework which combines data and expert judgement to assess likelihood of occurrence and magnitude of impact. An increasing relative scale is applied where numeric values are pre-defined to represent comparative levels of importance. Subsequently, an overall assessment of the level of risk associated is characterised by multiplying together allocated scores, to obtain a single discrete overall score per CEC. Guidelines to support implementation of the framework as far as soil (the initial receiving compartment and pathway to further protected targets) are developed and applied. The approach is demonstrated through its application to clarithromycin, where results indicate that – under the considered scenario - there is limited possibility of its occurrence in soil in a bioavailable form. The role of a qualitative risk assessment approach is considered and the opportunity for its outputs to inform future research agendas described.

Keywords Qualitative risk assessment; treated wastewater reuse; chemicals of emerging concern; agricultural irrigation; minimum water quality requirements

1. Introduction
Facilitating the reuse of treated wastewater (TWW) is a priority objective towards the achievement of sustainable water resources both internationally (UN SDG 6, 2015) and within several European Union strategies (EU 2012 and 2015). As an alternative source of irrigation water, TWW offers a range of potential benefits including a predictable water quantity, a reduced need for chemical fertilisers and improved soil conditioning leading to increased crop yield (Navarro et al., 2015). However, despite these practical and economic benefits, TWW is an under-exploited water resource. In Europe it is estimated that only 2.4% of TWW is reused, rising to 5-12% in the more water-scarce Mediterranean countries (Saliba et al., 2018). While the needs for additional infrastructure to transfer and/or store TWW are identified as barriers to uptake, a key issue limiting its use is public concern over potential impacts on human and environmental health (Maryam and Buyukgungor, 2017; Garcia and Pargament, 2016). A range of guidelines have been developed to support the safe use of TWW in agriculture (e.g. WHO, 2006; FAO, 1992, ISO 2015) and the European Commission recently published draft regulations on minimum quality requirements for reuse (EC, 2018). However, the focus of these guidelines is the protection of human health through a reduction of pathogenic risks and little, if any, attention has been paid to the risks (perceived or actual) associated with chemicals present in TWW (Gardner et al., 2013).

Selected guidelines (e.g. US EPA, 2012) identify limit values for a range of metals however, TWW may contain a myriad of further organic and inorganic substances, as a combined function of catchment-specific land use activities and wastewater treatment plant design. The risks associated with many of these chemical substances have yet to be robustly assessed, particularly chemicals of emerging concern (CECs; defined here as substances which are not regulated under existing EU water quality regulations but which have been identified as having the potential to impact negatively on human health and/or environmental endpoints). CECs represent a diverse group of substances and include various pharmaceuticals, perfluoroalkyl substances, biocides, plasticisers, plastics components, pesticides and oestrogenic compounds (NEREUS D20, 2018; EC, 2017).

With the increasing drive from both policy and practice to facilitate TWW reuse in agricultural irrigation, there is an urgent need to identify and characterise the risks associated with the occurrence of CECs in TWW. However, despite considerable activities undertaken to comply with, for example, the EU REACH requirements, the human and environmental health impacts of only a fraction of the 95,872 substances registered to-date have been fully evaluated (ECHA, 2019, EC, 2017). There is a lack of knowledge on CECs compositions in different products, relevant hazard data and /or details on levels of exposure (EC, 2017). In the absence of these data sets, it is not possible to undertake a quantitative risk assessment of the problems posed to human and environmental health by the occurrence of CECs in TWW. However, with the drive to reuse TWW accelerating, this paper presents a novel framework which combines data and (where this is not available) expert judgement to support a qualitative assessment of risks associated with the occurrence of CECs in TWW used in agricultural irrigation. Guidelines to support the application of the framework are identified up to the receiving soil environment, which represents the primary receiving compartment leading to a host of protection targets (including humans, plants and animals). Hence the specific risk evaluated is the occurrence of a CEC in soil in a bioavailable form. The developed approach is applied to clarithromycin (an advanced generation macrolide antibiotic which is included on both the WHO Model list of Essential Medicines (WHO, 2013) and the 2nd Watch List of Substances under the EU WFD; JRC, 2018) to illustrate the use of the methodology and the opportunities for its use within emerging research and policy agendas.

