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# Assessment of potential risks associated with chemicals in wastewater used for irrigation in arid and semiarid Zones (A review)

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10 Abstract:

11 Irrigation with raw, partially and treated wastewater is a widespread practice in many arid and semi-arid zones. The importance of wastewater for agriculture has 12 13 increasingly been recognised not only as a valuable water resource but also for its 14 nutrient value. However, inappropriate management of irrigation with wastewater can 15 pose substantial risks to public health and the surrounding environment as a result of 16 its microbial and toxic components. In this review, we summarise recent research 17 and provide a broad overview of the potential risks associated with the chemicals in wastewater used for irrigation including their environmental, and health impacts, 18 19 factors that may affect the fate of these chemicals, and available mitigation methods 20 and management options to reduce their impacts. A primary aim of this review is to 21 construct a generalised ranking of the risks from the chemical constituents of 22 wastewater used for irrigation in arid and semi -arid zones.

23

## 24 Keywords: irrigation with wastewater, environmental

- risks, chemical constituents, wastewater
- <sup>26</sup> management, arid zones

## 27 Introduction

Water scarcity is a growing concern especially in many arid and semi-arid zones where the limited natural water resources are heavily exploited. Increasing water scarcity threatens economic development and the sustainability of human livelihoods as well as the environment especially in developing countries (Scott et al., 2004). The challenges posed by water scarcity will become even greater in the future due to population growth, urbanisation, climatic change and the growing food demand which will contribute to increasing the gap between water supply and demand for water(Hussain et al., 2002). It is estimated that around 40% of the global population are currently experiencing water stress (Calzadilla et al., 2011)

37 Globally, agriculture is the largest consumer of water, accounting for approximately 38 70% of all freshwater extraction (Winpenny et al., 2010). Due to growing competition 39 between the agricultural and higher-economic-value urban and industrial uses of 40 freshwater supplies as a result of the increasing demand for water, wastewater has 41 increasingly become the predominant low cost and reliable alternative to 42 conventional irrigation water in many countries especially arid and semi-arid zones 43 (Scott et al., 2004). Currently, reuse of wastewater in urban and peri-urban 44 agriculture is already a widespread practice in different parts of the world (Jiménez et 45 al., 2010, Winpenny et al., 2010). It estimated that at least 10 % of the global 46 population consume foods produced by irrigation with wastewater (WHO, 2006) and 47 more than 20 million hectares are irrigated with untreated, partly treated/diluted or 48 treated wastewater around the world (Jiménez et al., 2010). It also has been 49 reported that approximately 44 countries are reusing over 15 million m<sup>3</sup>/day of 50 reclaimed water for irrigation purposes (Winpenny et al., 2010)

51 To a large extent, wastewater can be considered as a reliable source of water and 52 nutrients that is available all year around. Its availability and nutrient properties are 53 important factors that make it a valuable resource particularly in arid and semi-arid 54 zones (Jiménez et al., 2010, Winpenny et al., 2010). Nevertheless, wastewater is a 55 complex resource and while it may have many benefits, concern regarding the risks 56 to human health and environmental quality as a result of the microbial and toxic 57 components is a serious obstacle for wastewater reuse in agriculture. Most of the 58 existing research has tended to focus on the microbial risks regarding the use of 59 wastewater and guidelines for the safe use of wastewater in agriculture. This may be 60 due to the immediate effects of microbiological components on public health 61 compared to the longer term risks posed by chemical exposure ((WHO, 2006, Bos et 62 al., 2010). Generally, using wastewater in agriculture is unlikely to contribute to direct 63 health impacts from chemicals hazards unless the wastewater is heavily 64 contaminated with discharges from industrial sources. Another explanation may be

65 the difficulty in assessing the health impacts of toxic chemicals in wastewater as it 66 usually has a long latency period (Bos et al., 2010).

67 Inappropriate management of wastewater irrigation can contribute to serious 68 environmental problems especially in arid and semi-arid zones where wastewater could be the predominant water supply for agriculture (Pescod, 1992, Ayers and 69 70 Westcot, 1985, WHO, 2006, Simmons et al., 2010). Wastewater irrigation could lead 71 to negative impacts on soil properties and fertility, crop yields, groundwater and 72 surface water quality, and the aquatic ecosystem. The magnitude of the potential 73 impacts will depend on the concentration of the chemicals, their solubility and 74 inherent toxicity. Other important factors the rate and frequency of wastewater 75 application, the type of crop, and target yields, inhertent soil properties and condition, 76 the vulnerability of the aquifer, climatic conditions, and technology level and the 77 social-economic status of the farmers. In order to ensure good crop yields and 78 minimise the environmental risks associated with the chemical constituents in 79 wastewater, a risk assessment should be carried out and appropriate mitigation 80 measures should be applied. That will require an understanding of the fate, transport 81 and availability of these chemicals within the environment. Most of the environmental 82 studies in last few decades have primarily focussed on the effects and management 83 of salinity and heavy metals although more recently some studies have also 84 addressed the effects of other chemical constituents of wastewater such as 85 emerging contaminants.

This structured review attempts to provide a comprehensive overview of the 86 87 environmental impacts and risks from irrigation with wastewater particularly in arid 88 and semi -arid zones. The main objectives of this review are: (1) provide a review of 89 the chemicals present in raw, partially and treated wastewater used for irrigation, (2) 90 provide a review of the impacts of these chemicals on the environment (soil, plant, 91 water resources) and health from irrigation with wastewater, (3) identify the factors 92 that could influence their fate in the environment (4) review the available mitigation 93 and management options to allow the reuse wastewater for irrigation; (5) rank the 94 risks from these components based on the potential and the significance of their 95 effects on arid and semi- arid zones

## Negative impacts from the chemical constituents in wastewater used for irrigation

Wastewater contains various types and concentrations of contaminants depending on its source and the degree of treatment. In general, the critical water quality problems in relation to the chemical risks from wastewater reuse for irrigation are excessive concentrations of salt, heavy metals, nutrients, toxic organic compounds, and organic matter (WHO, 2006, Toze, 2006a, Qadir and Scott, 2010, Qadir et al., 2015).

The likelihood and magnitude of their negative impacts depends on their concentration, their solubility and inherent toxicity together with rate and frequency of wastewater application, the type of crop, and target yields, inhertent soil properties and condition, the vulnerability of the aquifer, climatic conditions, and technology level and the social-economic status of the farmers. (WHO, 2006). In the following sections, findings relating to each of the five main topic areas are summarised.

#### 110

#### 1.1. Excessive levels of Salt

Wastewater usually has a higher concentration of total dissolved solids and major ions and a higher electrical conductivity than fresh water especially in regions with hot climates due to the long dry season and the high rate of evaporation. These can originate from many sources such as detergents and washing material, the chemicals used during the treatment process and other sources (Toze, 2006a, Qadir and Scott, 2010, Muyen et al., 2011, Becerra-Castro et al., 2015).

117 Conventional wastewater treatment processes are inefficient for the removal of 118 excessive salt and sodium (Bahri, 1998). Generally, salt removal requires advanced 119 treatment such as reverse osmosis or the use of cation exchange resins which are 120 very expensive and may, therefore, be uneconomic for the production of water for 121 irrigation (Qadir and Scott, 2010, Chen et al., 2013a, Toze, 2006a). If excessive salt 122 is not removed, it may result in accumulation in the soil, particularly in the topsoil as 123 a result of high rates of evaporation. It may also lead to elevated levels of 124 exchangeable sodium concentrations and the exchangeable sodium cation (Na<sup>+</sup>) 125 percentage (ESP) (Qadir and Scott, 2010, García and Hernández, 1996, Rietz and 126 Haynes, 2003, Hamilton et al., 2005). For example, a study conducted in Jordan 127 shows that irrigation with wastewater increased soil salinity two to three times 128 compared to a control site (Al-Zu'bi, 2007). It was also found that long-term 129 wastewater irrigation (up to 80 years) in the Valley of Mezquital in Mexico led to 130 increasing soil salinization, and especially Na saturation (Friedel et al., 2000). 131 Another example from arid and semiarid western USA shows that irrigation with 132 recycled wastewater has exhibited 187% higher EC and 481% higher sodium 133 adsorption ratio (SAR) Compared with sites irrigated with fresh water(Qian and 134 Mecham, 2005).

135 It has been estimated that an annual application of 1000 mm of irrigation water with 136 500 mg/l of TDS may lead to an additional 5 tons/ha/year of salt in the soil unless it 137 is properly drained (Muyen et al., 2011). Increased soil EC, exchangeable Na and 138 ESP has significant effects on soil properties and plant growth and can result in a 139 decrease in soil productivity and crop yields. A study conducted in 1993 showed that 140 irrigation with wastewater increases Maize and Sorghum crop yield until the salinity 141 level reached 2330 mg/I TDS) after which the yield slightly decreased (Muyen et al., 142 2011). It may also contribute to groundwater pollution particularly in areas with 143 shallow groundwater (Qadir and Scott, 2010, García and Hernández, 1996, Rietz 144 and Haynes, 2003, Hamilton et al., 2005). Table 1 provides a summary of the main 145 potential effects from the excessive level of salts and sodium in wastewater.

#### 146 **1.1.1. Factors influencing the impacts of salinity and sodicity:**

Salinity and sodicity- related characteristics and impacts are affected by many factors including: the type of salt, the efficiency of leaching and the drainage system, irrigation system type, sensitivity of crops, and soil properties (Ayers and Westcot, 1985, Mohammad and Mazahreh, 2003, Rietz and Haynes, 2003, Chen et al., 2013a, Simmons et al., 2010, Hamilton et al., 2005, Malash et al., 2005, Leal et al., 2009). As a result, the significance of the salinity and sodicity risk will vary greatly under different wastewater irrigation regimes.

The suitability of reusing wastewater for irrigation is not only affected by the quantity of dissolved salts but also by the type of salts that are present (Maas and Grattan, 1999). Generally, wastewater can be classified into saline wastewater that contains excess levels of soluble salts and TDS, sodic wastewater containing excess sodium Na<sup>+</sup>, and saline-sodic wastewater which is characterised by both excessive salt and sodium Na<sup>+</sup>. The type and the degree of the effects will vary depending on the type
of wastewater being reused. (Simmons et al., 2010, Hillel, 2000).

Significant long-term problems of soil salinity and/or sodicity due to the application of saline irrigation water results primarily from poor irrigation management and inadequate soil drainage systems (Simmons et al., 2010, Carr, 2011). This is more pronounced in arid and semi- arid zones where rainfall is low and there are high rates of evaporation meaning accumulated salt ions are rarely removed naturally from soils by leaching or flushing (Emongor and Ramolemana, 2004, Simmons et al., 2010).

168 The type of irrigation system used directly affects both the efficiency of water use 169 and the way salts accumulate. Each irrigation technique has certain advantages and 170 disadvantages and these should be considered in order to improve salinity control 171 (Maas and Grattan, 1999). For example, while sprinkler irrigation can improve salt 172 leaching downwards below the root zone, it can increase the effect of ion toxicity as 173 the salt may accumulate in the leaves of certain sensitive crops. (Hamilton et al., 174 2005, Simmons et al., 2010). Drip systems may be recognised as more efficient 175 when using saline water, however they can lead to salt accumulation between drip 176 points due to radial water movement in the soil (Chen et al., 2010a, Malash et al., 177 2005, Hamilton et al., 2005, Al-Nakshabandi et al., 1997).

