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Beneficial and Negative Impacts on Soil by the Reuse of Treated/Untreated Municipal Wastewater for Agricultural Irrigation – A Review of the Current Knowledge and Future Perspectives

Juan C. Durán–Álvarez and Blanca Jiménez–Cisneros

Additional information is available at the end of the chapter

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1. Introduction

The scarcity of water for human use, such as food and energy production, manufacturing, drinking water and ecosystem conservation is a global problem for which the solution goes beyond merely the preservation of freshwater sources [1–2]. Although three quarters of the Earth's surface is covered by water, most of this water is either contained in oceans or confined in glaciers [3]. The volume of freshwater available for human activities (less than 1%) is unequally distributed throughout the globe; in some cases this water is confined to the deep sub-soil or is polluted [4]. Furthermore, the desertification of large areas caused by climate change has intensified the lack of water sources in cities and rural areas throughout the world [5]. Water scarcity results in food scarcity, since 70% of the water withdrawn for human activities goes to agriculture [6]. In zones where rain-fed agriculture is practiced, decay in crop yields is observed when droughts occur, which results not only in the scarcity of food but also the decrease in incomes due to falling crop sales [7]. The use of freshwater for agricultural irrigation limits the volume of freshwater available for human consumption; therefore, recycling of water becomes necessary for agricultural irrigation in dry zones. The idea of reusing wastewater to irrigate is not new; it actually originated around 3000 B.C. People in these ancient civilizations knew that wastewater contained both water and compounds that benefited the soil and thus they used it in a planned way to increase crop yields [8].

Commonly, reusing wastewater in agriculture is considered a deleterious practice since it may introduce pollutants to the environment, spread waterborne diseases, generate odor problems and result in aversion to the crops. Nevertheless, this kind of reuse may result in some benefits

for soils, crops and farmers. Nowadays, the reuse of wastewater in agriculture is seen in some countries as a convenient environmental strategy [9–10]; municipal wastewater is therefore considered an appropriate option for reuse. This kind of wastewater contains a significant load of biodegradable organic material (carbon and nitrogen) as well as most of the mineral macronutrients (e.g. phosphorous, potassium, magnesium and boron) and micronutrients (e.g. molybdenum, selenium and copper) which are necessary for the growth of crops. Accumulation of organic matter in soil by irrigation with wastewater can be beneficial as it may result in the enhancement of the physical structure of the soil, the increase in the soil microbial activity and the improvement of soil performance as a filter and degrading media for pollutants. Conversely, a fraction of the organic matter contained in wastewater is due to the occurrence of organic pollutants (e.g. polyaromatic hydrocarbons and polychlorinated biphenyls) and pathogenic microbial agents [11–12]. Because of the presence of organic, inorganic and microbial pollutants in wastewater, a prior step of depuration is necessary before reuse in irrigation in order to avoid the pollution of soil, crops and the nearby water sources, and thus the dissemination of waterborne diseases or the degradation of soil. The extent at which wastewater has to be treated prior to irrigation depends on the restrictions established in local or international water quality criteria for irrigation [13]. Primary treatment schemes (coagulation–flocculation with sedimentation or aerobic/anaerobic stabilization ponds) are used for treating wastewater to irrigate crops that are not intended for human consumption (e.g. fodder), while secondary treatment of wastewater (biological treatment followed by disinfection) is recommended when unrestricted crops are irrigated [14–15]. In developing countries, most or the whole volume of wastewater produced in cities is treated prior to irrigation, while in low income countries wastewater treatment is not a priority, and thus untreated or partially treated wastewater or a mixture of treated and untreated wastewater is commonly used for agricultural purposes [12, 16]. In Mexico, China, India and Pakistan, for instance, large areas exist where untreated wastewater has been reused in agricultural irrigation for a considerable time [17]. The World Health Organization estimates that nearly 20 million hectares throughout the world are irrigated using untreated wastewater [18]. It is also reported that in some cities up to 80% of the vegetables locally consumed are produced using wastewater for irrigation [19]. The application of wastewater to soil, particularly untreated wastewater, followed by its infiltration poses a significant risk of pollution, not only to soil and crops but also to the surface and subterranean water sources surrounding the irrigated area [20–21].

Pollution by pathogenic agents is the main cause of concern regarding the application of treated/untreated wastewater to soil. Due to the variety of microorganisms entering the soil via the wastewater there is a high risk of enteric disease outbreaks for farmers and consumers [22–23]. This chapter addresses the contamination of wastewater irrigated soils by helminths (intestinal worms) and pathogenic bacteria common in developing countries (where untreated wastewater is used to a greater extent), as well as the risk of outbreaks of parasitic diseases for both farmers and consumers in agricultural areas where untreated wastewater is reused. The occurrence of antibiotic resistance in indigenous organisms of soil and pathogens reaching soil via wastewater is gaining the attention of scientists and health organizations around the world [24–25], thus a review of what it is known and the research opportunities in this field are presented in the text. With regard to organic pollution, a current topic of interest is the entry

to the soil and potential risks within crops of so-called “contaminants of emerging concern”. These pollutants are substances that have not previously been considered as pollutants since they are part of everyday products; however, due to the subtle but harmful effects that these substances may cause in a variety of aquatic and terrestrial organisms, concerns have risen due to their continuous entry into the environment via wastewater [26]. A review on the presence of some organic contaminants of emerging concern, such as pharmaceutical substances, personal care products and industrial additives, in wastewater-irrigated agricultural soils is presented in this chapter along with some of the known potential effects caused to soil organisms, plants and consumers. Such effects have just begun to be elucidated, and only for some groups of contaminants of emerging concern [27–28], even though it is now known that up to 7 million commercially available chemicals are routinely disposed of in sewage after use [29]. In this regard, this chapter makes some suggestions regarding the next steps in the toxicity studies for this class of pollutants, such as testing the synergistic effects of mixtures of contaminants of emerging concern in soil organisms.

In spite of the variety and quantity of contaminants that soil regularly receives through wastewater irrigation, this ecosystem possesses self-purification processes that maintain homeostasis within the system. Such self-purification processes may either inactivate or reduce the population of pathogenic microorganisms reaching the soil via wastewater through predation by the indigenous microbiota within the soil [30–31], the production of antibiotics by some organisms in the rhizosphere [32] and by retention of microorganisms in the surface layers of the soil profile through physical and chemical processes. For organic pollutants, mechanisms such as photolysis and biodegradation promote the dissipation of contaminants in the soil, while adsorption onto the soil particles lead to the retention –and the potential confinement– of organics within the solid matrix [33]. In this chapter, current knowledge concerning the environmental fate of pathogen and organic contaminants of emerging concern in wastewater irrigated soils is discussed, highlighting the laboratory approaches that show the best results in simulation of the conditions in the field. Knowledge of the environmental fate of contaminants in irrigated soils is important in order to perform more accurate risk assessment studies on contamination of water sources, soil and crops in wastewater irrigated areas; furthermore, it provides information to policy makers to make proper legislation aimed at promoting environmentally responsible management of treated/untreated wastewater in agricultural irrigation.

Depuration of wastewater prior to its reuse is the most plausible option to prevent soil pollution by wastewater reuse. However, since wastewater represents a cheap source of water and fertilizer for farmers [34], it is necessary to consider the needs of users before planning schemes of wastewater treatment. The use of wastewater treatment systems aimed at removing carbon, nitrogen, phosphorous and minerals in wastewater leads to the reduction in quality of effluents as fertilizers, impacting crop yields and thus in the livelihood of farmers. In this sense, the use of advanced primary treatment systems could be a feasible option to: a) remove suspended solids, pathogens and heavy metals in wastewater without significantly impacting the content of nutrients in effluent; b) preserve the quality of agricultural soils to properly perform ecosystem services such as the production of food; and, c) fulfill the needs of farmers

that use wastewater as a source of water and nutrients. Treating wastewater by these kinds of systems may be an opportunity to couple sanitation with reuse within a program of comprehensive management of wastewater, the recycling of nutrients and the use of soil as a food producer and purification system.

This chapter aims to describe what it is known and what it is unknown regarding the positive and negative impacts of the reuse of treated/untreated wastewater in agricultural irrigation. It will be shown in detail how this practice can benefit soil and farmers, while at the same time posing a risk of contamination to the ecosystem. Emphasis is given to the purification processes occurring in the soil and how soil manages the continuous entrance of pollutants via wastewater. Lastly, some perspectives for further studies on the presence and environmental fate of pollutants in wastewater irrigated soils are proposed.

2. Impacts of wastewater reuse in agriculture

The reuse of wastewater results in both beneficial and negative impacts on soil, some of which are explained in this section. The aim is to identify both and to understand their origins in order to assist scientists and policy makers to balance them and even to greater advantage of the benefits compared to the drawbacks in certain situations.