2. Methodological approach to framework development

A conventional risk assessment (RA) approach involves identification of the hazards within an exposure scenario, followed by analysis of available data on its likelihood of occurrence (LO) and magnitude of impact (MI) to inform both risk characterisation and management decisions (US NRC, 1983). While the OECD (2018) has published a range of exposure scenarios as part of its approach to chemical risk assessment, a standardised exposure scenario pertaining to the reuse of TWW irrigation has yet to be developed. The key variables with the potential to influence the fate of CECs present in TWW reused within agricultural irrigation have been identified (NEREUS D20, 2018), and are presented as a source-pathway-receptor (SPR) model (Figure 1) to inform development of the risk scenario utilised within the worked example (which considers pathways as far as the soil only; see Section 4).

Add Figure 1 here

Within the context of the use of TWW in agricultural irrigation, LO refers to frequency of occurrence of specific CECs in TWW and MI is considered in terms of whether a direct effect can be detected within the environment (e.g. change in soil microbial composition) and whether detected changes are considered to be permanent or reversible following cessation of TWW irrigation. Standard approaches to quantifying LO and MI typically draw on the use of dose response models (in human health RA) or ‘no observable effect levels’ data (environmental RA). However, data on the behaviour and fate of many CECs is limited, with models to predict CECs exposure to either humans or environmental receptors still in the early stages of development. Where data are not yet available to support a quantitative RA, a qualitative approach can be adopted (DEFRA, 2004; Standards Australia 2004, USDA, 2003). Both LO and MI may be assessed using an increasing relative scale where numeric values are pre-defined to represent the comparative seriousness of the problem as indicated in Table 1 for the discharge of a specific CEC within a TWW flow which comes into contact with a protected target.

Add Table 1 here

The values presented in Table 1 are ordinal in nature and therefore represent only, for example, the order of LO of specific CECs in TWW at point of use relative to other CECs and do not have an exact quantitative meaning. For both LO and MI, scores are allocated across a range of 1 – 4, where a score of 1 indicates least likelihood/impact to up to a maximum of 4 (highest likelihood/impact). respectively. An overall assessment of the level of risk associated with a specific CEC in TWW used in agricultural irrigation can then be deduced by multiplying together the ranked scores allocated to LO and MI, developing a single discrete overall score per CEC.

3. Results and discussions

The scoring approach set out in Table 1 has been applied to the SPR model presented in Figure 1. Due to the lack of field data, dose response models and understanding of cumulative exposures, it is currently only possible to apply the approach as far as soil as the target receptor.

3.1 Benchmarking the likelihood of CECs reaching the soil environment

The likelihood of a CEC reaching the soil environment is identified as a function of the untreated WW characteristics, the type of treatment applied, whether the TWW is subjected to transportation/storage prior to use and the type of irrigation used. The following sections discuss each of these influencing factors and draw on a combination of literature data and expert judgement (provided by the NEREUS network; a global network of 380 researchers working in the field of TWW in a variety of disciplines) to inform the application of the approach set out in Table 1 within an agricultural irrigation context.

3.1.1 Dependence on sources of wastewater

CECs may be discharged into the WW treatment system from a range of urban and non-urban sources. The latter will be mainly rural residential areas from which WW will potentially contain CECs from a diversity of everyday activities, including the washing of textiles, the disposal of unused items and, in the case of pharmaceuticals, due to excretion in an unchanged state. In addition to housing, urban areas will additionally include hospitals and commerce/industry which, in the absence of on-site treatment facilities, are potentially major sources of CECs (Vidal-Dorsch et al., 2012; Fairbairn et al., 2016). The greater the variety of sources, the greater the likelihood that CECs will be present in the WW directed to the wastewater treatment plant (WWTP). However, a proposed rank scoring needs to take into account the different combinations of sources which may contribute CECs to WW and the relative importance of their contribution as shown in Table 2 (column 1). In the case of pharmaceuticals, the LO is greatest when the WWTP influent contains effluent from pharmaceutical industries followed by hospitals, residential areas and other industry (Brown et al., 2006; Santos et al., 2013).