178 The toxic effect of excessive salt and major ions on crops depends on the type of 179 crop and the stage of growth (Maas and Grattan, 1999, Hillel, 2000). Some crops are 180 more tolerant to excessive salt than others and in general, salt tolerance can be 181 divided into four classes: sensitive, moderately sensitive, moderately tolerant, and 182 tolerant (Maas and Grattan, 1999, Simmons et al., 2010, Hillel, 2000). Salt sensitivity 183 changes significantly during plant development with most crops being relatively salt 184 tolerant during germination. Substantial evidence indicates that the early seedling 185 period is the most salt- sensitive stage and the plant becomes increasingly tolerant 186 as its growth proceeds. In addition, certain parts of plants uptake salt ions more 187 readily than others, for example, Na<sup>+</sup>and Cl<sup>-</sup> entry into many horticultural crops is 188 easier through the leaves than the roots (Maas and Grattan, 1999, Hamilton et al., 189 2005, Munns and Gilliham, 2015). Soil texture and mineralogy is a dominant factor 190 affecting soil salinity and sodicity. Field investigation shows that salts may be 191 leached downwards more easily in loamy and sandy soils compared to soils with a 192 high clay content as they may be intercepted by clay particles (Chen et al., 2013b). It 193 has also been found that soils that have more clay content are more susceptible to 194 sodic conditions (Qadir and Schubert, 2002, Qian and Mecham, 2005, Leal et al., 195 2009). Organic matter and organic carbon also influence the impacts of excessive 196 salts and sodium. Adding organic matter to soil can enhance the total porosity and 197 subsequently increase the hydraulic conductivity and holding capacity leading to a 198 reduction in the adverse effect of excessive salts particularly when using sodic water 199 (Qadir and Scott, 2010). Increasing soil organic carbon may also lead to more salts 200 being dissolved due to chelation and movement of the salts to lower layers in the soil 201 (Chen et al., 2013b). The electrical conductivity of the soil solution can play an 202 important role in controlling sodicity effects and it has been reported that its effects 203 can be reduced with increased electrical conductivity of soil solution (Qadir and 204 Schubert, 2002, Muyen et al., 2011).

Implication	Compound	Effects	Comment	Reference	
Soil	Salt accumulation in soil (TDS, EC)	Causing salinity problem (lateral drainage is increased, soil erodes more easily, oxygenation limited negative, the effect on microbiological activity, and loss of soil productive capacity and fertility).	Major problem in arid and semi- arid zones as evaporation rate would be higher and accumulated salt is not flushed regularly from the soil profile by rainfall	(Toze, 2006a, Leal et al., 2009, Muyen et al., 2011, Qadir and Scott, 2010, Malash et al., 2005, Hamilton et al., 2005, Qadir and Schubert, 2002, Rietz and Havnes, 2003, Friedel et al.,	
	Excessive exchangeable sodium cation Na <sup>+</sup> concentrations related to magnesium and calcium(SAR), exchangeable sodium percentage (ESP)	Leads to sodicity problems which can cause deterioration of soil structure, clay dispersion with subsequent blocking of pores, negative effects of hydraulic properties such as causing soil impermeability		2000, Sou/Dakouré et al., 2013, García and Hernández, 1996)	
	Excess level of carbonate and bicarbonate	Leads to elevated PH of the soil solution, dissolves Humus and sodium humate precipitates which give the black color for the black alkali soils.			
Plants	Excess salt (salinity) leading to changes in the osmotic pressure in the root zone,	Osmotic effects depress makes the water less available to the plants leading to plant stress and growth reduction		(Muyen et al., 2011, Mohammad and Mazahreh, 2003, Hamilton et al., 2005, Ayers and Westcot, 1985, Pedrero and Alarcon, 2009,	
	Excessive exchangeable sodium cation Na <sup>+</sup> concentrations related to magnesium and calcium(SAR), exchangeable sodium percentage (ESP) (sodicity), Excess level of carbonate and bicarbonate (alkalinity)	Cause photo-toxicity, plants nutrients deficiency (e.g., phosphorus, potassium), and N losses due to NH <sub>3</sub> <sup>+</sup> volatilization, seedling emergence problems, plant root growth restriction and cropping difficulties		Katerji et al., 2003, Garcia and Hernández, 1996, Qadir and Schubert, 2002)	
	Excessive chloride, sodium, and boron	Specific ion toxicity			
Groundwater	Salts and ions leach each to groundwater	Water quality deterioration	TDS>500 Cause flavor but do not affect human health; High level of TDS can cause	(Toze, 2006a, Yu et al., 2012, Kass et al., 2005, Hamilton et al., 2005, WHO,	
Surface water	Salts and irons reach surface water via drainage systems or soil erosion	Water quality deterioration	<ul> <li>corrosion of water distribution equipment.</li> </ul>	2006)	

#### 205 Table 1 The effects of excessive concentrations of salts and major ions in wastewater used for irrigation

Very high concentration may limit its use
Boron which is not removed by treatment, absorbed by plants or wholly retained in the soil can be toxic. Accumulation in water bodies limits their use in agriculture

#### 206 **1.1.2. Salinity and sodicity management options:**

207 Removing salts from wastewater for irrigation purposes is prohibitively expensive. 208 Therefore, there is a need for specific measures and management strategies to 209 prevent and control the effects of salinity and sodicity during irrigation with 210 wastewater.

211 One important option for salinity control is regular application of effective leaching of 212 water to transfer solutes through the soil profile and ensure the leaching of excess 213 salt below the root zone (Carr, 2011, Maas and Grattan, 1999, Letey et al., 2011, 214 Hillel, 2000). To achieve leaching requirements, an adequate soil drainage system is 215 an essential prerequisite. This can be facilitated through natural drainage if the soil 216 has sufficient storage capacity or permeable subsurface layers, or via artificial 217 drainage systems. In addition to soil drainage, adequate groundwater depth and land 218 levelling are also important components to control salinity in the root zone (Simmons 219 et al., 2010).

220 Crop selection was found to be the principal factor for the sustainability of 221 wastewater irrigation since certain crops can be irrigated with wastewater without 222 any negative impact on yield. A number of field crops, fruit trees, forage grasses and 223 others have been identified in the literature to suit various salt-affected environments 224 (Simmons et al., 2010, Avers and Westcot, 1985, Maas and Grattan, 1999, Grattan 225 et al., 2004). As it was mentioned earlier, salt tolerance can be divided into four 226 classes including those that are sensitive (Sesame, Carrot, Onion, Almond and 227 apple), moderately sensitive (Corn, Peanut, Alfalfa, Tomato, Cucumber and Grape), 228 moderately tolerant (Sorghum, Soybean, Wheat, Squash, Fig and Olive and tolerant 229 (Barley, Cotton, Oat, Date palm and Currant) (Maas and Grattan, 1999). Crop choice 230 will depend on soil conditions, water quality and climate. Suitable crops should also 231 demonstrate the following characteristics: (i) high water and N demand, and 232 tolerance to salinity; (ii) good potential end use; (iii) marketable (da Fonseca et al., 233 2007).

Another management option to mitigate the salinity impact of wastewater irrigation is the use of the wastewater in conjunction with fresh water, if available, via blending or alternating approaches which provide more flexibility to suit different situations (Ayers and Westcot, 1985, Malash et al., 2005, Yu et al., 2012). Different field 238 studies have evaluated various aspects of these approaches and one study 239 suggested that the optimum ratio of mixing fresh water to wastewater is between 2:1 240 and 1:2 for plant growth (Yu et al., 2012). Another study carried out by Malash et al. 241 (2005) found that a mixed management strategy with a 60% fresh water 40% saline 242 water ratio in combination with a drip irrigation system gave the highest values of 243 yield and growth in tomato production. An alternating strategy of fresh and saline 244 water can also provide many advantages including the ability to grow a broad range 245 of crops, flexibility to use conventional irrigation methods and control of soil salinity in 246 topsoil during seeding stage to a lower level over time.

Since most crops are sensitive during their seeding stage especially grains (Barley, Wheat and Rice) Sesbania, Cotton, tomato, Corn, and sugar beets (Hanson et al., 1999); it may be possible to reduce the effects of salinity by using modifications of planting practice to minimise salt accumulation around the seeds. This may include sowing near the bottom of the sloping sides of furrows; increased plant density (the seedling rate per unit area) which could compensate for reduced germination; and growing seedlings with fresh water (Minhas, 1996, Ayers and Westcot, 1985).

254 The application method could also directly affect the efficiency of water use and the 255 way salts accumulate in the soil profile. Some methods are more suitable for use 256 with saline water than others. Several parameters in relation to risk reduction could 257 be used to choose the most suitable method including leaf damage, salt 258 accumulation in the root zone, ability to maintain high soil water potential and ability 259 to handle saline water without significant yield loss. Each irrigation method has a 260 combination of impacts on these parameters, which should be considered before any 261 attempt to improve salinity and sodicity control by changing the irrigation method is 262 undertaken (Maas and Grattan, 1999, Hillel, 2000, Pescod, 1992). In the case of 263 sodicity problems, soil treatment is a particularly useful option to mitigate the effect of 264 soil sodicity. Mitigating the effect of excess sodium on soil and crops can be 265 achieved through improving soil physical properties and infiltration rate by adding 266 chemical amendments such as gypsum (Simmons et al., 2010, Ayers and Westcot, 267 1985, Hillel, 2000). Leaving plant residues or adding organic matter to the field can 268 also enhance the physical and chemical condition of soils irrigated with sodic water 269 (Simmons et al., 2010).

Where available, water with a high electrical conductivity and an adequate proportion of divalent cations (mainly calcium) could also be used to improve sodic and salinesodic water without the need for a calcium-supplying amendment (Simmons et al., 273 2010)

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#### 1.2. Metalloids and heavy metals:

Typically, municipal wastewater has lower concentrations of inorganic chemicals compared to industrial effluents, and usually conventional treatment processes are capable of significantly reducing their concentration as most will accumulate in the sludge (bio-solid) (Hamilton et al., 2007, Chen et al., 2013a, Toze, 2006a).

279 In general, the risk from inorganic chemicals particularly heavy metals present in 280 wastewater is higher when industrial wastewater is mixed with municipal wastewater, 281 a common condition in developing countries where industrialisation is accelerating 282 and mixed wastewater is used untreated or partially treated (WHO, 2006). Where 283 industrial effluent is used the heavy metal concentration in plant tissues were 284 reportedly higher than permissible limits even when water and soil samples comply 285 with established safe standards (Chen et al., 2013b, Khan et al., 2008). Table 4 286 illustrates the main potential effects from heavy metals in irrigation with wastewater.

287 Many metals pose little hazard to humans through contamination of the food chain 288 due to the fact that they pose significant photo-toxic effects in low concentrations 289 which are not toxic to humans and therefore inhibit plant growth. Generally, cadmium 290 is the major relevant heavy metal which presents a risk to human health due to its 291 high mobility and also the fact that it is bio-available to plants at very low 292 concentrations that are not photo-toxic but could pose a health risk to human 293 (Hamilton et al., 2007, WHO, 2006, Chen et al., 2013c, Khan et al., 2013). Based on 294 many studies carried out in Southeast Asian countries such as Pakistan, India, and 295 China, where industrial effluent with sewage (diluted or untreated) is widely used for 296 irrigation, found that cadmium followed by Lead were the major metals which pose a 297 risk to health (Khan et al., 2013, Tiwari et al., 2011, Khan et al., 2008, Singh et al., 298 2010, Lu et al., 2014, Verma et al., 2015, Gupta et al., 2008). In most of these case 299 studies the concentration of cadmium and lead exceeded the permissible limits for 300 heavy metals in irrigation water, i.e. WHO/FAO standards 0.01 and 5.0 gm/L for Cd and Pb respectively (Khan et al., 2013, Tiwari et al., 2011, Verma et al., 2015, Guptaet al., 2008)

303 **1.2.1. Factors influencing the impacts of heavy metals:** 

304 The magnitude of the risk from heavy metal in wastewater depends largely on the 305 type of effluent. Typically, most domestic treated or partially treated wastewater has 306 low levels of trace elements and usually within the permissible limits for irrigation 307 water quality (Klay et al., 2010, Al Omron et al., 2012, Mohammad Rusan et al., 308 2007). Table 2 provide a summary of the average metal concentration in treated wastewater effluents used for irrigation in different countries. Many studies have 309 310 estimated that domestic treated or partially treated wastewater can be used safely 311 for up to a century without any negative effects to crops, groundwater or the food 312 chain (Chen et al., 2013c, Smith et al., 1996, Tarchouna Gharbi et al., 2010).