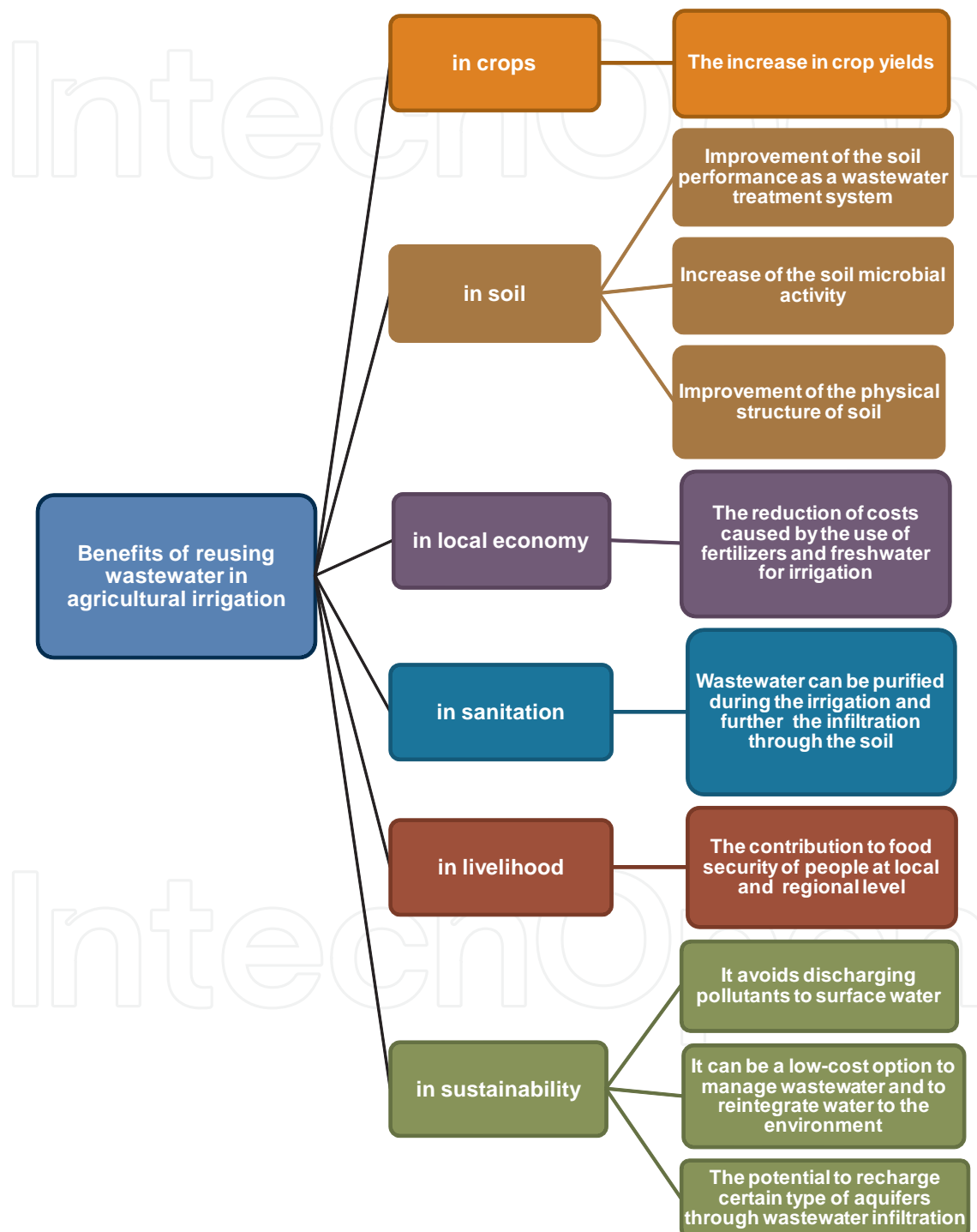
2.1. Benefits of wastewater reuse in agriculture

Figure 1 summarizes the positive impacts of reusing wastewater in agricultural irrigation in all of its forms. The extent of the positive impacts depends on local conditions of the specific project.

2.1.1. *Benefits in crops*

Since wastewater is produced constantly and thus is always available, it is possible to select a wider range of crops to be sown year-round, specifically those of high profitability which normally have higher and more stringent water demands in terms of quantity and timing. The consistent use of wastewater in irrigation may stabilize the content of nutrients in the soil, even when growing crops with high nutritional requirements; this is because the continuous withdrawal of nutrients by plants is compensated by the constant input of organic and mineral components into the soil via wastewater. Examples of how the reuse of wastewater has led to increases in crop yields in arid zones can be found worldwide. Studies conducted in Hubli-Dharwad, India, showed that irrigation with treated and untreated wastewater made it possible to produce vegetables during the dry season; yields and selling prices increased by 3–5 times compared to the kharif (monsoon) season [35]. In Pakistan, Ghana and Senegal the reliability and flexibility of wastewater supply allows rural and urban farmers to cultivate profitable crops in a shorter time, resulting in several harvests per year (3 to 6) [36–37]. Treated/untreated wastewater is a source of organic matter and the same large diversity of nutrients contained in any formulated fertilizer. It is estimated that 1,000 m³ of municipal wastewater applied to one hectare can contribute 16–62 kg of organic nitrogen, 4–24 kg of phosphorus, 269

kg of potassium, 18–208 kg of calcium and 9–110 kg of magnesium each year [16]. Table 1 shows the contribution of water and nutrients that untreated wastewater make to several crops.



With information of references [14, 18, 21, 36, 37]

Figure 1. Beneficial impacts of reusing wastewater for agricultural irrigation

Nitrogen is a plant macronutrient which can be found in the form of nitrate ions (N-NO_3), mostly in treated wastewater, or as ammoniacal nitrogen (N-NH_4^+) and organic nitrogen in untreated wastewater. The sum of all these forms is known as total nitrogen (TN). Most crops absorb nitrates to the greatest extent (85% of the nitrate contained in wastewater); whereas 50% of ammoniacal and less than 30% of organic nitrogen contained in wastewater can be assimilated as it is by plants. The remaining nitrogen is taken up by soil microorganisms and transformed into nitrates or volatilized as N_2 . In wastewater irrigated soils, organic nitrogen is transformed into nitrates by soil microorganisms to a greater extent than that observed in non-irrigated agricultural soils [38]. Problems related to high inputs of nitrate ions are due to their high solubility in water, and thus their rapid percolation through the soil to the aquifer.

Crop	Water requirements (mm/year)	Nutrients and sodium contribution by WW (kg ha/year)					
		N _{total}	P _{total}	K	Ca	Mg	Na
Maize	673	108–418	27–162	13–465	121–1401	61–741	182–1226
Green tomatoes	653	104–405	26–157	13–451	118–1358	59–718	176–1188
Chili	601	96–373	24–144	12–415	108–1250	54–661	162–1094
Beans	370	59–229	7–89	7–255	67–770	33–407	100–673
Wheat	520	83–322	21–125	10–359	94–1082	47–572	140–946
Barley	516	83–320	21–124	10–356	93–1074	46–568	139–939
Alfalfa	1360	218–843	54–326	27–938	245–2829	122–843	367–2475
Marrow	364	58–226	15–87	7–251	66–757	33–400	98–662
Oats	353.6	57–219	14–85	7–244	64–735	32–389	95–644

Source: reference [16]

Table 1. Contribution of nutrients and sodium from untreated wastewater and water requirements of demandant crops

A significant quantity of nitrate leaching through soil subsequently becomes unavailable for plants; this does not necessarily represent a problem, as nitrate is continuously supplied to soil via wastewater. More important, the presence of nitrates in subterranean water is related to occurrence of methemoglobinemia disease in infants ingesting nitrate at levels higher than 45 mg/L via drinking water [39]. The quantity of nitrogen washed out from soil depends on the irrigation rate, the frequency of rain events, the type of crops sown and the characteristics of the soil [40]. The amount of nitrogen that can be applied to soil to produce minimal nitrate leaching rates depends on the demand of crops, which usually varies between 50 and 350 kg of nitrogen per hectare [40]. Such demand is within or slightly above the amount of nitrate supplied by treated wastewater. In this sense, the limited removal of nitrogen by wastewater treatment would not significantly affect the input of this macronutrient to agricultural soils.

Phosphorous is another plant macronutrient, which is very scarce in soil, at the point it needs to be added through the application of fertilizers. Due to its stability and low solubility, this nutrient can be accumulated in soil. Wastewater normally contains small amounts of phosphorous, so its use for irrigation is beneficial to plants and it does not impact negatively upon the environment, even if applied consistently for long periods of time [40–41]. The recycling of phosphorous and nitrogen in wastewater-irrigated soils is important because it allows closure the P cycle rather than its breakage. Breakage of the cycle occurs when phosphorous is removed from wastewater during treatment, becoming trapped in sludge and dumped to confinement sites or landfills. An advantage of the availability of phosphorus in wastewater is that it is partly bound to organic components and thus it cannot form complexes with iron or aluminum ions upon its entry to soils [16]. In contrast to phosphorous, potassium is contained in soil at high concentrations (around 3% of the lithosphere) but in chemical forms that impede its bioavailability. As a result it is necessary to add potassium to soils via fertilizers. Approximately 185 kg of potassium per hectare are required to cultivate some crops [16]. Sewage contains low concentrations of potassium, insufficient to cover the theoretical demand in most cases. Meeting the demand for potassium in irrigated soils will depend on the amount of wastewater supplied at each irrigation event, the wastewater quality and the frequency of irrigation. Fertilization with potassium has not resulted in adverse impacts to the environment [42]. Recycling nutrients by the reuse of wastewater promotes savings in energy, which would otherwise be consumed in the production of fertilizers [43]. In particular, the recycling of phosphorus is important since the world's phosphorus reserves are becoming scarce [44]. Fertilizing agricultural soils by the reuse of wastewater invariably leads to the increase of crop yields. An example of this can be found in Mezquital Valley, Mexico [45]; in this respect, Table 2 shows the differences in the agricultural production in croplands of Mezquital Valley when either untreated wastewater or groundwater is used for agricultural irrigation.

Crop	Crop yield (tons/ha)		Increment (%)
	Untreated wastewater	Groundwater	
Corn	5.0	2.0	150
Barley	4.0	2.0	100
Tomato	35.0	18.0	94
Oats for forage	22.0	12.0	83
Alfalfa	120.0	70.0	71
Chili	12.0	7.0	70
Wheat	3.0	1.8	67

Source: references [16, 52]

Table 2. Comparison of crop yields for some vegetables in plots where wastewater and groundwater are used for agricultural irrigation (Mezquital Valley, central Mexico)

The use of wastewater in Mezquital Valley has also contributed to changing the landscape of the zone, transforming barren soils into productive and green vibrant soils, as shown in Figure 2.



Figure 2. Comparison of untreated wastewater irrigated (right side) and rain-fed (left side) croplands from Mezquital Valley, central Mexico

2.1.2. *Benefits in soil quality*

In order to define the improvements in soil quality produced by the application of treated/untreated wastewater it is necessary to establish the use of the irrigated soil. It is known that soil complies with five ecological functions: a) a medium for plant growth (including agriculture); b) a biodiversity pool and habitat for plants and (micro and micro) fauna; c) a carbon sink; d) a storage, filter and transforming medium for nutrients, pollutants and water; and, e) a landscaping and engineering medium. [46]. This chapter focuses on the functions of soil as a medium for plant growth as well as in its role as a transforming medium for nutrients and pollutants.

In addition to the continuous supply of nutrients to the soil, irrigation with treated/untreated wastewater confers significant improvements in soil quality. Favorable changes reported in irrigated soils comprise: a) an improvement in the physical structure of soil; b) an increase in soil microbial activity; and, c) the improvement of the soil performance as a wastewater treatment system.