3.1.2 Level of wastewater treatment

Although it has been recommended that secondary TWW should not be used for agricultural irrigation in the EU (JRC, 2017), the highest rank score (4) is allocated to this category of TWW as there may still be circumstances under which it could be used (Table 2; column 2). Conventional treatment systems (e.g. activated sludge) are typically not designed to treat CECs with the result that a high proportion of the parent compounds and their metabolites can be discharged. This is particularly true of surfactants, pharmaceuticals and personal care products (PPCPs) and polar pesticides (Petrovic et al., 2003). The increased efficiency achieved in microbiological WW treatment through the use of membrane bioreactors (MBR) is indicated by allocating a rank score of 3 to this treatment (Table 2). Gonzalez et al. (2016) report that MBR systems enhance the removal of many CECs compared to activated sludge systems, particularly in the case of hydrophobic compounds which have lengthy residence times. Although high levels of elimination (>90%) have been observed for many compounds there are some PCCPs, for example amitriptyline, diazepam and sulfamethoxazole, for which removal is less efficient (24-68%) (Trinh et al., 2012).

Tertiary and advanced wastewater treatments include adsorption, ozonation and advanced oxidation processes. Light-driven oxidation (with or without H_2O_2) and ozonation processes may involve the formation of unwanted toxic by-products, which is recognised by allocating a lower rank score (1) where there is the possibility of producing toxic by-products compared to a treatment scenario where this is known not to be the case (rank score 2) (Table 2; column 2). Potentially toxic by-products associated with the ozonation of WW include nitrosamine and N-Nitrosodimethylamine (Hollender et al., 2009).

Insert Table 2 here

The treatment of secondary effluents with high doses of ozone has demonstrated increased toxicity due to the formation of toxic by-products (Petala et al., 2008). Similar problems are associated with advanced oxidation processes (AOPs) such as UV/H_2O_2, photo-Fenton, heterogeneous photocatalysis, and O_3/H_2O_2. Although ozonation generally provides efficient removal of CECs (Nakada et al., 2007) there are some compounds which are resistant to this process including mecoprop, benzotrizole and sucralose (Margot et al., 2013; Reungoat et al., 2012). Adsorption techniques using activated carbon are widely practised treatment processes with removal efficiency depending on contact time and the physico-chemical properties of the adsorbate and the adsorbent. Removal efficiency increases as a substance's octanol-water partitioning coefficient (pK_{ow}) increases with pK_{ow} values >4 indicating a high potential for sorption to activated carbon (AC) (Margot et al., 2013). Granulated AC is reported to be capable of removing a range of different PPCPs and flame retardants to levels below detection limits (Kim et al., 2007). Together with sand filtration, AC filtration is recommended for the removal of oxidation by-products (Rizzo et al., 2019; Krzeminski et al., 2019).

3.1.3 Effect of storage and transportation prior to use

If TWW is stored before irrigation, CECs may be degraded to daughter products which are either less toxic, or more toxic, than the original substance. A critical factor will be the time between the TWW discharge from the WWTP and its use for irrigation, including both transfer within a distribution system and storage within either an open or closed system. CEC properties will also determine its susceptibility to physical (e.g. adsorption to suspended solids), chemical (e.g. hydrolysis) and biological (e.g. biodegradation) processes. The efficiency of biotic/abiotic degradation processes varies widely between CECs. Ryan et al. (2011) found that allowing photolysis in WW stabilisation ponds led to enhanced PPCP removal, although direct UV radiation is reported as ineffective for the removal of antibiotics (Adams et al., 2002). There is also disagreement regarding the role of hydrolysis reactions with data showing only limited evidence of ciprofloxacin, sulfamethoxazole and trimethoprim removal (Alexy et al., 2004). Where degradation does occur, the occurrence of increased toxicity of daughter products needs to be considered. The worst TWW storage scenarios would be where there is either no degradation of the original CEC or degradation results in the formation of a toxic daughter product. These scenarios are both allocated a rank score of 2 compared to a rank score of 1 where the degradation of the original CEC results in the formation of a non-toxic daughter product (Table 2; column 3), with scores of 2 and 1 reflective of the current limited understanding of the behaviour of CECs in stored/distributed TWW.