Table 2 Average metal concentrations in treated wastewater effluents used for
 irrigation in different countries

Metal	Tunisia <sup>1</sup>	Jordan <sup>2</sup>	Spain <sup>3</sup>	Saudi Arabia <sup>4</sup>	RMC <sup>a 5</sup>
Cd	0.005	0.02	0.03	0.0006	0.01
Со	0.019	-C	-	0.0005	0.05
Cr	0.016	-	0.02	0.037	0.1
Cu	0.017	0.01	0.02	0.014	0.2
Pb	0.044	0.77	0.02	0.0048	5
Zn	0.36	0.19	0.11	0.0055	2
Ni	0.034	-	0.12	0.0044	0.2
Mn	0.054	-	0.03	0.0055	0.2

a) RMC=Recommended maximum concentrations for crops production; b) not available; c) ND=not detected

 316
 Sources: 1.(Bahri, 1998)2(Mohammad Rusan et al., 2007)., 3(Pedrero and Alarcon, 2009) 4.(Al Omron et al., 2012) 5.(Pescod, 1992, WHO, 2006),

The major concern with regard to the potential effects of heavy metals on agricultural

319 production and human health would be related to the use of untreated wastewater or

320 the use of biosolids as fertilizers (Hamilton et al., 2007). Moreover, heavy metals

would be a critical issue when industrial wastewater is used or blended with
domestic wastewater and used for irrigation (Mapanda et al., 2005, Chen et al.,
2013a, Toze, 2006a). Long-term reuse of wastewater containing industrial discharge
leads to accumulation of heavy metals in both soil and plants (Liang et al., 2011).

325 The period over which the application of wastewater containing heavy metals takes 326 place has also has an impact on the change of heavy metal concentrations irrigated 327 soils. Many studies show that heavy metal accumulation starts to occur after 5 to 8 328 years of application (Xu et al., 2010, Rattan et al., 2005). The process of 329 accumulation of metals in soils can take a long time (e.g. several decades to a 330 century) before causing any negative effects to crops, groundwater or risks to human 331 health. (Klay et al., 2010, Siebe and Fischer, 1996, Zhang et al., 2008). However, 332 eventually, it may lead to increase the concentration of metals in soils to levels 333 beyond soil capacity and subsequently increasing their mobility and plant uptake 334 (Sridhara Chary et al., 2008, Friedel et al., 2000).

335 Another factor that could affect metal accumulation and plant uptake is soil 336 properties since some soils have a high capacity to absorb and retain heavy metals. 337 In such soils, wastewater with an average metals concentration may be applied to 338 land for several decades without fully exhausting the soil capacity (Hamilton et al., 339 2007, da Fonseca et al., 2007). However, when the capacity of the soil to retain 340 heavy metals is reduced as a result of continuous application of wastewater or a 341 change in soil PH, the metals enter a mobile phase, and may be released to 342 groundwater or to be available for plant uptake (Kumar Sharma et al., 2007, 343 Mapanda et al., 2005)

344 Metal mobility and bioavailability in the soil will vary considerably with soil properties 345 for similar total soil metal concentrations (Hamilton et al., 2007). Mobility and 346 bioavailability is a function of the amount of organic matter, clay minerals such as 347 montmorillonite in soils (Usman et al., 2005, Olaniran et al., 2013), CaCO<sub>3</sub> content 348 (Avci and Deveci, 2013), and soil pH (WHO, 2006, Mapanda et al., 2005, Sridhara 349 Chary et al., 2008, Friedel et al., 2000, Siebe and Fischer, 1996, Kiziloglul et al., 350 2007). It has been found that alkaline soils (pH >6.5) or/and high levels of organic 351 matter combined with clay contribute to decreasing the mobilisation of heavy metals 352 consequently reducing their availability for plant uptake or leaching. Soil CaCO<sub>3</sub> has also been found to increase the retention capacity for metals in soils (Brar et al.,
2000, Mapanda et al., 2005, Friedel et al., 2000, Siebe and Fischer, 1996).

Soil pH has great influence on mobility and bioavailability of heavy metals and in general metals are more available to plants from acidic soils than from neutral or alkaline soils (WHO2006). Soil pH changes depending on the pH of the irrigation water and consequently the application of wastewater with a low PH could lead to decreased soil pH and this in turn could cause an increase in the mobility of heavy metal which would then become available for plant uptake or leaching to lower soil layers (Xu et al., 2010)

Since soil organic matter has the capacity to form stable complexes with metal ions, it will affect their solubility and bioavailability in soils (da Fonseca et al., 2007, Klay et al., 2010). If the organic matter is in the solid form it will improve the heavy metal adsorption capacities of soils. However on the other hand, dissolved organic components enhance the solubility of metals thereby increasing their mobility and bioavailability particularly at low loading rates (Klay et al., 2010, Siebe and Fischer, 1996).

The rate at which heavy metals accumulate in plants depends on the plant species. The efficiency of metal absorption can be facilitated by either plant uptake or the soil-plant transfer factor of metals (Khan et al., 2008). Many studies have found that leafy vegetables such as spinach, mint, and coriander tend to accumulate more heavy metals in their edible parts compared to non-leafy vegetables such as root crops (carrot, garlic), grains (wheat and corn) and fruits (tomato) (Khan et al., 2013, Avci and Deveci, 2013, Ghosh et al., 2012, Simmons et al., 2010).

376 Furthermore, heavy metal concentrations in the different parts of the plant will also 377 vary. Usually plants accumulate metals more readily in their roots compared to other 378 parts of the plant such as the leaves, fruits, and seeds. As a result, the roots act as a 379 barrier against heavy metals translocation. In general, heavy metal concentrations in 380 different portions of plants follow the order of root>stem>leaves>fruits> seeds 381 (Liang et al., 2011, Ghosh et al., 2012, Keser, 2013, Mireles et al., 2004). Table 3 provides heavy metals concentration in edible parts of some crops found in the 382 383 literature.

Table 3 Heavy metal concentrations (mg/kg dry weight) in the edible portions of food crops grown in
 wastewater-irrigated soil, and selected regulatory limits.

Crops	Statistics	Cr	Ni	Pb	Cd	References
Coriander	Range	1.29-9.47 1.02-	2.95-5.89 0.12-0.60	21.04 - 53.15	3.38-4.39 0.17-1.03	(Khan et al., 2013)
		3.11		NA <sup>*</sup>		(Ghosh et al., 2012)
Spinach	Range	3.30-7.75	3.79-5.05	19.19- 25.10	1.83-4.48	(Khan et al., 2013)
		0.11-0.35	0.35-1.79	NA	0.34-2.06	(Ghosh et al., 2012)
Mint	Range	1.72-5.15	3.0-4.62	20.3-55.36	3.10-7.67	(Khan et al., 2013)
		2.60-5.50	3.00-6.70	0.40-1.90	0.02-0.05	(Avci and Deveci, 2013)
Onion	Range	1.29-5.59	3.79-7.16	33.59- 52.78	3.48-3.93	(Khan et al., 2013)
Garlic	Range	2.15-3.01	3.36-6.73	24.36- 33.39	2.29-3.48	(Khan et al., 2013)
Carrot	Range	0.86-5.59	2.95-6.31	23.99-	2.28-2.84	(Khan et al., 2013)
		0.34-1.04	0.24-1.19	NA	0.085-0.52	(Ghosh et al., 2012)
Radish	Range	0.86-3.44	2.95-7.16	28.42-	2.47-3.02	(Khan et al., 2013)
		0.45-1.38	0.41-2.09	NA	0.24-1.44	(Ghosh et al., 2012)
Okra	Range	1.29-5.59	2.53-5.89	23.99- 47.61	1.74-2.38	(Khan et al., 2013)
Tomato	Range	0.86-2.15	3.37 -6.31	29.89-	1.83-2.75	(Khan et al., 2013)
		1.02-3.11	0.29-1.49	NA	0.085-0.52	(Ghosh et al.,
		2.00-4.20	1.80-6.10	0.10-0.70	0.02-0.53	2012) (Avci and Deveci,
Eggplant	Range	2.60-5.50	0.6-2.70	0.30-4.50	0.01-0.34	(Avci and Deveci,
Wheat	Range	1.72-3.87	2.10-3.79	22.51- 37.65	1.00-1.65	(Khan et al., 2013)
Corn	Range	2.00 - 3.40	0.60-3.50	0.20-3.50	<0.01	(Avci and Deveci, 2013)
FAO/WHO limits 2002	-	-	0.20	0.5-0.10	0.02-0.20	(Avci and Deveci, 2013)

386 \*NA: not available

#### 387 **1.2.2. Heavy metal management options:**

Although wastewater treatment is the best choice in managing wastewater in agriculture biological treatments are generally designed to remove organic compounds and microorganisms and therefore the removal of heavy metal by biological treatment may be regarded as a side benefit (Chipasa, 2003). The 392 efficiency of metal removal by biological treatment processes will vary depending on 393 the types of metals which are present and their concentration. Physical, chemical 394 and biological factors will also affect the outcome, for example, heavy metal removal 395 from activated sludge depends on pH and dissolved organic matter and an increase 396 in pH will increase the removal as metals precipitate as hydroxides (Chipasa, 2003). 397 High concentrations of heavy metals can be toxic to microorganisms and reduce 398 microbial activity resulting in an adverse effect on biological treatment processes 399 (Chipasa, 2003). In recent years, various treatment technologies for heavy metal 400 removal from sewage, industrial and mining waste effluents have been extensively 401 include chemical precipitation, studied. These technologies ion-exchange, 402 adsorption, coagulation, cementation, electrochemical treatment technologies, 403 membrane filtration and reverse osmosis (Fu and Wang, 2011). Each of these 404 methods offers many advantages and also limitations for their use for the removal of 405 heavy metals from wastewater. For instance, chemical precipitation has traditionally 406 been used for metal removal from aqueous solutions due to its simplicity and low 407 capital and operational costs, however, its efficiency can be affected by pH and the 408 presence of another ions, it is also ineffective when metal concentration is very low 409 (Fu and Wang, 2011, Baysal et al., 2013). Ion exchange, membrane filtration, and 410 adsorption are alternative methods which have been wildly studied for heavy metal 411 removal. Ion exchange has successfully been used to remove heavy metals from 412 wastewater. Membrane filtration and adsorption have a high efficiency for the 413 removal of heavy metals from wastewaters with low concentrations of heavy metal. 414 However, these technologies have high capital and operational costs which limit their 415 use especially on a large scale (Fu and Wang, 2011, Baysal et al., 2013).

The selection of the most suitable treatment method will depend on many factors including the metal concentration, other wastewater components, plant flexibility and reliability, capital investment and operational cost, and environmental impact.