Improvement of the physical structure of soil. The physical structure of soil is defined as the arrangement of the solid particles and the size, shape and interconnection of pores and voids. Soil structure is closely related to its capacity to store and transport gases and water (and thus dissolved substances) [47]. Gas exchange between the soil and the atmosphere determines whether aerobic, anoxic or anaerobic conditions prevail within the soil. This in turn regulates the metabolism of soil microorganisms and impacts, inter alia, upon the nitrogen fixation, the transformation of soil organic matter and the degradation of pollutants. Additionally, the physical structure of soil affects the plant growth by influencing root distribution and thus the ability to take up water and nutrients [48]. Improvements in the physical structure of soil are

related to the increase in both the stability of the soil aggregates and soil porosity. The enhancement of the physical structure of soil results in a rise in agronomic productivity, the augmentation of water infiltration through soil to the aquifer and a decrease in erodibility [49]. The hierarchical theory of aggregation proposes that microaggregates (particle size below 250 μm) in the soil are formed initially by the attachment of organic material to some inorganic components of soils (e.g. clay and hydroxides); in turn these microaggregates join together to form macroaggregates (particle size above 250 μm). Alternatively, macroaggregates can form around the particulate organic matter, while exudates produced by soil microorganisms serve as cementing agents, making micro and macroaggregates more stable [50]. Microaggregates can be also formed from bacterial colony clusters which use bacterial polysaccharide exudates to bind with clay particles. The clay particles act as a protective shell for clusters and macroaggregate formation continues as described above [51].

Since the formation of aggregates in the soil is related to the presence of organic matter, and in some cases microorganisms, it might be expected that the continuous supply of these two elements via wastewater would result in the increased formation and stability of soil aggregates and thus an improvement in the physical structure of soil. For example, the study referred in [52] establishes that increased soil microbial activity due to the augmentation of organic carbon content by the application of wastewater impacts positively upon the stability of soil aggregates. Furthermore, there are substances contained in wastewater other than organic matter and microorganisms that may contribute to the formation and stability of soil aggregates. Calcium and magnesium cations, which are abundant in wastewater, increase the formation of microaggregates through cationic bridging between clay and organic matter, resulting in aggregation. In arid soils and soils with low organic matter contents, insoluble calcium and magnesium carbonates can trigger the formation of soil micro and macroaggregates [51]. Additionally, calcium can inhibit clay dispersion, and thus the breakup of aggregates, when sodium concentration increases in soil [53]. Dissolved organic matter in wastewater can form complexes with iron and aluminum in soil forming mobile organo-metallic compounds which can further precipitate and act as cores for microaggregates formation. Particulate organic matter (i.e. suspended solids in wastewater) may enhance the binding of microaggregates to subsequently form macroaggregates; for instance, extracellular polysaccharides of microorganisms in the surface of suspended solids can act as binding agents in the formation of macroaggregates [54]. In the case of phosphorous, the formation of insoluble aluminum and calcium phosphates in the soil can induce the formation of microaggregates and additionally it may act as a macroaggregate binding agent [55]. The entry of certain chemicals to the soil via wastewater increases the stability of soil aggregates. For example, hydrophobic substances (e.g. surfactants, lipids and hydrocarbons) decrease the wettability of aggregates by inducing water repellency, which in turn leads to increased cohesiveness and low decomposition rates of soil aggregates [51]. Agricultural activities in wastewater irrigated soils may also contribute to the improvement of the physical structure of soil. Previous studies have found that some crops (i.e. maize, alfalfa and leguminous plants) have beneficial effects on the conservation of the physical structure of soil. Aggregation of soil particles tends to increase when planting crops characterized by high density and long length of roots; this is because chemicals released by roots (i.e. mucilage) enhance the stability of soil

aggregates in the rhizosphere by increasing the bond strength and decreasing the wetting rate [56]. According to the study reported in reference [57], roots of leguminous crops increase the aggregation of soil particles. Corn (*Zea mays*) residues (leaves and shoots) also increase aggregation of soil particles compared with other crops; this is attributable to the liberation of phenolic compounds from plant tissues, since phenols favor the agglutination of particles and prevent wetting [57–58]. Municipal and industrial wastewater may also be a source of phenolic compounds to soil through irrigation, producing similar effects to those of corn wastes [59]. The study referred to in [58] demonstrated that the stability of soil aggregates is high for continuous cultivation of alfalfa (*Medicago sativa*), while the opposite effect was observed for soybean. This is attributable to the low concentration of phenols in the latter [60]. Some studies have addressed the changes in the physical structure of agricultural soils caused by long-term irrigation with wastewater. The results of these studies show a decrease in soil porosity caused either by occlusion of pores by the suspended solids contained in wastewater or by the augmentation of micropores (radius < 0.01 μm) in the soil matrix [61–62]. Depending on the method of water application during irrigation, an increase in the compaction of soil may be observed in the plot after an irrigation event [63]. Soils irrigated by flooding exhibit high compaction while water dropping effects (erosion) may be observed in soils irrigated by spraying. In any of both cases, wastewater irrigated soils exhibit large populations of earthworms which may assist in the formation and connection of pores within the soil matrix. Undoubtedly wastewater contains agents that improve the physical structure of soil. However, studies performed so far show contrasting results, either an increase in the soil microporosity or soil compaction. It is therefore necessary to carry out studies aimed at measuring changes in the physical structure of soil throughout several irrigation cycles and for longer periods (months or years); additionally, it is of interest to assess changes in the physical structure of soil at landscape level (piedmont or catena), as it may be useful for evaluating the horizontal displacement of soil particles and nutrients.

Increase of soil microbial activity. Either due to the extra supply of organic carbon or because of the addition of microorganisms via wastewater, microbial activity in wastewater irrigated soils tends to be higher than that found in non-irrigated soils [64–65]. This increase in the microbial activity of the soil brings benefits to both agriculture and the development of flora and fauna in the soil ecosystem. According to the study reported in reference [66], the C/N ratio in soils irrigated with wastewater for long periods tends to decrease by up to 45%, which implies an improvement in the nutritional conditions for soil microorganisms. The authors report an increase in the population of copiotrophic and oligotrophic bacteria (234 and 217%, respectively), as well as in the populations of actinomycetes (234%) and fungi (206%) in soils irrigated with wastewater for 100 years compared with those populations found in non-irrigated soils. Rises in the metabolic activity of soil, measured as the production of ATP and enzymatic activity have been also reported [65–66]. According to reference [66], soil enzymatic activity remained unchanged 20 years after wastewater irrigation ceased. In contrast, the study referred to in [67] shows that elevated microbial activity in soils irrigated with treated wastewater decreases after few days without irrigation. Due to the augmentation of the populations of bacteria, actinomycetes and fungi in the irrigated soil, a rise in the rhizospheric activity is experienced, resulting in: a) the increase in the growth and development of plants;

b) high rates in stabilization of organic matter entering the soil through wastewater; c) higher performance of the depuration of wastewater and degradation of the pollutants fixed in the soil in comparison with non-irrigated soils; and, d) the improvement in the formation and stability of soil aggregates. The latter may be explained by the role of polysaccharides exuded by bacteria as transient binding agents, which initialize aggregation of soil microaggregates [67]. The transformation of carbon and nitrogen by soil microorganisms supports the proliferation of soil (micro and macro) fauna which is essential for soil formation as well as for the development of plants. According to the work referred to in [68], the use of treated wastewater to irrigate an agricultural soil over 20 years has resulted in the improvement of the metabolic efficiency of soil microflora to transform carbonaceous and phosphorous substances into nutrients readily available to plants and macrofauna.

Soil biomass has proven to be capable of adsorbing a certain proportion of heavy metals contained in the wastewater. For instance, the study referred to in [69] found biosorption rates for cadmium and nickel within the range of 5 to 55 mg/g of biomass in a soil that had been irrigated with wastewater for two decades. In that soil, the predominant bacteria after irrigation were *Enterobacteriaceae* and *Pseudomonas*.

The effect of wastewater irrigation on soil nitrogen fixing organisms has been little studied. An increase in soil nitrifying activity accompanied by a low rate of denitrification has been observed in wastewater irrigated forest soils [70], while in the study referred to in [71] a peak in N_2O production in a soil irrigated with treated wastewater was reported, followed by an immediate drop in gas production. So far, the metabolic processes performed by different soil microbial species in wastewater irrigated soils have been little explored. However, it is important to keep in mind the important role that soil microorganisms play in both the development of the soil and plants as well as in the purification of wastewater when planning agricultural systems based on the reuse of wastewater. Even when soil microbial populations show some kind of resilience to a wide variety of contaminants, some other chemicals can cause not only toxic effects to soil microorganisms but the proliferation of pathogenic organisms and the occurrence of antibiotic resistance within the agricultural soils.

Improvement of soil performance as a wastewater treatment system. As it is known, the application and infiltration of wastewater through soil results in its purification. In practice, specific wastewater treatment systems are based on soil infiltration, which have been demonstrated to improve water quality to levels obtained using tertiary treatment systems [72–73]. Purification of wastewater is one of the ecological functions of soil; through this mechanism, soil maintains, at least partially, the quality of surface and groundwater bodies. The extent at which this natural system works is highly variable, from almost nonexistent to very high, depending on local conditions and types of pollutants. Table 3 shows the extent to which pollutants in wastewater are removed by infiltration through the soil. The application of wastewater to soil reduces the content of pathogenic microorganisms by 6–7 log units for bacteria and 100% for helminths and other protozoa. Total organic carbon can be reduced by up to 90%, while levels of recalcitrant compounds in wastewater, such as phosphorus (20–90%), nitrogen (20–70%), and metals (70–95%) are also reduced dramatically. In sewage, organic phosphorus (5–50 mg/L) is biologically converted to phosphate; subsequently, in

alkaline or calcareous soils, phosphate precipitates with calcium to form calcium phosphate and remains available for plants. In contrast, in acidic soils phosphate reacts with iron and aluminum oxides to form insoluble compounds, which are unavailable to plants. Sometimes soluble phosphate is initially immobilized by adsorption onto soil particles and then slowly returns to insoluble forms, allowing for further adsorption of mobile phosphate. This process is generally known as phosphate aging [72].

Variable	Effect
Organic matter	Biodegradable material is reduced by more than 90%, while less readily biodegradable material is adsorbed and later biodegraded or volatilized.
Nitrogen	Nitrogen is removed from water at a level similar to tertiary treatment systems by transformation in soil as well as by assimilation by soil microorganisms and plants.
Phosphorus	Phosphorous is reduced to levels of 1 mg/L or less by assimilation by plants.
Microorganisms	Helminth eggs and protozoa are easily removed by straining in the soil surface; bacteria and viruses can also be adsorbed onto the soil particles and then desiccated or killed by indigenous soil microorganisms. The performance of these processes depends on the texture, physical structure and organic matter content of soil.
Heavy Metals	Heavy metals can be removed by the formation of complexes with soil organic matter, precipitation or methylation at efficiencies of 70–95%.
Toxic organic compounds	Most are retained in soil and then biodegraded at different rates.