3.1.4 Technique used for soil irrigation

The efficiency with which TWW, and hence the CECs, reach the receiving soil is dependent on the irrigation method. Four categories of irrigation (surface, spray/sprinkler, drip irrigation and sub-surface) system were identified (Doneen and Westcot, 1988), all of which have the potential to contaminate the soils. However, drip irrigation and sub-surface irrigation represent a targeted process of TWW delivery in which the supply of TWW to the soil is regulated to crop requirements. This limits TWW percolation to groundwater and/or CEC build-up in the soil. Therefore, both these irrigation procedures have been given a rank score of 1 (Table 2; column 4). The same level of control is not possible with surface irrigation where gravity systems are employed to effectively flood the irrigated area. The increased potential for soil contamination merits a rank score of 2. In spray/sprinkler irrigation, which is correctly adjusted to avoid surface ponding, the level soil contamination will be less severe but the potential for direct contamination of the plant surfaces also merits a rank score of 2 (Table 2). The allocation of scores of 1 and 2 (as opposed to for example, 3 and 4) within this binary approach is reflective of the relatively limited data sets pertaining to CECs in TWW used in agricultural irrigation.

3.2 Benchmarking the magnitude of the impact of CECs in the soil environment

The MI of a CEC reaching the soil environment is considered to be a combined function of CEC load in TWW, the environmental behaviour of a specific CEC within the receiving soil environment and the type of soil management practices applied. The following sections discuss each of these factors to inform the application of the scoring scheme set out in Table 1.

3.2.1 Dependence on CEC load in TWW

The potential impact to the receiving soil will be influenced by the quantity of CEC delivered during the irrigation process. On the basis that constant irrigation flow rates will be used it is possible to use CEC concentrations as a surrogate for pollutant loads. The influent and effluent concentrations for a range of pharmaceuticals associated with a traditional activated sludge municipal treatment plant receiving a mean daily load of ~25 million gallons per day have been reported by Du et al. (2014). Influent concentrations ranged from 104 ng/l (diclofenac) to 47,500 ng/l (sucralose). The variabilities in treatment efficiencies and therefore effluent concentrations (16.1 to 39,425 ng/L) require that this breadth of values is considered when assigning scores for the assessment of the impact of contaminants to the receiving soil (Table 3; column 1).

3.2.2 Dependence on the CEC bioavailability/bioaccessibility in the soil

CEC bioavailability in soil pore-water is dependent on sorption/desorption and transformation processes which, in turn, are influenced by the soil properties and the chemical form of the CEC. The physical nature of a soil as well as the existence of voids/channels affect the ease of movement of solutes and contaminants. The heterogeneous nature of agricultural soils in terms of both organic content (e.g. soil organic matter; SOM) and mineral fractions control the availability of CECs as a result of partitioning between pore-water and soil solids according to the distribution coefficient (K_d). This parameter together with the octanol-water partition coefficient (K_{ow}; reflecting the degree of hydrophobicity of a contaminant), are critical parameters for assessment of soil-contaminant behaviour. Colloids can play an important role in sorption processes and CECs strongly associated with colloidal particles have limited bioaccessibility/bioavailability.

Insert Table 3 here

Hydrophobicity-independent mechanisms which contribute to reduced CEC availability include cation exchange/bridging, surface complexation and hydrogen bonding (Yamamoto et al., 2009). CECs may vary from being highly hydrophilic (log K_{ow} <1; e.g. sucralose) to hydrophobic in nature (log K_{ow} >4; e.g. ciprofloxacin) affecting their affinity for the soil-water phase. They can also occur as neutral or ionic forms depending on the value of the acid dissociation constant (pK_a) relative to the soil pH.

The binding of CECs to soils can result in the formation of non-extractable residues (NER). This is often a controlling factor in relation to the fate and persistence of pesticides and may also apply to pharmaceuticals. Acetaminophen has been shown to be rapidly converted to bound residue (73.4-93.3%), compared to carbamazepine (retained at <4.2% in the same soil) (Li et al., 2013). Sulfadiazine and triclosan have also exhibited irreversible formation of NER. In contrast, it is the reversibly sorbed fractions together with dissolved species which are readily available for migration. The bioavailability of CECs introduced into soils can be reduced by biodegradation, volatilisation and photodegradation. Microorganisms have been shown to biodegrade diclofenac (Xu et al., 2009) whereas less than 1.2% of carbamazepine was mineralised (Dodgen et al., 2016). The volatility of CECs from topsoil is limited (Undeman et al., 2009). Photodegradation of soluble pharmaceuticals can be a significant removal pathway (e.g. Fatta-Kassinos et al., 2011) but is confined to the soil surface.

The overall bioavailability of CECs is hence determined by their ease of movement through the soil, the established sorption/desorption equilibria and the existence of transformation processes. The latter are either of minimal importance or, as in the case of biodegradation, occur relatively slowly. Therefore, a scoring scheme (Table 3; column 2) has been developed based on the balance between the ease of movement of the CEC within the soil and its bioavailability based on soil properties and the chemical characteristics of the CEC.