419 Tabl	e 4 the effects of metalloids and hea	avy metals in irrigation with wastewater			
Implication	compound	effects	Comment		
Soil	Aluminum and Iron	Aluminum blocks productivity in acid soils as a result of reducing nutrient mobility especially phosphorus Iron can contribute to acidification and reduce phosphorus mobility	In alkaline soils with pH >7 the impact of aluminum is negligible due to ion precipitation.	(Simmons et al., 2010, Mapanda et al., 2005, WHO, 2006, Zhang et al., 2008)	
		Depending on pH, organic matter and metals content, metal can bind to soil particles and accumulate or mobilize into groundwater	Particularly in rapidly industrializing regions where industrial wastewater is mixed with domestic wastewater		
	High concentration of heavy metal	Once accumulated in soil removal can be difficult. Contamination can endure for hundreds of years due to long biological half-life.			
		Negative impact on soil microbial biomass, microbial structure, microbial diversity, and bacterial abundance after long-term exposure			
Plants:				(Hamilton et al., 2005,	
	Aluminum and iron	Could be toxic and also cause Phosphorus deficiencies depending on type of soil and pH,		vv FTO, 2006)	
	Arsenic, mercury, lead	As strongly adsorbed by soil only can be uptake by plant root but not translocation to shoots Generally phytotoxic at high concentration	Arsenic toxicity range from 12 mg/l to less than 0.05mg/l, mercury and lead not phytotoxic except at very high concentration,	(Sridhara Chary et al., 2008, Hamilton et al., 2005)	
	copper, manganese, nickel, zinc	Less strongly adsorbed by soil, readily taken up by plants. Phytotoxic to plants at concentration before the concentration to be toxic to human. pose little risk to human health	Toxicity to plant reduce in neutral or alkaline PH, soil plants barrier protects food chain from these elements	(Hamilton et al., 2005, WHO, 2006, Sridhara Chary et al., 2008)	
			Copper could be harmful to animals at low concentration to visibly affect plants		
	Cadmium, cobalt, selenium, molybdenum	Bioaccumulation in plants tissue. Generally, not phytotoxic to plants and pose risk to animal and human health	Cobalt tends to be inactive in neutral and alkaline soils	(Hamilton et al., 2005, WHO, 2006)	

Ground Water	Leach form acid soil and /or highly permeable and shallow water table conditions	Contaminate water and pose risk to human health if it used for drinking purpose.		(Gwenzi and Munondo, 2008, WHO, 2006)
			Particularly cadmium, lead, and mercury	
Surface water	If metals became mobile can reach surface water through runoff or drainage systems	Contaminate water and pose risk to aquatic life and can reach to human via food chine	-	

In the absence of treatment options to remove heavy metals from wastewater, other management measures at farm level could be very useful to reduce heavy metal transfer into the food chain. However, these measures may be more effective on soils with low or medium levels of contamination. Each of them has advantages and drawbacks and the effectiveness of using one or combinations of these measures will depend on the specific site conditions. One of the most effective options are plant-based treatment and soil based treatment

427 Plant based treatment includes growing of photo-remediation crops, growing 428 industrial crops and selecting crops with low metals uptake. Certain plant species 429 can be used to absorb and uptake trace elements from soil to above-ground 430 biomass. These plants are known as hyper-accumulators and have the ability to 431 accumulate high concentrations of metals up to 100 time greater compared to other 432 non-accumulator plants grown in the same contaminated soil (Chaney et al., 2007). 433 Currently, there are around 400 species categorized as hyper-accumulators of 434 metals such as Thlaspi caerulescens, Thlaspi caerulescens, Aeolanthus 435 biformifolius, and Alyxia rubricaulis (Cobbett, 2003, Chaney et al., 2007)

The cultivation of industrial plants including fibre plants (flax, cotton etc.) and energy crops (Salix trees and reed canary grass) has been considered as a valuable option for agricultural use in areas where soils are impacted by heavy metals (Puschenreiter et al., 2005). In addition to industrial plants, aromatic crops could be grown on heavy-metals enriched soil without causing any significant risk of metals transfer from soil to oil and alteration in essential oil composition (Lal et al., 2013).

442 Selecting crops with low metals uptake could also be a very useful option to reduce 443 any potential health risks via the food chain. Some crops such as leafy vegetables 444 accumulate certain metals in their edible parts in greater amounts than non-leafy 445 crops. Metals usually accumulate in leaves and roots more so than in the seeds and 446 fruits, suggesting that legumes such as peas, and grains may be more appropriate 447 crops than vegetables such as cauliflower, lettuce, spinach and carrots where heavy 448 metals are present. In addition, fodder crops may be preferred since they pose a 449 lower risk to human health as the process of transfer of metals via the food chain will 450 be longer (Puschenreiter et al., 2005, Simmons et al., 2010).

451 Soil amendment is another farm based measure that could mitigate against pant 452 uptake of heavy metals. Soil amendment can be classified into organic and inorganic 453 amendment. Organic amendments such as farmyard manure (FYM), compost, 454 biosolids or biosolid compost could effectively decrease the mobility and 455 bioavailability of heavy metals in soils as a result of its high content of organic 456 matter and high concentrations of P and Fe (Puschenreiter et al., 2005, Bolan et al., 457 2003). Inorganic amendments such as gypsum, lime CaCO<sub>3</sub>, synthetic zeolites, 458 phosphate material, Mn and Fe oxides and clay minerals are very effective in 459 reducing metal mobility and bioavailability due to pH effects and the introduction of 460 additional binding sites for heavy metals (Chen et al., 2003, Brown et al., 2004, Oste 461 et al., 2002, Puschenreiter et al., 2005, Hettiarachchi and Pierzynski, 2002). Many of 462 these amendments are by-products of industrial activities which are available in large 463 amounts and are relatively inexpensive (Puschenreiter et al., 2005).

464 **1.3. Nutrients** 

Wastewater commonly contains high concentrations of nutrients in the form of nitrogen, phosphorus and potassium, although concentrations will vary significantly, depending on whether untreated, diluted or treated wastewater is used. Table 5 provides a summary of the typical nutrient concentration ranges in untreated wastewater and in treated effluent from secondary and advanced tertiary processes

470

Constituent (mg/L)	Untreated Wastewater	Conventional activated sludge <sup>a</sup>	Activated sludge with BNR <sup>b</sup>	Activated sludge with BNR, microfiltration, and Reverse osmosis <sup>c</sup>
Total nitrogen	35-60	15-35	3-8	≤1
Ammonia –N	20-45	1-10	1-3	≤0.1
NO <sub>3</sub> –N	0-trace	10-30	2-8	≤ 1
Total Phosphorus	4-15	4-10	1-2	≤0.5

471 <u>Table 5 Typical nutrient concentration ranges in untreated and treated effluent</u>

472 473 474

a. Secondary treatment: activated sludge including a nitrification step

b. Tertiary treatment: activated sludge and biological nutrient removal of nitrogen and phosphorus

C. Tertiary treatment: activated sludge and biological nutrient removal combined with advanced treatment

475 Sources: (Sperling and de Lemos Chernicharo, 2005)and (Carey and Migliaccio, 2009)

Although the nutrient supply capacity is considered to be one of drivers for
wastewater use in agriculture, nutrients contained in wastewater can reach levels
which are excessive. This could result in possible negative effects of oversupply of

479 nutrients especially nitrogen and phosphorus. Oversupply of nitrogen through 480 irrigation with wastewater could lead to excessive vegetative growth, delay in 481 maturity and reduced crop size and quality which will result in low economic yield 482 (WHO, 2006, Hamilton et al., 2005, Qadir and Scott, 2010, Chen et al., 2013a) . 483 Nitrate leaching is another concern associated with nitrogen in wastewater which 484 may lead to contamination of groundwater causing health problems including 485 methaemoglobinemia in neonates (WHO, 2006, Hamilton et al., 2005, da Fonseca et 486 al., 2007, Gwenzi and Munondo, 2008, Knobeloch et al., 2000, Candela et al., 2007). 487 Furthermore, excessive nitrogen and phosphorous in irrigation water may impact soil 488 microbial communities, in particular the microbial activities associated with cycling 489 these elements (Becerra-Castro et al., 2015). The excess of nutrients can disturb the 490 autochthonous soil microbial communities, for example the accumulation of 491 inorganic-N (NO<sub>3</sub>-N and NH<sub>4</sub><sup>+</sup>-N) in soils could affect the microbial catabolic activity, 492 especially the biodegradation of recalcitrant carbon compounds that are present in 493 soil (DeForest et al., 2004, Ramirez et al., 2012). Both N (in the form of NO<sub>3</sub>-N) and 494 P can reach surface water via drainage systems or soil erosion and cause 495 eutrophication or toxicity in other habitats (Hamilton et al., 2005, WHO, 2006, Wu, 496 1999). Table 6 illustrates the potential effects of excessive nutrients.

497

#### 498 **1.3.1. Nitrogen**:

The amount of nitrogen taken up by the plant, leached to groundwater, or lost via soil erosion and volatilization depends on the nitrogen concentration in the effluent and the soil, the type of soil, crop demand, soil permeability, irrigation rate and the vulnerability of the aquifer. Nitrogen supplied via irrigation is removed primarily through nitrification and subsequent ready uptake by plants as ammonium NH<sub>4</sub>+-N and nitrate NO<sub>3</sub>-N. However when they are applied in excessive amounts they can affect the quality of crops (Chen et al., 2013a).

506 The concentration of ammonium NH<sub>4</sub><sup>+</sup> in treated wastewater is normally greater than 507 nitrate and it usually binds to soil particles and is not leached. However it can easily 508 be converted to nitrate via nitrification by soil bacteria, Nitrates are highly dissolved 509 in the soil solution and they can easily be moved through wastewater irrigated soils 510 especially highly permeable soils (Qadir and Scott, 2010). When they are applied in 511 levels in excess of plant requirements there may be a risk of leaching into 512 groundwater (da Fonseca et al., 2007).

#### 513 **1.3.2.** Phosphorus:

Normally wastewater contains low concentrations of phosphorus. Phosphorus is stable in soils and is therefore considered beneficial with no negative impacts on the environment. This is the case even if wastewater effluents with high concentrations of phosphorus are applied over long periods of time (WHO, 2006). However, because phosphorus accumulates at or near the soil surface over the time, it can reach surface water through soil erosion and runoff contributing to eutrophication. (WHO, 2006, Qadir and Scott, 2010, Wu, 1999)

#### 521 **1.3.3. Potassium**:

522 Potassium is not bioavailable from the soil as it is bound to other compounds and 523 therefore, it usually needs to be added to the soil as fertiliser. In general, wastewater 524 contains low levels of potassium and normally this is not sufficient to meet crops 525 requirement, Therefore the use of wastewater for irrigation does not usually pose 526 any risk to the environment associated with the presence of potassium (Emongor 527 and Ramolemana, 2004, WHO, 2006)

#### 528

#### 1.3.4. Nutrient management options:

529 Wastewater treatment plants typically provide various physical, chemical, and 530 biological methods to improve effluent quality however nutrient removal from 531 wastewater requires tertiary treatment and infrastructure that may be economically 532 prohibitive (Carey and Migliaccio, 2009). An alternative approach that can also be 533 used to remove excess nutrient from irrigation wastewater is to place on farm 534 treatment options that work as effective sinks for nutrients such as the use of 535 wetlands or duckweed ponds (Simmons et al., 2010, WHO, 2006, Qadir et al., 2015).

536 Excessive addition of nutrients particularly N could be avoided by selecting crops 537 that can take advantage of high concentrations of nutrients such as fodder grass 538 (Simmons et al., 2010) or utilising the practice of crop rotation to enable the removal 539 of any excess nutrients (Hamilton et al., 2005). Hamilton et al. (2005) and Snow et 540 al (1998,1999) claim that the risk of nitrate leaching to groundwater could be 541 significantly reduced by appropriate matching of crops and plant production systems

- 542 to climate and effluent characteristics. For instance, in arid zones high yielding crops 543 with large concentrations of nitrogen in their biomass (such as leafy vegetable and 544 fodder grass) are likely to be more effective than tree plantations for decreasing 545 nitrate leaching (Simmons et al., 2010, Hamilton et al., 2005).
- 546 Similar to salinity over fertilisation from wastewater application could be reduced by
- 547 using wastewater blended with fresh water or water with low nutrient concentrations.
- 548 However, this option would only be possible when fresh water is available (Hamilton
- 549 et al., 2005, Simmons et al., 2010, WHO, 2006, Qadir et al., 2015).