Table 3. Processes in soil that improve the quality of the wastewater, relative to selected parameters

Most of the organic compounds (natural and synthetic) in sewage are rapidly transformed in soil to stable, and in some cases non-toxic, organic compounds (e.g. humic and fulvic acids). Actually, soil biodegrades a greater amount and variety of organic pollutants than that reported for water streams. Wastewater application to soil under controlled conditions (e.g. limited irrigation rate and intermittent flooding) permits the biodegradation of hundreds of kilograms of carbonaceous substances per hectare per day, with no impact on the environment [72]. Total organic carbon levels in wastewater are dramatically reduced from levels of 80–200 mg/L to 1–5 mg/L in the infiltrated water [74]. Heavy metals can be removed from wastewater during soil infiltration and confined within the organic domain of the soil for several hundred years. Metals are retained in the surface layer of the soil either by complexation with soil organic matter or by precipitation at high pH values. Only a small fraction of metals infiltrates to lower layers of the soil profile and even less can be assimilated by crops. For instance, around 80–94% of cadmium, copper, nickel, and zinc can be removed in the first 5–15 cm of the soil profile, 5–15% is leached to lower layers and only 1–8% can be absorbed by grass [75]. A similar process occurs with fluorine [76]. This phytoremediation process is used to treat wastewater in planned natural treatment systems such as wetlands. However, it is necessary to be aware that some edible crops are able to take up heavy metals to a greater degree than grasses [77].

The capability of soil to act as a filter and transforming medium for wastewater pollutants can be observed in both long-term and newly wastewater irrigated soils [72, 78]. The operation of this natural purification system is closely related to the physical and chemical properties of the soil and thus modifications in soil characteristics caused by irrigation with wastewater may either improve or worsen the performance of this natural wastewater treatment system. The increase in the soil organic matter content is the main factor resulting in an improvement in the removal of biological, organic and inorganic pollutants as wastewater leaches through the soil. This is because soil organic matter promotes the immobilization of pollutants either by adsorption or formation of complexes, while at the same time stimulating the proliferation of degrading microorganisms [78–79]. Regularly, heavy metals are fixed in the upper layers of the soil profile by complexation with organic matter [65], thus organic matter enrichment in wastewater irrigated soils results in greater retention of heavy metals by the solid matrix. Heavy metals cannot be biodegraded but they may be modified by soil microorganisms. Biological methylation of metals and metalloids, such as selenium, arsenic and mercury, has been reported in wastewater irrigated soils. It is expected that this process is elevated in wastewater irrigated soils, where microbial biomass occurs at higher levels than in non-irrigated soils. Methylation of heavy metals leads either to reduced toxicity or increased loss of metals in soil through volatilization [80–81]. Another process observed in long-term wastewater irrigated soils, related to those aforementioned, is the potential of soil microorganisms to develop resistance to the harmful effects caused by the presence of heavy metals in the solid matrix [69, 82]. Such resistance is similar to that developed to antibiotics and has been reported for cadmium, chromium, zinc and nickel in soils irrigated with wastewater over the long term [69, 83]. It is plausible that the expression of these resistances results in an increase of heavy metal methylation in the soil, which allows soil microorganisms to survive and to continue with those metabolic functions that increase agricultural productivity and purify wastewater. With regard to organic contaminants, the increase in the soil organic matter content produces, in most cases, an incremental boost in the adsorption of solutes onto soil particles. Studies referred to in [84] found increased adsorption of organic contaminants (i.e. pesticides, pharmaceuticals and estrogenic hormones) in long-term wastewater irrigated soils compared to rain-fed soils from the same agricultural area. Organic compounds displaying high hydrophobicity are adsorbed by soil not only faster and to a greater extent but with greater strength than is observed for semi-polar and polar compounds [85]. The increase in the hydrophobicity of soil due to the application of wastewater increases the capacity of such soils to strongly retain non-polar organic contaminants within the solid matrix. The increase in the adsorption of organic pollutants by soil results in an extended retention time in the solid matrix, encouraging biodegradation processes. Similar to the results reported for adsorption, higher rates of biodegradation of organic pollutants have been observed in treated/untreated wastewater irrigated soils compared to non-irrigated ones [86]. This may be caused, on the one hand, by the continuous supply of organic matter to the soil via wastewater, which can be used by soil microorganisms as co-substrate in the biodegradation of target organic pollutants, and on the other hand, by the prolonged exposure of soil organisms to pollutants. The latter case can be understood as the acclimation of the degrading organisms to the occurrence of organic pollutants in the soil followed in the short term by the acquisition of the capability for using organic contaminants as a carbon source. The increase in the soil organic matter content caused by wastewater irrigation has a positive impact not only in the adsorption of organic compounds but also on the retention by soil of wastewater–

borne pathogens. This is due to the high affinity of the cell membranes to the organic domain of soil. The study referred to in [87] reports a higher adsorption of enteric bacteria *Escherichia coli* and the enteric protozoa *Giardia lamblia* in long-term wastewater irrigated soils compared with long-term groundwater irrigated soils from the same agricultural zone.

In general terms, an increase in pH values has been observed in agricultural soils irrigated with treated/untreated wastewater; although in less cases soil pH tended to decrease following the application of wastewater [81]. The first phenomenon is attributed to the continuous addition of salts (carbonates, calcium, magnesium, sodium) in wastewater. The second case is explained by the high mineralization rate of organic matter in the irrigated soil, which is highly dependent on the soil type, the climatic conditions of the site, and the quality of wastewater, among other reasons. The increase in soil pH, in combination with the continuous supply of organic matter, results in the buffering of soil pH, which prevents the drop of soil pH values during rain events (including acid rain). Stabilization of soil pH values also contributes to the retention of heavy metals in the surface layers of the soil by the formation of insoluble basic salts. Furthermore, basic values of soil pH can facilitate the adsorption of neutral and basic organic contaminants; as these compounds tend to be better adsorbed to neutral and basic soils than to acidic ones.

Since wastewater irrigation improves the physical structure of soil (i.e. increased formation and greater stability of aggregates), aerobic conditions may be maintained within the soil matrix; which in turn contributes to an increase in the aerobic biodegradation rate of organic pollutants. Additionally, an increase in the adsorption of pollutants can be achieved in better structured soils due to the increase in the specific surface area of soil particles. Moreover, higher biodegradation of the adsorbed contaminants can be expected as long as they remain available to microorganisms after adsorption. In irrigated soils where occlusion of the pores by the suspended solids in wastewater occurs, anoxic conditions may be achieved. Under such conditions, toxic species of heavy metals are chemically reduced into non-toxic species (e.g. Cr^{+6} into Cr^{+3} and As^{+5} into As^{+3}), then they may be immobilized by the formation of insoluble hydroxides. The extent to which wastewater irrigation contributes to the function of the soil as filter and degradation medium for pollutants is just beginning to be studied. The potential of soil to act as an efficient wastewater depuration system is a powerful argument to convince policy makers that agricultural irrigation with treated/untreated wastewater can be an appropriate strategy to simultaneously solve problems of water stress and low agricultural productivity with no negative impacts in the quality of water sources surrounding the irrigation site. This, of course, is achieved when all of the appropriate precautions to avoid contamination are taken at each site.

2.2. Negative impacts of wastewater reuse in agriculture

The main drawback of reusing treated/untreated wastewater in agriculture is the pollution of soil, the potential contamination of crops and water sources, and the inherent risk of harmful effects that contamination poses to the exposed organisms. Even when soil acts as an efficient living filter to remove, inactivate and transform the pollutants contained in wastewater, it is not fully effective at eliminating some of them. Moreover, as a result of the increasing industrial

development, wastewater irrigated soils continuously receive newly synthesized substances, which may negatively impact the effectiveness of soil as a treatment system by poisoning the degrading microorganisms, destroying the physical structure of soil or damaging the natural cycles occurring within soil. The pollutants received by soil via wastewater may be different in developing and developed countries. Examples of this include pathogenic microbial agents. In developed countries most wastewater is treated prior to reuse and thus pathogens are not present in irrigation water, while in developing countries untreated wastewater is used in most of cases. Pathogens vary for different zones; for instance, the enteric protozoa *Giardia* is commonly found in wastewater of developing countries (Latin American and African countries), while the parasitic protozoa *Cryptosporidium* occurs in developed countries (United States and western European countries). Similar to microorganisms, some organic pollutants can be found in wastewater from developing countries and not in developed countries. Examples include some herbicides (e.g. DDT and atrazine) whose use is restricted in developed countries; on the other hand, nanomaterials and new-generation antibiotics, all of which are much more likely to occur in wastewater of developed countries. The determination of pollutants in soil initially requires specific sampling methods which take into consideration the heterogeneity of the soil matrix. In addition, specialized extraction techniques able to efficiently isolate analytes (or microorganisms) from soil are necessary prior to analysis. Specialized analytical methods have been developed and validated for the determination of trace contaminants and microorganisms in soil. However, in most cases, these methods are time-consuming, expensive and require the use of specialized reagents and personnel. It is therefore necessary to continue research towards the development of simpler and environmentally-friendly analytical techniques. Determining the occurrence and concentration of contaminants in soil is a task that requires a significant effort; however, this is only a part of the job. The study and understanding of the environmental fate of contaminants in soil is also a priority task to accomplish truly useful environmental risk assessment studies comprising soil, water sources, crops, farmers and consumers. Knowing the environmental fate of contaminants in the soil is necessary to understand the potentialities and limitations of each soil as a natural purification system of wastewater and an effective tool to define the capacity of each site to support wastewater irrigation in agriculture. Since soil is a complex and heterogeneous matrix, the fate of contaminants can vary significantly from one site to another. In this sense, it is worth defining which parameters are determinant in the fate of contaminants within soil and, on the basis of this knowledge, elucidating the fate of contaminants in other sites using mathematical tools to achieve such extrapolations. In this section, attention will be focused on pathogenic microbial agents, heavy metals and organic pollutants contained in municipal wastewater. The occurrence of such pollutants in wastewater-irrigated soil as well as their environmental fate in soil is addressed; additionally the most significant effects of these contaminants will be treated in some detail. Lastly, perspectives for further studies on the occurrence and fate of the studied pollutants in soil are presented.