3.2.3 Biosolid/fertiliser addition to soils and ploughing

The addition of biosolids/animal manures and the action of ploughing can influence the bioavailability of CECs in soils. Cultivation improves drainage and aeration, typically by breaking up undisturbed soil and reducing the size of soil aggregates. Ploughing can facilitate the transport of contaminants within soils (Dominguez et al., 2014). Application of biosolids or animal manures leads to an increase in SOM (enhancing adsorption and reducing CEC mobility) as well as elevated cation exchange capacity (facilitating CEC complexation). Biosolids are also sources of CECs with Kinney et al. (2006) detecting 30-45 contaminants per biosolid sample at sum total concentrations ranging from 64 to 1811 mg/kg. Animal manures have also been shown to contribute CECs to soil and therefore the possible introduction of an additional CEC load to soil has to be balanced against the advantages conferred by increased SOM as a result of non-composted biosolids or animal manure application.

Soil organic carbon content can inhibit PPCP biodegradation by reducing contaminant bioavailability and hence inhibiting contaminant availability to microbial populations (Stumpe and Marschner, 2010). Therefore, biosolid amendment of soils reduces biodegradation (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, further contributing to a reduced biodegradation. However, the major impact of biosolids is on CEC availability in the soil environment. The soil structural changes brought about by ploughing to some degree counteract the effects of biosolids/manure amendment by assisting CECs movement within the soil but at a considerably reduced level. Therefore, in developing a scoring system relating to the combined effect of biosolid/animal manure application and ploughing on CEC availability in soils the following order is proposed: no biosolids/manure + ploughing > manure (only) + ploughing or no ploughing > biosolds + ploughing > biosolids + no ploughing. The composting of animal manures, which has been demonstrated to degrade veterinary pharmaceuticals (Song and Guo, 2014), reduces CECs load associated with manure application and hence lowers the assigned score. The rank scores are allocated as shown in Table 3 (column 3).

3.3 Calculation of discrete scores for LO and MI

The different factors which influence the likelihood of CECs reaching the soil environment after irrigation with TWW (see Section 3.1) can be combined by multiplication of the individual ranking scores to give a single score indicating LO per CEC. These can be ranked to give a prioritised list varying from most likely (highest combined score) to least likely (lowest combined score). Likewise, in relation to MI, multiplying together each of the scores allocated to the factors that influence the impact of CEC bioavailability within soil generates a discrete combined score which can be used to indicate the relative MI of a CEC. The range of scores generated when calculating single combined values for either LO or MI range from 1 to 64 in both cases. These scores are grouped into four ranges and descriptors allocated to indicate an increasing overall likelihood of a CEC occurring in soil following irrigation with TWW or an escalating overall MI in terms of bioavailability within the soil environment. Ranges of scores and supporting LO and MI descriptors are as follows:

- scores 1-6: rare (LO: a lack of evidence but possible; MI: impact not detectable; integrated score = 1)
- scores 7-16: unlikely (LO: uncommon but know to occur; MI: uncommon but impact may occur; integrated score = 2)
- scores 17-36: possible (LO: may occur sometimes; MI: may create an impact sometimes; integrated score = 3)
- scores 37-64: LO: likely to occur; MI likely to exert an impact; integrated score = 4

3.4 Calculation of an overall risk score

Multiplying the LO and MI scores (described in Tables 2 and 3) together supports development of a ranked list of CECs with regard to their potential to occur in soil in a bioavailable form. As an ordinal dataset, it does not provide information on what, for example, a 'high probability' means, nor can it be used to determine how important the difference is between CECs ranked first as opposed to second. However, the ranked risk scores can be used to short-list CECs which are relatively of most concern and should be prioritised for further research. Whilst the score itself has no quantitative meaning, such risk scores are often interpreted using a 'traffic-light' style matrix. Despite their widespread use, there are no clear guidelines on how scores should be segregated into discrete ranges or how these sets of values should be interpreted. In the absence of specific guidelines, the approach below is proposed, together with an example of how score ranges can be interpreted:

- A risk score of 12-16 indicates a high probability of the occurrence and bioavailability of a CEC in soil resulting in uptake by a receptor;
- A risk score of 9-11 indicates the possibility of the occurrence and bioavailability of a CECs in soil resulting in uptake by a receptor;
- A risk score of 5-8 indicates the unlikely (or limited possibility of) the occurrence and bioavailability of a CEC in soil resulting in uptake by a receptor;
- A risk score of 1-4 indicates that only on very rare occasions would the occurrence and bioavailability of a CEC in soil result in uptake by a receptor;

4. Example of the application of the developed qualitative RA framework

The scenario considered focusses on clarithomycin and involves WW from a residential area (no major industrial or hospital contributions) undergoing secondary treatment with MBR. The TWW is piped directly to a closed tank, and is used for spray irrigation within 24 hours to a neutral, sandy soil. The soil is not amended with biosolids/animal manure but has been subjected to ploughing. By following the SPR model outlined in Figure 1 and considering the scoring systems described in Tables 2 and 3, the following assessments can be deduced.

4.1 The likelihood of CECs reaching the soil environment

This will be dependent on:

- source of WW: WW derived from a residential area without industrial or hospital sources is allocated a score of 2.
- level of wastewater treatment: enhanced secondary treatment with MBR receives a score of 3.
- effect of storage prior to use: TWW is transferred to the irrigation site in a closed system and used within 24 hours allowing limited time for breakdown of the clarithromycin by hydrolysis or biodegradation. Lack of exposure to light eliminates opportunity for photolysis hence a score of 2 is allocated.
- soil irrigation technique: spray irrigation is considered to pose an increased CEC risk due to increased opportunity for soil contamination and is allocated a score of 2.

Therefore, the overall score relating to the likelihood of CECs reaching the soil environment is 2 x 3 x 2 x 2 = 24. This falls within the '16-36' range indicating an integrated LO score of 3 which is indicative of the possibility of clarithromycin being found in the soil.

4.2 The MI of CEC bioavailability within the receiving soils

This will be dependent on:

- CEC load in TWW: Following conventional activated sludge treatment, effluent clarithromycin concentrations in the range 57-598 ng/L have been reported (Tuckwell, 2014). After primary and secondary clarifiers followed by sand filtration, McArdell et al. (2003) found clarithromycin concentrations of 57-135ng/L in TWW from a WWTP receiving WW from an urban catchment without industrial or hospital inputs. The level of treatment and the catchment type are considered similar to the described scenario, leading to the allocation of a score between 2 and 1.
- CEC bioavailability in soil: the bio-physico-chemical factors which need to be balanced against one another to provide an overall assessment of the bioavailability of a given CEC in a particular soil are outlined in Table 4. Clarithromycin movement in a sandy soil will be limited due to electrostatic attraction to negatively-charged soil minerals although clarithromycin is likely to exhibit only moderate interaction with SOM. Therefore, the category in Table 3 which best fits this behaviour is 'ready movement of CECs within soil'.
- biosolid/animal manure addition and ploughing: ploughing is practised but there is no application of biosolids/animal manure hence a score of 4 is allocated.

Insert Table 4 here

Therefore, the overall MI score relating to the impact of CEC bioavailability within the receiving soil is 2/1 x 2 x 4 = 16/8. This falls within the '7-16' range indicating an integrated MI score of 2 which is indicative of clarithromycin being unlikely to exert an impact in the soil environment.

4.3 Overall risk assessment score

Combination of the LO and MI scores yields an overall risk score of 6 (3x2) which fits into the '5-8' band (see Section 3.4) and corresponds to a scenario in which there is limited possibility of the occurrence and bioavailability of clarithromycin in the soil.