### 550 Table 6 The effects from nutrients contents in irrigation with wastewater

Implication	compound	Negative effects	Comment	References
Soil	Excessive level of nutrients	Disturbance of soil microbial communities, and Microbial catabolic activity		(DeForest et al., 2004, Ramirez et al., 2012)
Plants	Excessive level of nitrogen	Excessive vegetative growth Delay in maturity Reducing crop size and quality, Low economic yield	Forage being the main food for cattle can cause grass tetany caused by imbalance of nitrogen, potassium and magnesium in pasture grasses	(WHO, 2006, Hamilton et al., 2005, Qadir and Scott, 2010, Chen et al., 2013a)
	Excessive level of phosphorus	No effect		
Ground water	High level of nitrate (N-NO <sub>3)</sub>	Leaching of N particularly NO <sub>3</sub> could lead to contaminate groundwater and causing health problems mainly methaemoglobinemia problems	Nitrogen stable in ground water and can accumulate because of the reduction of microbial activities caused by limited carbon sources.	(WHO, 2006, Hamilton et al., 2005, da Fonseca et al., 2007, Gwenzi and Munondo, 2008, Knobeloch et al., 2000)
Surface water	Excessive level of nitrogen and phosphorus	Eutrophication	Particularly in arid and semi-arid zones	(Hamilton et al., 2005, WHO, 2006, Wu, 1999, Carey and Migliaccio, 2009)

#### **1.4.** Toxic organic compounds and emerging contaminants

552 Wastewater contains a wide variety of toxic organic compounds including priority 553 organic pollutants such as pesticides (DDT, 2,4-D, Aldrin), industrial compounds 554 (phthalates PCBs, non -ionic detergents), disinfection by-products, synthetic and 555 natural hormones, Pharmaceuticals and Personal Care Products (PPCPs) (WHO, 556 2006, Onesios et al., 2009, Bolong et al., 2009, Muñoz et al., 2009, Cizmas et al., 557 2015). Many of them can be difficult to detect due to the lack of suitable analysis 558 techniques that are able to directly detect them in low concentrations, Furthermore, 559 they vary considerably in their form and their mechanism of actions which makes the 560 identification and evaluation of these compounds a unique challenge (Bolong et al., 561 2009). These toxic pollutants may have carcinogenic, teratogenic and mutagenic 562 effects. In addition, many of them are Endocrine Disrupters Chemicals (EDCs) which 563 means that they may interfere with hormone functions in animals and humans. 564 (WHO, 2006, Qadir and Scott, 2010, Bolong et al., 2009, Cizmas et al., 2015, Wu et 565 al., 2015). Although direct evidence of negative human health effects are still being 566 debated (Bolong et al., 2009, WHO, 2006, Toze, 2006a, Onesios et al., 2009, 567 Bergman et al., 2013), relationships have been identified between endocrine 568 disruptors and increased incidences of endocrine-related cancers such as breast, 569 ovarian, prostate, testicular and thyroid cancer (Cizmas et al., 2015, Bergman et al., 570 2013). Abnormalities, altered immune function and population disruption due to 571 exposure to these pollutants have also been observed in birds, reptiles, mammals, 572 amphibians and invertebrates (WHO, 2006, Colborn et al., 1993, Bergman et al., 573 2013).

574 Many EDCs, and PPCPs could persist in the environment and may accumulate in 575 irrigated soils or eventually reach surface water or groundwater leading to human 576 exposure through drinking water (WHO, 2006, Chen et al., 2013a, Chen et al., 577 2011). From the data available in the literature, soil systems are better equipped 578 than water courses for the degradation of many of these compounds, with 579 mechanisms including microbial degradation or adsorption by soil organic matter 580 (Qadir and Scott, 2010, Chen et al., 2011, Dalkmann et al., 2014, Qin et al., 2015). 581 However, it is still possible that some of them such as PPCPS may be taken up by 582 crops or transferred to the edible surface of crops as a result of irrigation with 583 wastewater or soil that remains on the surface of crops after harvesting (WHO, 2006, 584 Wu et al., 2015). Most of the studies on pant uptake of PPCPs were conducted in 585 greenhouses or the laboratory and data on the accumulation of these chemicals in 586 crops irrigated with wastewater under realistic conditions is limited (Wu et al., 2015). 587 However, research findings reported to date would suggest that the potential for 588 these substances to enter edible parts of crops was low under normal field 589 conditions (Wu et al., 2015, Prosser and Sibley, 2015). The literature also suggested 590 that their effects on the quality of crops could be negligible (Chen et al., 2011, Wu et 591 al., 2015). The major concerns related to PPCPs are the potential development of 592 antibiotic resistance in soil and water microorganisms as result of discharging 593 antibiotics into the environment (Toze, 2006a, Chen et al., 2011, Cizmas et al., 594 2015). The potential environmental effects of these toxic pollutants as result of 595 irrigation with wastewater is summarised in Table 7.

596 Currently, considerable uncertainty exists regarding the potential risks of PPCPs and 597 their transformation products to agricultural and environmental health.(Qin et al., 598 2015, Bergman et al., 2013). Although the presence of these substances in the 599 environment and their potential ecological effects are generally alarming, their 600 concentration in water sources and other environmental receptors to date are very 601 low (Qadir and Scott, 2010), in addition, many of these chemicals have potential 602 short environmental half-lives (Toze, 2006a, Chen et al., 2011).

603

#### 1.4.1. Management options:

604 Many of the EDCs and PCPs tend to be resistant to conventional and even 605 advanced wastewater treatment (WHO, 2006, Bolong et al., 2009, Fang et al., 2012, 606 Wang et al., 2005). Certainly existing wastewater treatment plants have not been 607 designed for the removal of these pollutants and even if the best available treatment 608 technology is adopted, only a part of a wide range of emerging contaminants can be 609 removed especially by biological treatment (Luo et al., 2014). The reasons for this 610 are numerous and include the fact that these pollutants have a wide range of 611 chemical properties and their successful removal even in advanced treatment varies 612 significantly (Bolong et al., 2009, Yan et al., 2010, Luo et al., 2014). Secondly, there 613 is no existing regulation specifically targeted at wastewater or water treatment 614 criteria for these range of compounds (Bolong et al., 2009, Fatta-Kassinos et al., 615 2011). Finally the possibility of the existence of other potential unknown chemicalsof-concern makes it difficult to estimate the removal of all these chemicals under all
available treatment technologies or environmental conditions (Toze, 2006b,
Bergman et al., 2013)

Due to the lack of current knowledge on the actual effects of these chemicals on humans and the environment (Bergman et al., 2013), the mitigation measures that could be applied to manage their risks are limited to pre-treatment or segregation of industrial discharges (WHO, 2006, Simmons et al., 2010), the promotion of more clean production in industries and education of society to use less toxic compounds (WHO, 2006, Simmons et al., 2010).

### Table 7 The effects of toxic organic compounds and emerging contaminants in irrigation with wastewater

Implication	Negative effects	Comment	reference
Soil	Adsorbed by soil particles and organic matter may affect soils microorganism and microbial communities	Removal efficiencies are greater in soils reach in silt, clay and organic matter	(Qadir and Scott, 2010, Chen et al., 2011, WHO, 2006)
plants	Their large size and high molecular mass prevent them to be absorbed by plants Many can be uptake by plant soil or transferred to edible surface of crops via irrigation water or soil remain in the surface of crop	There are experimental studies indicate adverse effect on plants growth and biomass particularly by PPCPs There is lack of data related to human health effects through food- crop chain. Their effects on crops health assumed to be negligible	(Qadir and Scott, 2010, WHO, 2006,Chen et al., 2011,Wu et al. 2014)
Ground water	Could reach to ground water under highly permeable and shallow water table conditions or leach from poor organic matter soil, which lead to Groundwater contamination and they may contribute to adverse effect to human health if reach drinking water sources		(Chen et al., 2013a, Chen et al., 2011, WHO, 2006)
Surface water	Can reach to surface water via runoff and affect aquatic ecosystems		(Toze, 2006a, Chen et al., 2011, Qadir and Scott, 2010, Bolong et al., 2009, Muñoz et al., 2009)

#### 626 **1.5. Organic matter and suspended solids:**

627 Wastewater application will increase the organic matter content in soils, which may 628 be considered a beneficial impact. Adding organic matter to soil through wastewater 629 addition improves soil structure and moisture, enhances cation exchange capacity, 630 helps to retain metals and reduce their mobility and bioavailability and adds more 631 nutrients to soils (WHO, 2006, Qadir and Scott, 2010, Chen et al., 2010b). However, 632 high concentrations of organic matter and suspended solids can have an adverse 633 impact on soil porosity and favour anaerobic conditions in the root zone. In addition, 634 if agricultural runoff contains high concentrations of organic matter and this reaches 635 surface water, this may lead to depletion of dissolved oxygen in the water, resulting 636 in hypoxic conditions and increasing the mortality of aquatic species (WHO, 2006, 637 Qadir and Scott, 2010). High concentrations of organic matter and suspended solids 638 may also lead to plugging problems in micro irrigation systems such as sprinklers 639 and drippers (Qadir and Scott, 2010)

#### 640 **1.5.1. Management options:**

Reducing the effect of high concentrations of organic matter and suspended solids can primarily be achieved by enhanced removal of suspended solids and organic matter by pre-treatment, Ploughing soils when they are clogged and allowing soils to biodegrade organic matter by reducing the application frequency may also mitigate the potential effects (WHO, 2006).

## 646 Ranking the risks from chemical components of

## 647 irrigation with wastewater on arid and semi- arid 648 zones

649 Based on the outcome of the literature review presented above an assessment was 650 carried out to determine the relative environmental risk assessment associated with 651 the use of wastewater contaminated with a range of chemical pollutants in arid and 652 semi-arid zones. The key element for any valid risk assessment is to provide 653 procedures for determining appropriate consequences (the impacts) and the 654 likelihood (the probability of the hazard been realised) of each set of contaminants 655 under a range of environmental conditions as result of irrigation with wastewater. For 656 qualitative assessment, adequate descriptions for each level of consequences and 657 likelihood is required. Based on standards (standards Australia, 2004a, 2004b) each 658 of the sets has four levels of impact ranging from very low (no obvious and direct 659 impact with a score of 1) to high (irreversible with a score of 3), with medium (a score 660 of 2). The qualitative likelihood (Table 8) also has four levels ranging from Rare 661 (Lack of evidence but not impossible with a score of 1) to likely (expected to occur; 662 with a score of 4). The Risk value for each set was calculated based on a formal 663 judgement on the consequence and probability using the mathematical formal of:

664 Risk = impact level x Likelihood level

A simple risk matrix adopted from was used to evaluate the significance of the risk as illustrated in Figure **1** where risk value of 1-3 (green) are typically perceived as low risks and it can be accepted, while risk values of 8-16 (red) are perceived as high risks and should be unacceptable and it is important to manage these risks. Table 9 and Table 10 summarise the results of the evaluation.