2.2.1. Soil pollution by pathogenic microbial agents

Contamination of soil and crops by pathogenic agents is the effect of wastewater reuse in agriculture that receives most attention from environmentalists and scientists. Municipal

wastewater contains a huge quantity and variety of bacteria, protozoa and viruses passed from human and animal feces and urine; therefore this water is a vector for intestinal infections (although some other diseases can spread from the environment via wastewater). Exposure may be direct through contact or ingestion of wastewater and soil, or indirect through contact with sick people or by ingestion of polluted crops, meat or milk. There are four groups at risk: a) farmers and their families, b) crop handlers, c) product consumers and d) people living nearby to irrigated fields. For any of these groups children and elderly are the most vulnerable, especially when they are undernourished. The most affected group is agricultural workers due to their high exposure to wastewater and contaminated soils [18]. Table 4 shows the risk of infection of water-borne diseases for vulnerable groups in irrigated areas using treated/untreated wastewater.

Effects caused by microbial pollution in soil. Several diarrheal outbreaks have been associated with the use of wastewater to irrigate [18, 88]; however, since this occurs in places where sanitation, hygiene practices and drinking water are of low quality it is always difficult to define their specific contribution to the total diseases burden. Cholera, caused by the bacterium *Vibrio cholera*, is one infection closely linked to wastewater irrigation in poor countries. Other intestinal diseases related to the use of wastewater to irrigate are traveler's diarrhea caused by *Escherichia coli*, shigellosis caused by *Shigella* spp., gastric ulcers caused by *Helicobacter pylori*, giardiasis caused by the parasitic protozoan *Giardia intestinalis* and amebiasis caused by *Entamoeba histolytica*. Additionally, viral enteritis (caused by rotaviruses) and Hepatitis A are the most reported viral infections caused by consumption of polluted vegetables [89]. Some studies [90] report skin diseases, such as dermatitis (eczema), in farmers that come into contact with untreated wastewater and wastewater irrigated soil. Nail problems in farmers, such as *koilonychias* (spoon-formed nails), have also been reported as related to the presence of fungi in wastewater irrigated soils [91]. Health and growth problems have been observed in cattle that consume forage produced by wastewater irrigation. Furthermore, in low income areas where water is scarce, cattle are not only fed with fodder grown using wastewater but also they are allowed to drink the wastewater used for irrigation. Some protozoa can survive in the surface layers of soil or even in aerial parts of crops; animals can be infected after eating these crops, although this is a remote way of transmission. There is some evidence indicating that beef tapeworm (*Taenia saginata*) can be transmitted from livestock fed with wastewater-irrigated forage to meat consumers. Furthermore strong evidence indicates that cattle grazing on fields freshly irrigated with raw wastewater or drinking from raw wastewater canals or ponds can become heavily infected by *Cysticercus bovis*, the early stage of the *Taenia saginata* life cycle [88].

Microbial agents in wastewater irrigated soils. The study of microbial contamination by the use of treated/untreated wastewater in agricultural irrigation is focused in the pollution of crops rather than the soils receiving wastewater. This is because, on the one hand, a greater number of people are exposed to pathogenic microorganisms through consumption of contaminated crops, meat and milk than by direct contact with irrigated soils, and on the other hand, the difficulties in the analysis of microorganisms in soil; for instance, the inherent problems of extracting microorganisms from such a complex matrix as the soil. Studies in the

Group exposed	Helminth infections	Bacterial/viral infections	Protozoan infections
Consumers	Significant risk of <i>Ascaris</i> infection for both adults and children consuming vegetables contaminated with helminth ova.	Cholera, typhoid and shigellosis outbreaks reported due to the consumption of polluted crops. Seropositive responses for <i>Helicobacter pylori</i> in crop consumers. Increase in risks of suffering non-specific diarrhea when concentration of thermotolerant bacteria in wastewater used for irrigation exceeds 10^4 CFU/100 mL.	Evidence of parasitic protozoa found on the surface of wastewater-irrigated vegetables, but no direct evidence of disease transmission.
Farm workers and their families	Significant risks of <i>Ascaris</i> infection for both adults and children in contact with untreated wastewater and irrigated soils. Risk remains, especially for children, when wastewater presents more than 1 nematode egg per litre. Increased risk of hookworm infection in farmers.	Increased risk of diarrheal diseases for children in contact with wastewater when it exceeds 10^4 CFU/100 mL for thermotolerant coliforms. Elevated risk of <i>Salmonella</i> infection in children exposed to untreated wastewater and wastewater irrigated soil. Elevated seropositive responses to norovirus in adults exposed to partially treated wastewater and wastewater irrigated soil.	Risk of <i>Giardia intestinalis</i> infection insignificant for contact with both treated/untreated wastewater and soil. Increased risk of amoebiasis observed due to contact with untreated wastewater and wastewater irrigated soil.
Nearby communities	High risk of infections when flood and furrow irrigation is used. <i>Ascaris</i> transmission not studied for sprinkler irrigation.	Sprinkler irrigation with untreated wastewater and high aerosol exposure associated with increased rates of bacterial infections due to the use of partially treated wastewater (10^4 – 10^5 CFU/100 mL or less). No risks of viral infection associated with sprinkler irrigation.	No data of protozoan infections transmission during irrigation with wastewater.

Table 4. Summary of health risk associated with the use of wastewater in agriculture

Mezquital Valley, Central Mexico, found the occurrence of fecal contamination indicators (*Escherichia coli*). *Giardia lamblia* cysts and helminth eggs (*Ascaris lumbricoides*) at different depths of long-term wastewater irrigated soils. Results shown in Figure 3 evidence the accumulation of the three microorganisms in the first few centimeters of the soil profile, indicating that infectious agents are removed from wastewater at the beginning of percolation through soil; such removal can be achieved by several physical and chemical phenomena. In this study, the content of pathogenic microorganisms in soils with different time under irrigation was also evaluated. Results showed that the accumulation of microorganisms in the

tested soils is not related to the time under irrigation, suggesting that soils have mechanisms to inactivate and/or destroy these microorganisms after irrigation.

As mentioned above, different types of microorganisms can be found in wastewater irrigated soils depending on the zone where reuse is taking place. For example, the study referred in [92] showed a higher prevalence of *Cryptosporidium* spp. compared with *Giardia* spp. in wastewater irrigated and manure amended soils of dairy farms in southeastern New York. *Cryptosporidium* is a protozoan commonly found in developed countries, while different species of *Giardia* are widespread in developing countries. In this respect, the study referred in [93] found the occurrence of *Ascaris lumbricoides*, hookworm and *Trichiuris trichiura* in 69% of the soil samples taken in an untreated wastewater irrigated area in West Bengal, India.

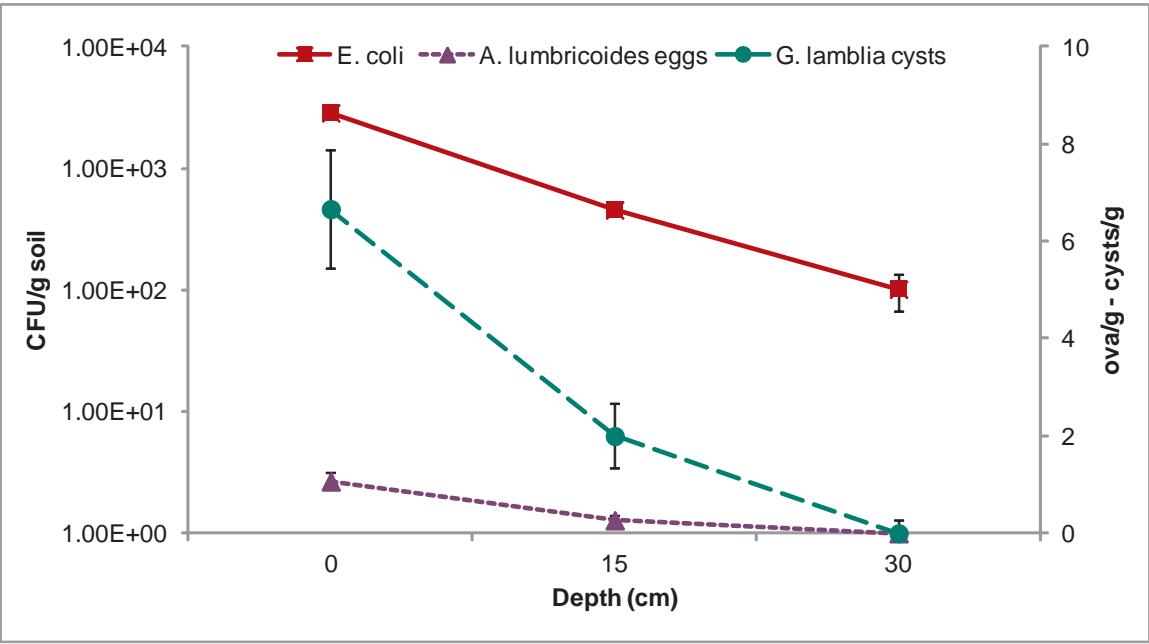


Figure 3. Abundance of three pathogenic microorganisms in a long-term wastewater irrigated soil at different depths