5. Conclusions

Recognising that the development of complete data sets on the occurrence, behaviour and fate of CECs in TWW reused in agriculture is a long-term goal, this paper sets out a novel approach to qualitatively characterising the risk that a CEC will occur in soil in a bioavailable form. The utility of the approach is demonstrated through its application to clarithromycin and the scope for this approach to be applied to further CECs is clear. However, the identity of substances to be evaluated to inform a robust assessment of risks to human and environmental health from TWW reuse in this application is less so. The development of a short-list of priority CECs is a dynamic target influenced by both the development of new products (e.g. levels of CECs) and the perspective of the list-maker (e.g. a focus on potential to be bioaccumulated as opposed to those most resistant to treatment etc.). An initiative which could make a significant contribution to identifying a short(-er) list of CECs is the European Chemical Agency's chemical screening programme, involving the evaluation of data on hazardous properties to identify all 'substances of very high concern' (SVHCs) by 2020. Whilst the ECHA SVHCs short-list itself would not be fully fit for purpose (see Deviller et al., (under review) for a comprehensive evaluation of existing chemical legislation in relation to sources of CECs potentially present in TWW), it will provide a useful starting-point to which further CECs of concern can be added on a systematic basis. The results of the application of the developed approach to a prioritised list of CECs will enable future research and policy initiatives to focus on CECs in TWW reused in agricultural irrigation from the perspective of potential to occur in a bioavailable form. This represents a significant step forwarding in understanding, and one which can underpin efforts to address a further critical research question: do CECs identified as having a high probability of being present in soils in a bioavailable form have the potential to accumulate within an identified receptor and – if so – to what level?

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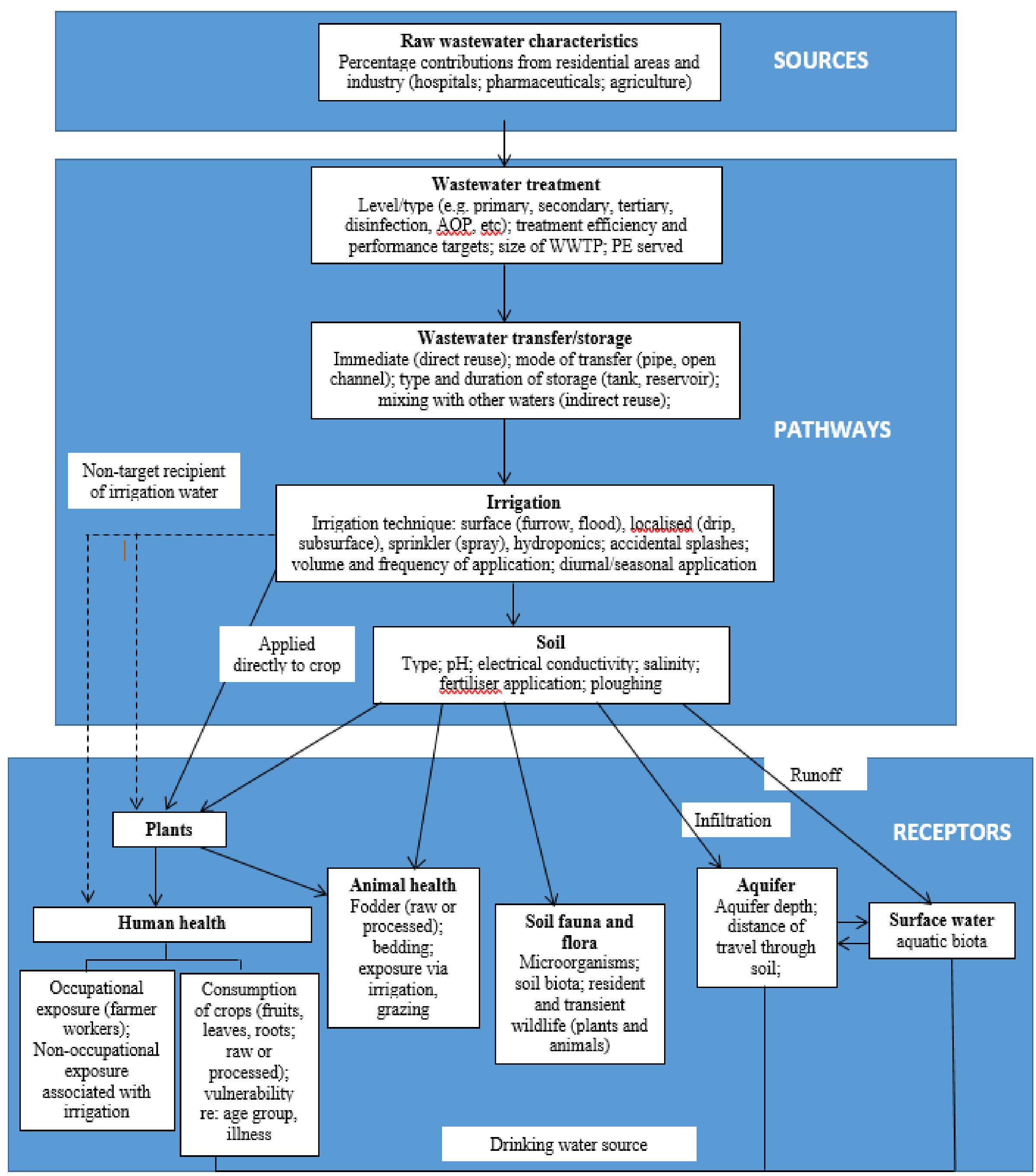
Table 1. Descriptors and scores to benchmark the likelihood of a specific CEC occurring in TWW and the magnitude of the impact occurring when a specific CEC is discharged in TWW