670 Table 8 Likelihood definitions derived from standards (standards Australia, 2004a,
 671 2004b)

Level	Score	Descriptor		
Likely	4	It is expected to occur		
Possible	3	May occur sometimes		
Unlikely	2	Uncommon but has been known to occur		
Rare	1	Lake of evidence but not impossible		

672

		impact						
		High (4)	medium (3)	low (2)	very low (2)			
рс	likely (4)	16	12	8	4			
hoc	possible (3)	12	9	6	3			
keli	Unlikely (2)	8	6	4	2			
ij	Rare (1)	4	3	2	1			

Figure 1 the method for assessing the environmental risks of irrigation with wastewater

The analysis shows that in arid and semi-arid zones where surface water and rainfall are limited the most significant environmental issue with respect to irrigation with 677 wastewater would be salinity and sodicity. As a result of the high evaporation rate 678 and the lack of rainfall, excessive salts are not naturally flushed out and accumulate 679 in the soil profile causing soil salinity and/or sodicity leading to serious environmental 680 problems that contribute to a loss of soil productivity and fertility, and potential yield 681 losses.

Excessive nitrogen supply can also be an important concern. Managing appropriate levels of nitrogen could be a challenging task particularly in developing countries where most irrigation rates are designed to match water requirements rather than nutrient requirements, and oversupply of nitrogen may greatly affect the quality of crops and consequently reduce economic yields. Groundwater contamination from excessive levels of nitrate is a further area of concern.

Heavy metals present health risks since their impact on the environment and agricultural productivity is long term (from a few decades to a century depending on the type of effluent used). Health impacts associated with their transmission into the food chain are likely to arise long before they have a negative effect on the environment.

693 The potential adverse impact of exposure to emerging chemicals particularly EDCs 694 have mainly been reported in aquatic environments (Qadir and Scott, 2010, Bolong 695 et al., 2009, Toze, 2006a, Muñoz et al., 2009) and animals in direct contact with 696 polluted water (mainly surface water)(WHO, 2006, Toze, 2006a). Whilst the risks 697 associated with emerging contaminants in treated wastewater used for irrigation are 698 still controversial and not fully known, some studies have claimed that these 699 contaminants are unlikely to pose a serious threat to groundwater, soil environments 700 or human health as a result of its agricultural application (Chen et al., 2013a, Chen et 701 al., 2011, WHO, 2006, Wu et al., 2014, Wu et al., 2015). Nevertheless, there is a 702 significant lack of studies concerning the prevalence and fate of emerging 703 contaminants as a result of reusing wastewater for irrigation in terms of their 704 potentially adverse effects on the terrestrial ecosystem, crop uptake and potential 705 health impacts through the food-chain (Qadir and Scott, 2010, Muñoz et al., 2009, 706 Chen et al., 2011, Fatta-Kassinos et al., 2011, Qin et al., 2015, Prosser and Sibley, 707 2015).

	soil			plants		Groundwater		Surface water		health	
Hazards	Likelihood	Impact	Likelihood	Impact	Likelihood	Impact	Likelihood	Impact	Likelihood	Impact	
Salinity	Likely	high	likely	high	possible	medium	unlikely	low	unlikely	low	
Excessive Nutrient											
• nitrogen	possible	low	possible	high	possible	high	possible	high	possible	high	
Phosphorous	possible	low	possible	low	unlikely	low	possible	high	rare	Very low	
Heavy Metal	possible	high	possible	medium	possible	medium	unlikely	low	possible	high	
Toxic organic compounds and emerging contaminants	possible	low	possible	low	unlikely	Very Iow	unlikely	high	unlikely	low	
Organic matter & suspended solid	possible	low	unlikely	Very low	unlikely	Very Iow	unlikely	medium	rare	Very Iow	

#### 708 Table 9 Assessing the likelihood and the impacts and of chemical pollutants in irrigation with wastewater on related environments:

## 718 Table <u>10 Rank of the risks from wastewater reuse in agriculture</u>

hazards	score of the risk from irrigation with wastewater				
	soil	plants	Groundwater	Surface water	health
Salinity and sodicity	16	16	9	4	4
Excessive Nitrogen	6	12	12	12	12
Excessive phosphorous	6	6	4	12	1
Heavy Metal	12	9	6	4	12
Toxic organic compounds and emerging contaminants	6	6	2	8	4
Organic matter & suspended solid	6	2	2	6	1

## 720 **Conclusion:**

721 Wastewater availability and its nutrient properties make it a valuable alternative 722 water supply for irrigation practice in arid and semi-arid zones. However, 723 inappropriate management of irrigation with wastewater can contribute to serious 724 environmental and health problems. This review was conducted in order to provide a 725 comprehensive overview of the environmental and health risks associated with the 726 chemical components of irrigation with wastewater aiming to evaluate and rank the 727 risks from these constituents particularly on arid and semi-arid zones. Based on this 728 review it can be concluded that salinity and sodicity followed by excessive nitrogen 729 supply are the most significant environmental risks from irrigation with wastewater in 730 arid and semi-arid zones where surface water and rainfall are scarce while heavy 731 metals could be considered as a potential health risk more than an environmental 732 concern. Although there is a substantial range of literature dealing with the 733 environmental and health risks from heavy metals as a result of irrigation with 734 wastewater, more intensive studies are required on the effects of heavy metals on 735 plant nutritional components. There remains a lack of studies that evaluate and 736 quantify the environmental risks associated with PPCPs and emergent contaminants 737 on terrestrial ecosystems due to wastewater and biosolids reuse in agriculture. In 738 addition, further research is needed to understate the influence of soils properties 739 and plant factors on the uptake and translocation of PPCPs and emergent 740 contaminates in plants. The health risks of the exposure to mixture of PPCPs via 741 food crop chain as a result of irrigation with wastewater requires more investigation.

742

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## 754 **References:**

- AL-NAKSHABANDI, G. A., SAQQAR, M. M., SHATANAWI, M. R., FAYYAD, M. &
  AL-HORANI, H. 1997. Some environmental problems associated with the use of
  treated wastewater for irrigation in Jordan. Agricultural Water Management, 34, 8194.
- AL-ZU'BI, Y. 2007. Effect of irrigation water on agricultural soil in Jordan valley: An example from arid area conditions. Journal of Arid Environments, 70, 63-79.
- AL OMRON, A. M., EL-MAGHRABY, S. E., NADEEM, M. E. A., EL-ETER, A. M. & ALMOHANI, H. 2012. Long term effect of irrigation with the treated sewage effluent on
  some soil properties of Al-Hassa Governorate, Saudi Arabia. Journal of the Saudi
  Society of Agricultural Sciences, 11, 15-18.
- AUSTRALIA, S. 2004a. Risk Management Guidelines: Companion to AS/NZS4360: 2004.
   sydney Australia: Standards Australia International Ltd,Homebush,NSW.
- AUSTRALIA, S. 2004b. Risk Management, 3rd edn. Standards Australia, . Homebush,
   NSW.
- AVCI, H. & DEVECI, T. 2013. Assessment of trace element concentrations in soil and plants
   from cropland irrigated with wastewater. Ecotoxicology and Environmental Safety,
   98, 283-291.
- AYERS, R. S. & WESTCOT, D. W. 1985. Water quality for agriculture.FAO Irrigation and
   Drainage Paper . No. 29 Rome.
- BAHRI, A. 1998. Fertilizing value and polluting load of reclaimed water in Tunisia. Water
   Research, 32, 3484-3489.
- BAYSAL, A., OZBEK, N. & AKMAN, S. 2013. Determination of Trace Metals in Waste
  Water and Their Removal Processes, INTECH Open Access Publisher.
- BECERRA-CASTRO, C., LOPES, A. R., VAZ-MOREIRA, I., SILVA, E. F., MANAIA, C.
  M. & NUNES, O. C. 2015. Wastewater reuse in irrigation: A microbiological perspective on implications in soil fertility and human and environmental health.
  Environment International, 75, 117-135.
- BERGMAN, Å., HEINDEL, J. J., JOBLING, S., KIDD, K. A., ZOELLER, R. T. &
  JOBLING, S. K. 2013. State of the science of endocrine disrupting chemicals 2012:
  an assessment of the state of the science of endocrine disruptors prepared by a group
  of experts for the United Nations Environment Programme and World Health
  Organization, World Health Organization.
- BOLAN, N. S., ADRIANO, D., NATESAN, R. & KOO, B.-J. 2003. Effects of organic
  amendments on the reduction and phytoavailability of chromate in mineral soil.
  Journal of Environmental Quality, 32, 120-128.
- BOLONG, N., ISMAIL, A. F., SALIM, M. R. & MATSUURA, T. 2009. A review of the
  effects of emerging contaminants in wastewater and options for their removal.
  Desalination, 239, 229-246.

- BOS, R., CARR, R. & KERAITA, B. 2010. Assessing and mitigating wastewater-related
  health risks in low-income countries: An introduction. Wastewater irrigation and
  health: Assessing and mitigating risk in low-income countries, 29-47.
- BRAR, M. S., MALHI, S. S., SINGH, A. P., ARORA, C. L. & GILL, K. S. 2000. Sewage
  water irrigation effects on some potentially toxic trace elements in soil and potato
  plants in northwestern India. Canadian Journal of Soil Science, 80, 465-471.
- BROWN, S., CHANEY, R., HALLFRISCH, J., RYAN, J. A. & BERTI, W. R. 2004. In Situ
  Soil Treatments to Reduce the Phyto- and Bioavailability of Lead, Zinc, and
  Cadmium. Journal of Environmental Quality, 33.
- CALZADILLA, A., REHDANZ, K. & TOL, R. S. 2011. Water scarcity and the impact of
   improved irrigation management: a computable general equilibrium analysis.
   Agricultural Economics, 42, 305-323.
- 805 CANDELA, L., FABREGAT, S., JOSA, A., SURIOL, J., VIGUÉS, N. & MAS, J. 2007.
  806 Assessment of soil and groundwater impacts by treated urban wastewater reuse. A
  807 case study: Application in a golf course (Girona, Spain). Science of The Total
  808 Environment, 374, 26-35.
- CAREY, R. & MIGLIACCIO, K. 2009. Contribution of Wastewater Treatment Plant
  Effluents to Nutrient Dynamics in Aquatic Systems: A Review. Environmental
  Management, 44, 205-217.
- CARR, G. 2011. Water reuse for irrigated agriculture in Jordan: soil sustainability,
   perceptions and management. Water, Life and Civilisation: Climate, Environment and
   Society in the Jordan Valley, 415.
- CHANEY, R. L., ANGLE, J. S., BROADHURST, C. L., PETERS, C. A., TAPPERO, R. V.
  & SPARKS, D. L. 2007. Improved Understanding of Hyperaccumulation Yields
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  Journal of Environmental Quality, 36.
- CHEN, F., YING, G.-G., KONG, L.-X., WANG, L., ZHAO, J.-L., ZHOU, L.-J. & ZHANG,
  L.-J. 2011. Distribution and accumulation of endocrine-disrupting chemicals and
  pharmaceuticals in wastewater irrigated soils in Hebei, China. Environmental
  Pollution, 159, 1490-1498.
- 826 CHEN, M., MA, L. Q., SINGH, S. P., CAO, R. X. & MELAMED, R. 2003. Field
  827 demonstration of in situ immobilization of soil Pb using P amendments. Advances in
  828 Environmental Research, 8, 93-102.
- 829 CHEN, W., LU, S., JIAO, W., WANG, M. & CHANG, A. C. 2013a. Reclaimed water: A
  830 safe irrigation water source? Environmental Development, 8, 74-83.
- CHEN, W., LU, S., PAN, N. & JIAO, W. 2013b. Impacts of long-term reclaimed water
  irrigation on soil salinity accumulation in urban green land in Beijing. Water
  Resources Research, 7401–7410.
- CHEN, W., LU, S., PENG, C., JIAO, W. & WANG, M. 2013c. Accumulation of Cd in agricultural soil under long-term reclaimed water irrigation. Environmental Pollution, 178, 294-299.