The entry of antibiotic-resistant pathogens (ARPs) and antibiotic resistance genes (ARGs) into the soil via wastewater is an emerging issue. Since municipal wastewater contains both sub-therapeutic amounts of antibiotics, ARPs and ARGs –which occur to a greater extent when sewer systems combine municipal and hospital wastewater– [94], these substances can reach the soil, modifying the dynamic of soil microbial populations. Antibiotic resistance may occur naturally in the soil, and to a greater extent in the rhizosphere, which functions as a hotspot for both antibiotic-resistant bacteria and ARGs [32]. Previous studies have found the presence of opportunistic pathogens (*Stenotrophomonas maltophilia*, responsible for respiratory tract infections and endocarditis) in the rhizosphere of *Brassicaceae* type plants [95]. The transfer of ARGs from these opportunistic bacteria to human pathogens reaching the soil through wastewater has not yet been demonstrated. The ARPs reaching the soil through wastewater may survive on the soil surface and, if conditions are appropriate, reproduce or migrate to

surface and groundwater sources. ARGs may be mobilized into aquifers by infiltration of wastewater or into surface water sources by runoff. So far a relationship between the presence of traces of antibiotics in wastewater and the occurrence of antibiotic resistance in the irrigated soil has not been categorically established. In previous studies the incidence of two sulfonamide resistance genes (*sul1* and *sul2*) was determined in the Mexico City wastewater, agricultural soils irrigated with such wastewater over different time periods and rain-fed soils [96]. The authors found the presence of ARGs in the three analyzed matrices; the concentration of resistance genes was 150 to 1500 times higher in irrigated soils than in non-irrigated ones. The occurrence of ARGs was positively related to the time under irrigation, with a higher content of resistance genes occurring in *Enterococci* bacteria living in soils irrigated for longer periods of time [96]. Such behavior may indicate that prolonged irrigation with wastewater promotes both the proliferation of indigenous ARPs in soil, due to the high and constant supply of nutrients via wastewater, and the increase in the assimilation of resistance genes due to the higher biomass content in old wastewater irrigated soils. Conversely, studies reported in [97] found that the abundance of isolates resistant to tetracycline, ciprofloxacin, sulfonamides and erythromycin were identical in wastewater irrigated soils and freshwater irrigated soils despite the high load of ARGs and ARPs in the wastewater used for irrigation. In this regard, the study in reference [98] found, by comparing the resistance of soils irrigated either with wastewater or groundwater, that *Enterococci* bacteria in freshwater irrigated soil were highly resistant to a greater number of antibiotics (erythromycin, tylosin, tetracycline, and ciprofloxacin) than long-term wastewater irrigated soil, which showed resistance to lincomycin and daptomycin. Furthermore, no differences were found in the content of ARPs when wastewater and freshwater irrigated soils were compared, suggesting that ARPs rarely survive after they enter soil via wastewater. Even though it seems unlikely that development of antibiotic resistance to human pathogens in wastewater irrigated soil is related to the input of antibiotics and resistant organisms via wastewater, it is worth, as a next step, studying the exchangeable genetic material (e.g. plasmids), since such material can be assimilated by soil microorganisms, inducing antibiotic resistance. Many questions remain about the mechanisms leading to the transference of this type of genetic material [99].

Microbial pollution in crops. Crops are polluted by direct contact with wastewater during irrigation. Pollution of the edible parts of plants depends not only on the quality of water, but also on the quantity applied to soil, the irrigation method and the type of crop. For example, zucchini when spray-irrigated with wastewater accumulate higher levels of pathogens on their surface than other crops. Zucchini have a hairy and sticky cover and grows close to the ground, which favors the attachment of pathogens. Microbial contamination of crops can occur not only as a result of wastewater irrigation but also during washing, packing, transportation and marketing. These problems are frequently not addressed, giving the impression that irrigation is the only source of microbial pollution [100]. In a previous study, referred in [101], it was found that less microbial pollution of crops is caused if irrigation is performed by subsurface dripping than through sprinklers, furrows or flooding. Moreover, the study reported in [102] showed that subsurface irrigation does not pollute crops even when using wastewater with $6-7 \times 10^5$ CFU/100 mL of fecal coliforms and 225 helminth ova/L. Microbial pollution of crops also depends on the type of crop. Fruits from trees are rarely polluted when

irrigation is not provided using sprinklers (this is not a common procedure used to apply wastewater since sprinkler heads tend to become clogged). Fruits grow far from the watering sites when furrow and flood methods are used. The microbial contamination of crops in wastewater irrigation systems is closely related to the survival of microorganisms. Table 5 shows the survival times of some pathogens in agricultural soils and crops irrigated with wastewater.

Pathogen	Survival time (days)	
	Soil	Crops
<i>Ascaris lumbricoides</i> eggs	180	30
<i>Salmonella</i> spp.	80	25
Fecal coliforms	<70, but usually <20	<30, but usually <15
<i>Vibrio cholera</i>	<20, but usually <10	<5, but usually <2
<i>Entamoeba histolytica</i>	<20	<10
<i>Trichuris trichiura</i> eggs	>180	<60, but usually <30
<i>Taenia saginata</i> eggs	>180	<60, but usually <30
Enterovirus	<40	<20

Source: references [105–106]

Table 5. Survival of selected pathogens in soil and crops irrigated with wastewater

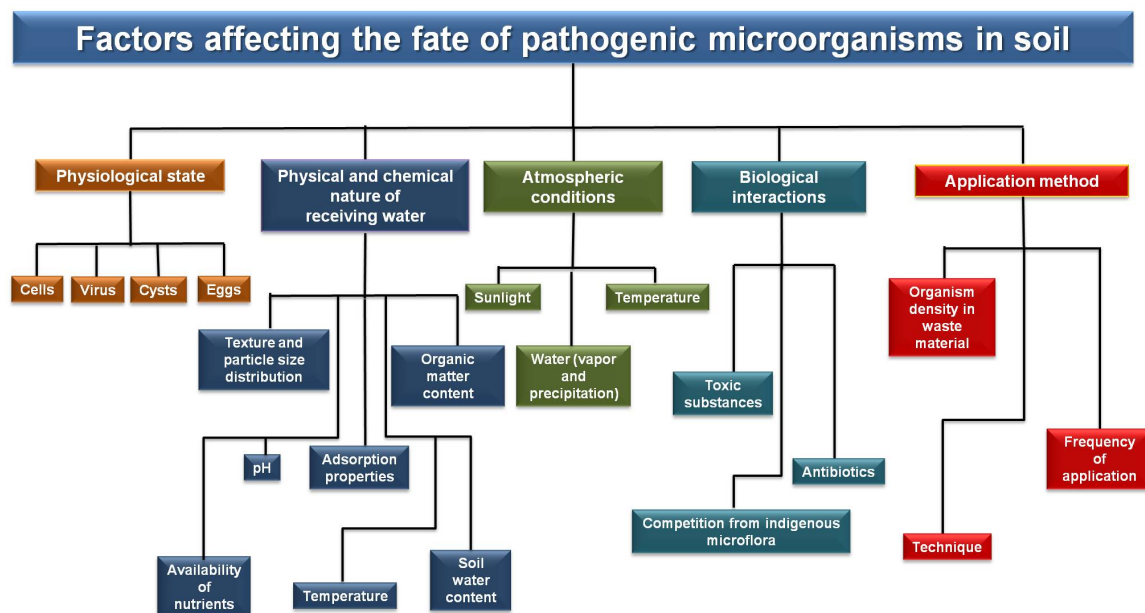
Both pathogenic and non-pathogenic microorganisms display differences in their survival in soil and crops. For instance, the non-pathogenic fecal coliform indicator *E. coli* can survive in soil for nearly a month, while the pathogenic strain of *E. coli* O157:H7 survives at most for 14 days in spinach leaves [103]. It is known in some detail that survival of pathogenic bacteria can increase by internalization within the plant tissues [104]. Previous studies indicate that *E. coli* can translocate from soil to leaves of lettuce through the root system [107]. In contrast, the results reported in reference [108] indicate that translocation of pathogenic bacteria to the edible parts of crops via the root system is quite unlikely. It is more likely that pathogens enter to the edible parts of crops through wounds in vegetal tissues [109]. Wounded tissues have been demonstrated allow the entrance of *Salmonella* and *E. coli* to lettuce and tomato plants [110–111]. Similarly, it is reported that *E. coli* can use the stomatal cavities in leaves to enter the internal structure of lettuce [115]. The pathway of this kind of entry is still unknown. Once inside the plant tissues, pathogen survival rates improve since they can use cellulose as their main source of carbon. Protozoa are larger in size than bacteria and thus they cannot access the internal parts of the plants; however, these pathogenic organisms can adhere to the surface of edible plants and remain there by the excretion of polymers which facilitate adhesion. Table 6 shows some examples of the occurrence of protozoa in crops irrigated with treated/untreated wastewater.

Pathogen	Crop	Occurrence	Reference
<i>Giardia lamblia</i>	Potatoes	5.1 cysts/kg	Crops irrigated using untreated wastewater in Marrakesh. [112]
	Coriander	254 cysts/kg	
	Mint	96 cysts/kg	
	Carrots	155 cysts/kg	
	Radish	59.1 cysts/kg	
<i>Ascaris lumbricoides</i>	Potatoes	0.18 eggs/kg	
	Turnip	0.27 eggs/kg	
	Coriander	2.7 eggs/kg	
	Mint	4.63 eggs/kg	
	Carrots	0.7 eggs/kg	
	Radish	1.64 eggs/kg	
<i>Enterobius vermicularis</i>	Lettuce	10–40 cysts/kg	Crops irrigated using treated and untreated wastewater in Kahramanmaras, Turkey. [113]
	Parsley	10–60 cysts/kg	
	Cress	10–20 cysts/kg	
	Spinach	1–3 cysts/kg	
<i>Entamoeba histolytica</i>	Lettuce	10–50 cysts/kg	
	Parsley	10–50 cysts/kg	
<i>Giardia lamblia</i>	Lettuce	10–20 cysts/kg	
<i>Ascaris lumbricoides</i>	Lettuce	10–30 eggs/kg	
	Parsley	10–30 eggs/kg	
<i>Trichuris trichiura</i>	Spinach	3.3% of the analyzed samples.	Crops grown in soils irrigated with raw wastewater in West Bengal, India. [93]
	Pudina	3.1% of the analyzed samples.	
	Coriander	5% of the analyzed samples.	
Hookworm	Lettuce	9.4% of the analyzed samples.	
	Parsley	3.3% of the analyzed samples.	
	Spinach	6.7% of the analyzed samples.	
	Pudina	9.4% of the analyzed samples.	
	Celery	3.6% of the analyzed samples.	
	Coriander	5% of the analyzed samples.	
<i>Ascaris lumbricoides</i>	Lettuce	43.8% of the analyzed samples.	
	Parsley	23.3% of the analyzed samples.	
	Spinach	36.7% of the analyzed samples.	
	Pudina	50% of the analyzed samples.	
	Celery	25% of the analyzed samples.	
	Coriander	35% of the analyzed samples.	
Helminth eggs	Leafy vegetables	100 eggs/kg	Vegetables irrigated with untreated wastewater in Faisalabad, Pakistan. [114]
	Cauliflower		

Table 6. Occurrence of some pathogen protozoa on the surface of crops irrigated using treated/untreated wastewater