Factor	Possible descriptors for relative grading	Ordinal value associated with identified factor
Likelihood of occurrence	Likely (expected to occur)	4
	Possible (may occur sometimes)	3
	Unlikely (uncommon but known to occur)	2
	Rare (lack of evidence but not impossible	1
Magnitude of impact	High (; available for uptake)	4
	Medium (; may be available for uptake)	3
	Low (; unlikely to be available for uptake)	2
	Very low (not available for uptake)	1



Key: AOP = advanced oxidation processes' PE = person equivalent

Figure 1 Source-pathway-receptor model related to the use of TWW in agricultural irrigation

Table 2 Example of an approach for developing a single combined score which represents the likelihood of CECs occurring in soil following irrigation with TWW.

Sources of wastewater				Characteristics of WW treatment				Storage prior to use		Soil irrigation			
Rural WW	Urban/Municipal WW			Secondary treatment (employing filter beds/ activated sludge aeration)	Enhanced secondary treatment (e.g. membrane bioreactors)	Tertiary/ advanced treatment; where oxidation processes can lead to toxic by-products	Tertiary/ advanced treatment; where there is NO possibility of toxic by-products	During the storage/ distribution process there is no breakdown of the original CECs or breakdown results in a toxic daughter product	During the storage/ distribution process breakdown of the original CECs results in a non-toxic daughter product	Surface irrigation	Spray/ sprinkler irrigation	Drip irrigate ion	Sub-surface irrigation
	Residential sources	Industrial/ hospital sources with on-site treatment	Industrial/ hospital sources with NO on-site treatment										
	4			4				2	1	2		1	
	3			3				2	1	2		1	
	2			2				2	1	2		1	
1				1				2	1	2		1	

Table 3 Example of an approach for developing a single score which represents the impact of CECs bioavailability within the soil environment

CECs load (concentration) in treated wastewater				**CECs bioavailability/bioaccessibility in the soil**				**CECs availability in the soil due to biosolids/fertiliser application and ploughing**			
CECs concentration in TWW exceeds 10,000 ng/L	CECs concentration range in TWW is 1,000 to 10,000 ng/L	CECs concentration range in TWW is 100 to 1,000 ng/L	CECs concentration in TWW is less than 100 ng/L	Ready movement of CECs within soil and ready availability for uptake	Limited movement of CECs within soil and ready availability for uptake	Ready movement of CECs within soil and limited availability for uptake	Limited movement of CECs within soil and limited availability for uptake	No biosolids/ animal manure application + ploughing	Animal manure (fresh or slurry) only application + ploughing or no ploughing	Biosolids/ composted animal manure application + ploughing	Biosolids/ composted animal manure application + no ploughing
4				4				4			
	3				3				3		
		2				2				2	
			1				1				1

Table 4 Factors influencing the bioavailability of clarithromycin in soil in the example

Influencing factor	**Situation for hypothetical scenario**	**Impact for soil bioavailability/bioaccessibility**
Soil structure	Sandy soil	No inhibition of movement
log K_{ow} for clarithromycin	3.16; indicative of moderate hydrophobicity	Some tendency for clarithromycin to associate with solid as opposed to aqueous phase
log K_{oc} for clarithromycin	2.17; 1.37 (calculated values from EPI suite); indicative of fairly weak sorption to organic soil particles	Limited tendency for clarithromycin to sorb to organic matter associated with soil particles
pK_a for clarithromycin	8.99; compared to soil pH of 7 indicates a tendency for clarithromycin to exist in cationic form	Cationic form of clarithromycin will promote sorption to predominantly negatively charged soil particles.
Biodegradation / volatilisation / photo-degradation	Not expected to readily occur in the soil environment.	Introduced clarithromycin levels in soil expected to be maintained.