- CHEN, W. P., HOU, Z. N., WU, L. S., LIANG, Y. C. & WEI, C. Z. 2010a. Evaluating
  salinity distribution in soil irrigated with saline water in arid regions of northwest
  China. Agricultural Water Management, 97, 2001-2008.
- CHEN, Y., DOSORETZ, C. G., KATZ, I., JÜESCHKE, E., MARSCHNER, B. &
  TARCHITZKY, J. 2010b. Organic Matter in Wastewater and Treated WastewaterIrrigated Soils: Properties and Effects. Treated Wastewater in Agriculture. WileyBlackwell.
- CHIPASA, K. B. 2003. Accumulation and fate of selected heavy metals in a biological
  wastewater treatment system. Waste Management, 23, 135-143.
- 846 CIZMAS, L., SHARMA, V., GRAY, C. & MCDONALD, T. 2015. Pharmaceuticals and
  847 personal care products in waters: occurrence, toxicity, and risk. Environmental
  848 Chemistry Letters, 13, 381-394.
- COBBETT, C. 2003. Heavy metals and plants-model systems and hyperaccumulators. New
   Phytologist, 159, 289-293.
- 851 COLBORN, T., VOM SAAL, F. S. & SOTO, A. M. 1993. Developmental effects of
  852 endocrine-disrupting chemicals in wildlife and humans. Environmental health
  853 perspectives, 101, 378.
- DA FONSECA, A. F., HERPIN, U., DE PAULA, A. M., VICTORIA, R. L. & MELFI, A. J.
  2007. Agricultural use of treated sewage effluents: Agronomic and environmental implications and perspectives for Brazil. Scientia Agricola, 64, 194-209.
- BALKMANN, P., SIEBE, C., AMELUNG, W., SCHLOTER, M. & SIEMENS, J. 2014.
  Does long-term irrigation with untreated wastewater accelerate the dissipation of pharmaceuticals in soil? Environmental science & technology, 48, 4963-4970.
- BEFOREST, J. L., ZAK, D. R., PREGITZER, K. S. & BURTON, A. J. 2004. Atmospheric
  nitrate deposition, microbial community composition, and enzyme activity in northern
  hardwood forests. Soil Science Society of America Journal, 68, 132-138.
- EMONGOR, V. & RAMOLEMANA, G. 2004. Treated sewage effluent (water) potential to
   be used for horticultural production in Botswana. Physics and Chemistry of the Earth,
   Parts A/B/C, 29, 1101-1108.
- FANG, Y., KARNJANAPIBOONWONG, A., CHASE, D. A., WANG, J., MORSE, A. N. &
   ANDERSON, T. A. 2012. Occurrence, fate, and persistence of gemfibrozil in water
   and soil. Environmental Toxicology and Chemistry, 31, 550-555.
- FATTA-KASSINOS, D., KALAVROUZIOTIS, I. K., KOUKOULAKIS, P. H. &
  VASQUEZ, M. I. 2011. The risks associated with wastewater reuse and xenobiotics
  in the agroecological environment. Science of The Total Environment, 409, 35553563.
- FRIEDEL, J., LANGER, T., SIEBE, C. & STAHR, K. 2000. Effects of long-term waste
  water irrigation on soil organic matter, soil microbial biomass and its activities in
  central Mexico. Biology and Fertility of Soils, 31, 414-421.
- FU, F. & WANG, Q. 2011. Removal of heavy metal ions from wastewaters: A review.
  Journal of Environmental Management, 92, 407-418.
- 878 GARCÍA, C. & HERNÁNDEZ, T. 1996. Influence of salinity on the biological and biochemical activity of a calciorthird soil. Plant and Soil, 178, 255-263.

- GHOSH, A. K., BHATT, M. A. & AGRAWAL, H. P. 2012. Effect of long-term application
  of treated sewage water on heavy metal accumulation in vegetables grown in
  Northern India. Environmental Monitoring and Assessment, 184, 1025-1036.
- 883 GRATTAN, S. R., GRIEVE, C. M., POSS, J. A., ROBINSON, P. H., SUAREZ, D. L. &
  884 BENES, S. E. 2004. Evaluation of salt-tolerant forages for sequential water reuse
  885 systems: I. Biomass production. Agricultural Water Management, 70, 109-120.
- 886 GUPTA, N., KHAN, D. K. & SANTRA, S. C. 2008. An Assessment of Heavy Metal
  887 Contamination in Vegetables Grown in Wastewater-Irrigated Areas of Titagarh, West
  888 Bengal, India. Bulletin of Environmental Contamination and Toxicology, 80, 115-118.
- 6WENZI, W. & MUNONDO, R. 2008. Long-term impacts of pasture irrigation with treated
   sewage effluent on shallow groundwater quality. Water Science and Technology, 58,
   2443-2452.
- HAMILTON, A. J., BOLAND, A.-M., STEVENS, D., KELLY, J., RADCLIFFE, J.,
  ZIEHRL, A., DILLON, P. & PAULIN, B. 2005. Position of the Australian
  horticultural industry with respect to the use of reclaimed water. Agricultural Water
  Management, 71, 181-209.
- HAMILTON, A. J., STAGNITTI, F., XIONG, X., KREIDL, S. L., BENKE, K. K. &
  MAHER, P. 2007. Wastewater irrigation: The state of play. Vadose Zone Journal, 6, 823-840.
- HANSON, B., GRATTAN, S. R. & FULTON, A. 1999. Agricultural salinity and drainage,
   University of California Irrigation Program, University of California, Davis.
- HETTIARACHCHI, G. M. & PIERZYNSKI, G. M. 2002. In situ stabilization of soil lead
   using phosphorus and manganese oxide. Journal of Environmental Quality, 31, 564 572.
- HILLEL, D. 2000. Salinity management for sustainable irrigation: integrating science,
   environment, and economics, World Bank Publications.
- 906 HUSSAIN, I., RASCHID, L., HANJRA, M. A., MARIKAR, F. & VAN DER HOEK, W.
  907 2002. Wastewater Use in Agriculture: Review of Impacts and Methodological Issues
  908 in Valuing Impacts: with an Extended List of Bibliographical References, Iwmi.
- JIMÉNEZ, B., DRECHSEL, P., KONÉ, D., BAHRI, A., RASCHID-SALLY, L. & QADIR,
  M. 2010. Wastewater, sludge and excreta use in developing countries: an overview.
  In: DRECHSEL, P., SCOTT, C. A., RASCHID-SALLY, L., REDWOOD, M. &
  BAHRI, A. (eds.) Wastewater Irrigation and Health: Assessing and Mitigating Risk in
  Low-Income Countries. London, UK: Earthscan.
- 814 KASS, A., GAVRIELI, I., YECHIELI, Y., VENGOSH, A. & STARINSKY, A. 2005. The
  815 impact of freshwater and wastewater irrigation on the chemistry of shallow
  816 groundwater: a case study from the Israeli Coastal Aquifer. Journal of Hydrology,
  817 300, 314-331.
- 8 KATERJI, N., VAN HOORN, J. W., HAMDY, A. & MASTRORILLI, M. 2003. Salinity
  8 effect on crop development and yield, analysis of salt tolerance according to several
  8 classification methods. Agricultural Water Management, 62, 37-66.
- KESER, G. 2013. Effects of irrigation with wastewater on the physiological properties and heavy metal content in Lepidium sativum L. and Eruca sativa (Mill.). Environmental Monitoring and Assessment, 185, 6209-6217.

- KHAN, M. U., MALIK, R. N. & MUHAMMAD, S. 2013. Human health risk from Heavy
  metal via food crops consumption with wastewater irrigation practices in Pakistan.
  Chemosphere, 93, 2230-2238.
- KHAN, S., CAO, Q., ZHENG, Y. M., HUANG, Y. Z. & ZHU, Y. G. 2008. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. Environmental Pollution, 152, 686-692.
- KIZILOGLUL, F. M., TURAN, M., SAHIN, U., ANGIN, I., ANAPALI, O. &
  OKUROGLU, M. 2007. Effects of wastewater irrigation on soil and cabbage-plant (brassica olerecea var. capitate cv. yalova-1) chemical properties. Journal of Plant Nutrition and Soil Science-Zeitschrift Fur Pflanzenernahrung Und Bodenkunde, 170, 166-172.
- 835 KLAY, S., CHAREF, A., AYED, L., HOUMAN, B. & REZGUI, F. 2010. Effect of irrigation
  836 with treated wastewater on geochemical properties (saltiness, C, N and heavy metals)
  937 of isohumic soils (Zaouit Sousse perimeter, Oriental Tunisia). Desalination, 253, 180938 187.
- 839 KNOBELOCH, L., SALNA, B., HOGAN, A., POSTLE, J. & ANDERSON, H. 2000. Blue
  940 babies and nitrate-contaminated well water. Environmental Health Perspectives, 108,
  941 675.
- 842 KUMAR SHARMA, R., AGRAWAL, M. & MARSHALL, F. 2007. Heavy metal
  943 contamination of soil and vegetables in suburban areas of Varanasi, India.
  944 Ecotoxicology and Environmental Safety, 66, 258-266.
- LAL, K., YADAV, R. K., KAUR, R., BUNDELA, D. S., KHAN, M. I., CHAUDHARY, M.,
  MEENA, R. L., DAR, S. R. & SINGH, G. 2013. Productivity, essential oil yield, and
  heavy metal accumulation in lemon grass (Cymbopogon flexuosus) under varied
  wastewater-groundwater irrigation regimes. Industrial Crops and Products, 45, 270278.
- LEAL, R. M. P., HERPIN, U., DA FONSECA, A. F., FIRME, L. P., MONTES, C. R. &
  MELFI, A. J. 2009. Sodicity and salinity in a Brazilian Oxisol cultivated with sugarcane irrigated with wastewater. Agricultural Water Management, 96, 307-316.
- LETEY, J., HOFFMAN, G. J., HOPMANS, J. W., GRATTAN, S. R., SUAREZ, D.,
  CORWIN, D. L., OSTER, J. D., WU, L. & AMRHEIN, C. 2011. Evaluation of soil
  salinity leaching requirement guidelines. Agricultural Water Management, 98, 502506.
- LIANG, J. T., CHEN, C. C., SONG, X. L., HAN, Y. L. & LIANG, Z. H. 2011. Assessment
  of Heavy Metal Pollution in Soil and Plants from Dunhua Sewage Irrigation Area.
  International Journal of Electrochemical Science, 6, 5314-5324.
- LU, Y., YAO, H., SHAN, D., JIANG, Y., ZHANG, S. & YANG, J. 2014. Heavy Metal
  Residues in Soil and Accumulation in Maize at Long-Term Wastewater Irrigation
  Area in Tongliao, China. Journal of Chemistry.
- LUO, Y., GUO, W., NGO, H. H., NGHIEM, L. D., HAI, F. I., ZHANG, J., LIANG, S. &
  WANG, X. C. 2014. A review on the occurrence of micropollutants in the aquatic
  environment and their fate and removal during wastewater treatment. Science of The
  Total Environment, 473–474, 619-641.