Fate of pathogenic microorganisms in soil. Upon their arrival to irrigated soils, microorganisms can either survive or be inactivated/killed by the physical and chemical processes naturally occurring in soil as well as by predation by indigenous soil organisms. Given the case that these microorganisms can survive in the soil, they may subsequently colonize soil particles, infiltrate the soil to the aquifer or migrate through across the landscape by runoff. Processes affecting the environmental fate of the pathogenic microorganisms in soil are shown in Figure 4. Previous experiments have demonstrated that some microorganisms can vertically and/or horizontally mobilize through the soil, travelling long distances from the initial point of contamination [116]. Bacterial migration in soil has been reported up to 830 meters, while for viruses such displacement is significantly lower, i.e. up to 408 m [117–118]. Survival of pathogens is related with their environmental fate since the longer the lifetime of the microorganisms the larger the distance they can travel. As indicated in Table 5, bacteria can survive for long periods compared to viruses, and thus bacteria can be transported farther. Climatic conditions also impact upon pathogen transportation; for instance, in frozen soils pathogens can survive longer and thus they can be transported farther than in tropical and desert soils [119]. Microorganisms can be more easily displaced through coarse textured soils than fine textured ones. The study referred to in [118] found greater mobilization of coliforms in sand–gravel soil than in fine sand. In fact, in coarse sandy soils, the vertical movement of microorganisms can be as rapid as that observed for inorganic tracers. In this regard, the results reported in reference [120] evidence that infiltration of streptomycin-resistant *E. coli* can be compared with that of the chloride tracer in undisturbed soil columns, even when different soil textures are compared. Since the transportation of microorganisms is similar to that observed for tracers, the physical structure of soil is the determinant factor in them reaching the aquifer; therefore, a greater occurrence and interconnection of pores within the solid matrix may result in efficient infiltration of water and thus bacteria. Studies on the movement of pathogens in the field confirm the rapid movement of pathogenic bacteria observed in laboratory tests. These studies also found a high concentration of bacteria and viruses in groundwater [121]. In addition to the higher quantity and interconnection of pores, the increased transport of bacteria and viruses through the soil can be explained by the presence of preferential paths within the soil matrix. Such preferential paths are referred to cracks, fractures, worm holes and channels formed by plant roots or fauna in the soil. Studies reported in reference [122] show that larger microorganisms (*E. coli*) can mobilize deeper into soil than smaller coliphages. Moreover, the study referred to in [123] confirms that bacterial cells smaller than 1 μm in diameter are more rapidly transported through soil than larger organisms.

The chemical properties of soil can also impact upon the vertical and horizontal transport of microorganisms. The mineral composition of soil can favor adhesion of microbial cells, eggs or cysts onto soil particles. Several types of bacterial cells have been shown to strongly adhere to the mineral domain of soil and aquifer material [124]; once adhered, bacteria can replicate and form biofilms on the surface of soil particles. In wastewater irrigated soils, the accumulated organic matter as well as the continuous input of dissolved organic matter via wastewater may enhance the proliferation of bacteria. With regard to parasites, the study referenced in [87] found that *Ascairs lumbricoides* eggs and *Giardia lamblia* cysts adhere to the mineral fraction of wastewater irrigated soils more rapidly and more strongly than to the organic domain. In the



Source: modified from [121]

Figure 4. Factors affecting the environmental fate of pathogenic microorganisms in wastewater irrigated agricultural soils

case of *Ascaris* eggs, adhesion occurs with the silica in sand particles. In contrast to protozoan eggs, studies referred to in [125] suggest that adhesion or adsorption of protozoan cysts may be related to soil organic matter rather than the mineral fraction of soil. This has been attributed to the hydrophobic nature of the cysts walls. According to the findings reported in [126] detachment of bacteria from soil particles is effected by the composition of the irrigation water. In that study, *Pseudomonas* sp. showed enhanced transport when distilled water was used for detachment in column experiments, compared with 0.01 M NaCl. Such results suggest that clean water can efficiently wash off the polysaccharides excreted by bacterial cells which act as an adhesive between soil particles and bacteria. The opposite effect has been observed for *Ascaris* eggs. When soil is washed with NaOCl, eggs are effectively detached from soil particles; this is because sodium hypochlorite can destroy the albuminose layer that coats the surface of helminth eggs and which anchors with the soil particles [127]. According to the established in [87], the environmental relevance of studying the impact of this salt on the detachment of eggs from soil relies on the fact that NaOCl can be found in reclaimed water, as it is commonly used for disinfection of effluents.

Once microorganisms are retained by soil, either by adsorption/adhesion or straining, they can be inactivated or eliminated by desiccation. This phenomenon is particularly important in arid areas where high levels of solar radiation are reported. The environmental fate of microorganisms in soil also depends on the native microorganisms living in the solid matrix. Predators of wastewater-borne pathogenic bacteria in soil include Streptomycetes, Myxobacteria, *Bdellovibrio* and nematodes [121]. The presence of plants may affect the persistence and movement of microorganisms in soils. On the one hand, pathogen can found favorable conditions for survival in the rhizosphere due to the high content of nutrients in this zone; and

on the other hand, native bacteria in rhizosphere can be natural predator of those pathogens, while roots may excrete antibiotics that inhibit or kill pathogenic microorganisms.

2.2.2. Soil pollution by heavy metals

Given that most agricultural wastewater irrigation is performed using municipal wastewater, which contains negligible amounts of heavy metals [11], the occurrence of these elements in wastewater irrigated soils is usually significantly lower than the maximum permissible concentrations established by international regulations. However, there are some cases where care should be taken when reusing wastewater in irrigation, e.g. close to tanneries, metal processing or mining areas [91]. Different levels of risk are perceived for the different heavy metals. While some of them are nutrients for plants at trace concentrations, others have been shown to produce harmful effects on exposed organisms, or are absorbed by plants and accumulated through the food web. Table 7 presents the risks that are incurred by the presence of some heavy metals in soil.

Risks characteristics	Metal
Low risk	Mn, Fe, Zn, Cu, Se, Sb
High risk	Cr, As, Pb, Hg, Ni, Al, Cd
Essential micronutrient to plants	Cu, Fe, Mn, Mo, Zn, Ni
Beneficial for some crops	Co, Na, Si
Can accumulate in crops to levels that are toxic for consumers	Cd, Cu, Mo
No human toxicological threshold established for wastewater intended for irrigation	Hg
Relatively high threshold for wastewater used in irrigation	Cu, Fe, Mn, Zn
Low absorption by plants	Co, Cu, Mn, Zn

Source: with information from [75]

Table 7. Heavy metal risk characteristics during irrigation

Cadmium is the metal with the highest associated risk. It is toxic to humans and animals in doses much lower than those that visibly affect plants; furthermore crop uptake (which is notably high in acidic soils) can increase the dose consumed by organisms and in turn accumulation in animal tissue. Absorbed cadmium in animals is stored in kidney and liver, although meat and milk products have shown to be little affected by cadmium accumulation [75]. There is a relatively good knowledge to allow the setting of limits regarding the acceptable amount of heavy metals contained in wastewater used to irrigate. In the study referred to in [128], numerical calculation of the limits for the maximum tolerable pollutant concentration in wastewater irrigated soils was carried out (health-based targets). This was based on the acceptable daily human intake (ADI) for selected heavy metals and the amount that can be

“permitted” to accumulate in soil before harmful effects occur in consumers of crops (Table 8). This analysis assumed: a) only two exposure routes (wastewater → soil → plant → human; and, wastewater → crop → human); b) a global diet in which the daily intake of grains/cereals, vegetables, root/tuber crops and fruit accounts for ~75% of daily adult food consumption; c) a body mass for adults of 60 kg; d) all of the food grain, vegetables, root/tuber crops and fruits are obtained from land irrigated with wastewater; and, e) a total daily intake of pollutants by this consumption path of 50% of the ADI (the remaining 50% of the ADI was attributed to background exposure). Table 8 shows the inputs of heavy metals by wastewater to irrigated soils, assuming an application of treated wastewater of approximately 1.2 m/year, which is roughly the amount of water required to produce a crop cycle in an arid zone.

Element	Maximum input by wastewater (kg/ha/year)	Maximum tolerable concentration (mg/kg)
Arsenic	0.6–12	9
Cadmium	0.06–0.24	7
Chromium	1.2–60	3200
Lead	1.2–60	150
Mercury	0.12–0.12	5
Nickel	0.24–12	850
Selenium	0.24–0.6	140
Silver	1.2	3

Source: reference [128]

Table 8. Maximum tolerable concentration of heavy metals in wastewater irrigated soils

Health effects associated with the use of water heavily contaminated with industrial discharges for agricultural irrigation have been reported. In Japan, itai–itai disease, a bone and kidney disorder associated with chronic cadmium poisoning, occurred in areas where rice paddies were irrigated with water from the contaminated Jinzu River [129]. In some parts of China, the use of industrial wastewater for irrigation was associated with a 36% increase in hepatomegaly (enlarged liver) and 100% increase in both cancer and congenital malformation rates [130].

With regard to the occurrence of heavy metals in agricultural soils irrigated using wastewater, the study referred in [131] presents an inventory of sources of some heavy metals (zinc, copper, nickel, lead, chromium and cadmium) in agricultural soils of England and Wales. Results showed that the greatest contribution of heavy metals in those soils comes from the application of sludge from wastewater treatment plants, while irrigation appeared to be of little importance as a source of heavy metals in soils. According to this investigation, which followed the rates of deposition of heavy metals in the studied soils, the time required for metal concentrations to reach maximum values permitted by international regulations is 80 years for zinc

and at least 1256 years for cadmium. In this respect, study referred to in [132] showed that concentrations of heavy metals in long-term untreated-wastewater irrigated soils in central Mexico were 10 times lower than the limits set by the Danish regulations; moreover, the authors estimated that another century of irrigation is necessary to exceed these values. In most cases, metals have little impact on aquifers. According to the results reported in [133] the most toxic metals to humans –cadmium, lead, and mercury– were absent in groundwater at five sites in the United States after 30–40 years of applying secondary and primary effluents at rates between 0.8 m/year and 8.6 m/year to different crops. The reason given was that the pH values greater than 6.5 in soil and wastewater resulted in the precipitation of the entire amount of metals. Metals are normally bonded into the organic matter through the formation of organo-metallic complexes, which are not bioavailable to plants. The addition of lime and wastewater to soil assists the precipitation of metals, while the addition of chemical fertilizers has the opposite effect, since over the long term they tend to lower the soil pH and thus solubilize metals.