- MAAS, E. & GRATTAN, S. 1999. 3 Crop Yields as Affected by Salinity. In: SKAGGS, R.
  W. & SCHILFGAARDE, J. V. (eds.) Agricultural drainage. Madison, WI ASA-CSSA-SSSA.
- MALASH, N., FLOWERS, T. J. & RAGAB, R. 2005. Effect of irrigation systems and water
   management practices using saline and non-saline water on tomato production.
   Agricultural Water Management, 78, 25-38.
- MAPANDA, F., MANGWAYANA, E. N., NYAMANGARA, J. & GILLER, K. E. 2005.
  The effect of long-term irrigation using wastewater on heavy metal contents of soils under vegetables in Harare, Zimbabwe. Agriculture, Ecosystems & Environment, 107, 151-165.
- MINHAS, P. S. 1996. Saline water management for irrigation in India. Agricultural Water
   Management, 30, 1-24.
- MIRELES, A., SOLÍS, C., ANDRADE, E., LAGUNAS-SOLAR, M., PIÑA, C. &
  FLOCCHINI, R. G. 2004. Heavy metal accumulation in plants and soil irrigated with
  wastewater from Mexico city. Nuclear Instruments and Methods in Physics Research
  Section B: Beam Interactions with Materials and Atoms, 219–220, 187-190.
- MOHAMMAD, M. J. & MAZAHREH, N. 2003. Changes in Soil Fertility Parameters in
  Response to Irrigation of Forage Crops with Secondary Treated Wastewater.
  Communications in Soil Science and Plant Analysis, 34, 1281-1294.
- 986 MOHAMMAD RUSAN, M. J., HINNAWI, S. & ROUSAN, L. 2007. Long term effect of
  987 wastewater irrigation of forage crops on soil and plant quality parameters.
  988 Desalination, 215, 143-152.
- 989 MUNNS, R. & GILLIHAM, M. 2015. Salinity tolerance of crops what is the cost? New
   990 Phytologist, 208, 668-673.
- MUÑOZ, I., GÓMEZ-RAMOS, M. J., AGÜERA, A., FERNÁNDEZ-ALBA, A. R.,
  GARCÍA-REYES, J. F. & MOLINA-DÍAZ, A. 2009. Chemical evaluation of
  contaminants in wastewater effluents and the environmental risk of reusing effluents
  in agriculture. TrAC Trends in Analytical Chemistry, 28, 676-694.
- MUYEN, Z., MOORE, G. A. & WRIGLEY, R. J. 2011. Soil salinity and sodicity effects of
   wastewater irrigation in South East Australia. Agricultural Water Management, 99,
   33-41.
- 998 OLANIRAN, A. O., BALGOBIND, A. & PILLAY, B. 2013. Bioavailability of Heavy
   999 Metals in Soil: Impact on Microbial Biodegradation of Organic Compounds and
   1000 Possible Improvement Strategies. International Journal of Molecular Sciences, 14,
   1001 10197-10228.
- ONESIOS, K. M., JIM, T. Y. & BOUWER, E. J. 2009. Biodegradation and removal of pharmaceuticals and personal care products in treatment systems: a review.
   Biodegradation, 20, 441-466.
- OSTE, L. A., LEXMOND, T. M. & VAN RIEMSDIJK, W. H. 2002. Metal immobilization
   in soils using synthetic zeolites. Journal of Environmental Quality, 31, 813-821.
- PEDRERO, F. & ALARCON, J. J. 2009. Effects of treated wastewater irrigation on lemon
   trees. Desalination, 246, 631-639.
- PESCOD, M. 1992. Wastewater treatment and use in agriculture. FAO irrigation and drainage paper 47. FAO,Roma.

- PROSSER, R. & SIBLEY, P. 2015. Human health risk assessment of pharmaceuticals and personal care products in plant tissue due to biosolids and manure amendments, and wastewater irrigation. Environment international, 75, 223-233.
- 1014 PUSCHENREITER, M., HORAK, O., FRIESL, W. & HARTL, W. 2005. Low-cost agricultural measures to reduce heavy metal transfer into the food chain-a review.
  1016 Plant Soil Environ, 51, 1-11.
- 1017 QADIR, M., MATEO-SAGASTA, J., JIMÉNEZ, B., SIEBE, C., SIEMENS, J. & HANJRA,
  1018 M. A. 2015. Environmental Risks and Cost-Effective Risk Management in
  1019 Wastewater Use Systems. In: DRECHSEL, P., QADIR, M. & WICHELNS, D. (eds.)
  1020 Wastewater :Economic Asset in an Urbanizing World. Springer.
- QADIR, M. & SCHUBERT, S. 2002. Degradation processes and nutrient constraints in sodic
   soils. Land Degradation & Development, 13, 275-294.
- 1023 QADIR, M. & SCOTT, C. A. 2010. Non-pathogenic trade-offs of wastewater irrigation. In:
  1024 DRECHSEL, P., SCOTT, C. A., RASCHID-SALLY, L., REDWOOD, M. & BAHRI,
  1025 A. (eds.) wastewater irrigation and health: Assessing and Mitigating Risk in Low
  1026 Income Countries. london: earthscan.
- QIAN, Y. L. & MECHAM, B. 2005. Long-Term Effects of Recycled Wastewater Irrigation on Soil Chemical Properties on Golf Course Fairways This report was financed in part by the U.S. Department of the Interior, Geological Survey, through the Colorado Water Resources Research Institute and Grant no. 01HQGR0077. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. government. Agron. J., 97, 717-721.
- QIN, Q., CHEN, X. & ZHUANG, J. 2015. The Fate and Impact of Pharmaceuticals and Personal Care Products in Agricultural Soils Irrigated With Reclaimed Water. Critical Reviews in Environmental Science and Technology, 45, 1379-1408.
- 1037 RAMIREZ, K. S., CRAINE, J. M. & FIERER, N. 2012. Consistent effects of nitrogen amendments on soil microbial communities and processes across biomes. Global 1039 Change Biology, 18, 1918-1927.
- 1040 RATTAN, R. K., DATTA, S. P., CHHONKAR, P. K., SURIBABU, K. & SINGH, A. K.
  1041 2005. Long-term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater—a case study. Agriculture, Ecosystems & Environment, 1043 109, 310-322.
- 1044 RIETZ, D. N. & HAYNES, R. J. 2003. Effects of irrigation-induced salinity and sodicity on 1045 soil microbial activity. Soil Biology and Biochemistry, 35, 845-854.
- SCOTT, C. A., FARUQUI, N. I. & RASCHID-SALLY, L. 2004. 1. Wastewater Use in Irrigated Agriculture: Management Challenges in Developing Countries. In: C. A
  SCOTT, FARUQUI, N. I., NASER, I. & RASCHID-SALLY, L. (eds.) Wastewater use in irrigated agriculture: confronting the livelihood and environmental realities.
  UK: CABI.
- SIEBE, C. & FISCHER, W. R. 1996. Effect of long-term irrigation with untreated sewage
   effluents on soil properties and heavy metal adsorption of leptosols and vertisols in
   Central Mexico. Zeitschrift für Pflanzenernährung und Bodenkunde, 159, 357-364.
- SIMMONS, R., QADIR, M. & DRECHSEL, P. 2010. Farm-based measures for reducing
   human and environmental health risks from chemical constituents in wastewater. In:

- 1056 RECHSEL, P., SCOTT, C. A., RASCHID-SALLY, L., REDWOOD, M. & BAHRI,
  1057 A. (eds.) Wastewater irrigation and health. Assessing and Mitigating Risk in Low1058 income Countries. London: Erthscan.
- SINGH, A., SHARMA, R. K., AGRAWAL, M. & MARSHALL, F. M. 2010. Health risk
  assessment of heavy metals via dietary intake of foodstuffs from the wastewater
  irrigated site of a dry tropical area of India. Food and Chemical Toxicology, 48, 611619.
- SMITH, C. J., HOPMANS, P. & COOK, F. J. 1996. Accumulation of Cr, Pb, Cu, Ni, Zn and
  Cd in soil following irrigation with treated urban effluent in Australia. Environmental
  Pollution, 94, 317-323.
- SOU/DAKOURÉ, M. Y., MERMOUD, A., YACOUBA, H. & BOIVIN, P. 2013. Impacts of
  irrigation with industrial treated wastewater on soil properties. Geoderma, 200–201,
  31-39.
- SPERLING, M. V. & DE LEMOS CHERNICHARO, C. A. 2005. Biological wastewater
   treatment in warm climate regions, IWA.
- 1071 SRIDHARA CHARY, N., KAMALA, C. T. & SAMUEL SUMAN RAJ, D. 2008. Assessing
   1072 risk of heavy metals from consuming food grown on sewage irrigated soils and food
   1073 chain transfer. Ecotoxicology and Environmental Safety, 69, 513-524.
- 1074 TARCHOUNA GHARBI, L., MERDY, P. & LUCAS, Y. 2010. Effects of long-term
  1075 irrigation with treated wastewater. Part II: Role of organic carbon on Cu, Pb and Cr
  1076 behaviour. Applied Geochemistry, 25, 1711-1721.
- 1077 TIWARI, K. K., SINGH, N. K., PATEL, M. P., TIWARI, M. R. & RAI, U. N. 2011. Metal
  1078 contamination of soil and translocation in vegetables growing under industrial
  1079 wastewater irrigated agricultural field of Vadodara, Gujarat, India. Ecotoxicology and
  1080 Environmental Safety, 74, 1670-1677.
- TOZE, S. 2006a. Reuse of effluent water—benefits and risks. Agricultural Water
   Management, 80, 147-159.
- 1083 TOZE, S. 2006b. Water reuse and health risks—real vs. perceived. Desalination, 187, 41-51.
- 1084 USMAN, A., KUZYAKOV, Y. & STAHR, K. 2005. Effect of Clay Minerals on
  1085 Immobilization of Heavy Metals and Microbial Activity in a Sewage Sludge1086 Contaminated Soil (8 pp). Journal of Soils and Sediments, 5, 245-252.
- 1087 VERMA, P., AGRAWAL, M. & SAGAR, R. 2015. Assessment of potential health risks due
  1088 to heavy metals through vegetable consumption in a tropical area irrigated by treated
  1089 wastewater. Environment Systems and Decisions, 35, 375-388.
- WANG, Y., HU, W., CAO, Z., FU, X. & ZHU, T. 2005. Occurrence of endocrine-disrupting
  compounds in reclaimed water from Tianjin, China. Analytical and Bioanalytical
  Chemistry, 383, 857-863.
- 1093 WHO 2006. Guidelines for the Safe Use of Wasterwater Excreta and Greywater, volume2:
   1094 wastewater use in agriculture, World Health Organisation, Geneva.
- WINPENNY, J. T., HEINZ, I., KOO-OSHIMA, S., WINPENNY, J. T. & WINPENNY, J. T.
  2010. The wealth of waste: The economics of wastewater use in agriculture, Food and
  Agriculture Organization of the United Nations.
- WU, R. 1999. Eutrophication, water borne pathogens and xenobiotic compounds:
   environmental risks and challenges. Marine Pollution Bulletin, 39, 11-22.

- WU, X., CONKLE, J. L., ERNST, F. & GAN, J. 2014. Treated wastewater irrigation: uptake
  of pharmaceutical and personal care products by common vegetables under field
  conditions. Environmental science & technology, 48, 11286-11293.
- WU, X., DODGEN, L. K., CONKLE, J. L. & GAN, J. 2015. Plant uptake of pharmaceutical and personal care products from recycled water and biosolids: a review. Science of The Total Environment, 536, 655-666.
- XU, J., WU, L., CHANG, A. C. & ZHANG, Y. 2010. Impact of long-term reclaimed
  wastewater irrigation on agricultural soils: A preliminary assessment. Journal of
  Hazardous Materials, 183, 780-786.
- YAN, S., SUBRAMANIAN, S., TYAGI, R., SURAMPALLI, R. & ZHANG, T. 2010.
  Emerging Contaminants of Environmental Concern: Source, Transport, Fate, and Treatment. Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management, 14, 2-20.
- YU, Y., WEN, B., YANG, Y. & LU, Z. H. 2012. The Effects of Treated Wastewater Irrigation on Soil Health. In: CHEN, R. & SUNG, W. P. (eds.) Biotechnology, Chemical and Materials Engineering, Pts 1-3. Stafa-Zurich: Trans Tech Publications Ltd.
- ZHANG, Y. L., DAI, J. L., WANG, R. Q. & ZHANG, J. 2008. Effects of long-term sewage
  irrigation on agricultural soil microbial structural and functional characterizations in
  Shandong, China. European Journal of Soil Biology, 44, 84-91.
- 1120