In contrast, agricultural soils have been reported in which the concentration of heavy metals, such as cadmium and zinc, are close to reaching the maximum levels set out in international regulations. In these cases, the factors leading to an exacerbated soil contamination and thus increased risk of groundwater and crop pollution are: a) sandy soil texture; b) acidic to neutral soil pH; c) low organic matter content; and/or, d) the use of industrial wastewater for agricultural irrigation [134–135]. In such cases, the cessation of agricultural irrigation with wastewater is recommended, together with allowing the recovery of soil through remediation techniques such as phytoremediation.

2.2.3. Soil pollution by organic compounds

Pollution of soil by organic substances has been a matter of concern to scientists and organizations regulating the quality of soil, water sources and food for several decades. An extensive body of work exists addressing the degradation of soil by conventional organic pollutants (e.g. pesticides, polyaromatic hydrocarbons, organochlorides, paraffin, organic solvents, etc.). However, in sites where treated/untreated wastewater is disposed of by agricultural irrigation one can find organic substances different to those commonly studied and reported in literature treating oil spills, mining zones or soil polluted by industrial wastewater. Most of the dissolved and particulate organic matter contained in municipal wastewater is produced by the degradation of human and animal excreta, hence organic matter in wastewater is composed mainly by saccharides, lipids, amino acids and proteins; however, a tiny fraction of the organic material in wastewater originates from chemicals contained in everyday consumer products used and disposed of via sewage by people in urban and rural areas. According to [24], thousands of organic compounds are contained in municipal wastewater at trace levels and there is a lack of knowledge regarding the effects that such substances may cause to the exposed organisms, either by themselves or in combination with other compounds or groups of organic compounds. This group of chemicals is referred as “organic pollutants of emerging concern” (OPECs) [136]; though they should actually be listed as priority pollutants in cases where wastewater is used to irrigate crops, since these contaminants are in contact with soils, crops

and water sources near the irrigation area [137]. Over the last three decades, significant work in the field of analytical chemistry has been carried out in order to extract, isolate and quantify some of these pollutants in wastewater and soils. Frequently found OPECs in such complex matrices are pharmaceutically active compounds (PACs) and their metabolites, personal care products (e.g. disinfectants, fragrances, insect repellents, sunscreens, etc.), sweeteners, stimulants (e.g. caffeine and psychoactive drugs), detergents and their metabolites, plasticizers and industrial additives (e.g. additives in gasoline) [137]. Almost all of the studies addressing the removal of OPECs in wastewater treatment plants report that most of these substances are partially degraded/removed in primary and secondary treatment systems –and some pollutants are only partially removed even in tertiary treatment systems– [138]. Because of this, OPECs occur in irrigated soils if either treated or untreated wastewater is used in irrigation. Effluents of wastewater treatment plants contain a small fraction of the parent substance as well as the by-products generated during treatment. However, some of the compounds may be retained and concentrated in the sludge produced during wastewater treatment and reach the environment via the use of sludge (or biosolids) as soil amendments in agriculture. Due to continuous industrial development, the number of organic substances contained in wastewater is constantly increasing; in fact, most of these substances are not tested before they are released onto the market, and therefore their potential risks or the side effects they cause in non-target organisms in soils or water bodies is yet unknown.

Effects caused by domestic wastewater-related organic pollutants in irrigated soils. As mentioned above, due to the ever growing pool of organic compounds discharged to the soil via wastewater, there is a general lack of knowledge regarding the effects that such substances cause to exposed organisms. In general terms, municipal wastewater is the main vector of OPECs to reach the environment, so that these substances are ubiquitous at sites where wastewater streams occur. Pharmaceutically active compounds (PACs) are designed to cause a defined effect on target organisms; however, when trace amounts of these substances are transported by wastewater into environment, they can interact with non-target organisms. One effect that has captured the attention of the scientific community in recent years is the development of antibiotic resistance by pathogenic microorganisms due to the occurrence of antibiotics in wastewater, surface water bodies and soils receiving wastewater [139–140]. However, a large number of studies on this subject report that proliferation of antibiotic-resistant pathogens is quite unlikely in wastewater irrigated soils [97–99]. Conversely, the study referenced in [96] attempts to relate the occurrence of sulfonamide and fluoroquinolone antibiotics with the emergence of antibiotic resistances in wastewater and long-term wastewater irrigated soils. The authors reported a relationship between time under irrigation and the frequency of detection of antibiotic resistance genes in soils. In the case of non-antibiotic PACs, the most studied compounds –because they are the most used worldwide– are the analgesic and anti-inflammatory drugs [141]. Compounds such as ibuprofen, naproxen, diclofenac, paracetamol and ketoprofen have been shown to cause systemic damages in aquatic species; damages in liver, gills and kidney are commonly reported [142]. The non-steroidal anti-inflammatory drug diclofenac has been demonstrated to cause visceral gout in vultures; in fact, the presence of diclofenac in livestock was the cause of the mass death of three species of vulture in India and Africa [143]. Other studies show that chronic exposure to traces

of anti-inflammatory drugs leads to a lessening in the development of human embryo cells [144]. The occurrence of psychotropic agents at trace levels in water bodies polluted by wastewater discharges has been shown to alter the behavior of some fish species, suppressing their survival instincts against predators [145]. With regard to OPECs that are not pharmaceutically active compounds, there is significant concern that they may alter hormone homeostasis in organisms. These substances, known as endocrine disruptors, can mimic or compete with natural hormones by binding with active sites on hormone receptors, causing reduced or disproportionate hormonal responses in the affected organisms [146]. The most potent endocrine disruptors found so far in municipal wastewater are the natural and artificial estrogenic hormones—the latter are used as birth control agents—and the regulators of thyroidal function, followed by plasticizers (e.g. phthalates and bisphenols), surfactants and their metabolites and some industrial additives [147]. Endocrine disruptors are suspected of causing the feminization or masculinization of fish and reptile populations as well as the occurrence of breast cancer, imbalances in thyroidal function, teratogenic effects (e.g. cryptorchid) in mammals, and even obesity in mammals (obesogens) [148–150]. There is a serious lack of knowledge regarding the effects caused by OPECs in soil organisms. Studies on this field have been little developed compared to those for water bodies. Table 9 shows some examples of effects caused to soil organism by the occurrence of OPECs.

The effects caused by this class of pollutants are not limited to soil organisms and impacts can be observed in the soil matrix. For example, surfactants can, on the one hand, decrease the capillarity and penetrability of soil as well as increase the solid–liquid contact angle, the shape factor and the sorptivity of soil particles. On the other hand, the input of these substances can increase the desorption of previously sorbed organic molecules on the soil particles, which in turn increases the bioavailability and mobility of the desorbed compounds [163]. To evaluate the toxic effects caused by the occurrence of OPECs to soil organisms two approaches are commonly used, i.e. acute and chronic toxicity studies. For the former, high concentrations of target pollutants are supplied to studied organisms under controlled conditions for a short period; chronic toxicity tests, on the other hand, are based on prolonged exposure of organisms to low (i.e. environmentally representative) doses of the studied pollutants. So far, most toxicity studies dealing with OPECs have been carried out using the acute toxicity approach. Even though these studies do not fully represent the conditions observed in the field, they provide valuable information on the subject of impacts caused by this kind of contaminants to soil organisms. Studies evaluating chronic toxic effects of pollutants are more representative of field conditions, i.e. toxic substances enter to soil in small doses over long periods. In this regard, conducting long-term toxicity studies that evaluate the chronic effects caused by OPECs in soil organisms are a priority. Several toxicity studies report that the effects of organic pollutants on soil organisms (i.e. reduction in soil respiration, enzymatic activity and nitrification/denitrification rates) are observed in the early days of exposition; then, after a short period (4 to 10 days) soil recovers to its basal conditions [153–154, 159, 161]. The next step in toxicity studies for these emerging pollutants is to determine the dynamics of the toxic effects on soil organisms after tens or hundreds of growing cycles in which target contaminants are continuously supplied; i.e. under conditions similar to what occurs in long-term irrigated areas.

Compound	Effect in soil organisms	Reference
Estrone, 17 β estradiol (hormones)	Negative impacts on the vegetative cycle of alfalfa (<i>Medicago sativa</i>).	[151]
Sex hormones	Shift in sex ratio of free life nematode communities in soil.	[152]
Triclosan (antibacterial agent)	Inhibition in plant growth (rice and cucumber). Effect concentrations 50 (EC50, i.e. 50% of exposed population was affected) were 57 and 108 mg/kg for rice and cucumber respectively. Inhibition of soil respiration and phosphatase activity at concentration levels higher than 10 mg/kg.	[153]
	Reduction in soil respiration 4 days after supplying the compound. The observed effects were dependent on the adsorption of the compound onto the soil.	[154]
Bisphenol A (plasticizer)	Shift in sex ratio to female individuals in isopod (soil arthropod) communities.	[155]
Abamectin (anthelminthic)	Negative impacts on reproduction of <i>Folsomia fimetaria</i> and <i>Folsomia candida</i> (soil arthropods) at concentrations of 0.25 and 0.5 mg/kg of soil (dry mass), respectively. Negative impacts on reproduction of soil earthworms at concentration levels of 0.06 mg/kg of soil (dry mass).	[156]
Fenbendazole and cypermethrin (antiparasitic)	Negative impacts on degrading microorganisms of dung.	[157]
Sulfonamide and tetracycline antibiotics	Inhibition of the soil microbial activity by 10% (ED10) at concentrations of 0.003–7.35 μ g/g of soil (dry mass). Shifts in fungi:bacteria ratio.	[158]
Sulfadiazine (antibiotic)	Decrease in denitrification rates when the input of antibiotic was 100 mg/kg of soil (dry mass).	[159]
	Significant decrease in the bacteria:fungi ratio	[160]
Chlortetracycline, tetracycline, tylosin, sulfamethoxazole, sulfamethazine and trimethoprim (antibiotics)	Decrease in crop growth (sweet oat, rice and cucumber). Inhibition of the microbial activity of soil (soil respiration and phosphatase enzyme activity).	[161]
Human and veterinary pharmaceutically active substances	Decrease in growth and development of <i>Phaseolus vulgaris</i> L., <i>Glycine max</i> , <i>Medicago sativa</i> , <i>Zea mays</i> , and several other crops.	[162]

Table 9. Summary of negative effects on soil organisms caused by the occurrence of pollutants of emerging concern at trace levels

Occurrence of domestic wastewater–related organic pollutants in irrigated soils. In spite of the fact that wastewater is the main vehicle allowing OPECs to reach soil, very few studies reporting the presence of these pollutants in wastewater irrigated soils have been carried out.

This finds an explanation, on the one hand, in the inherent difficulty of extracting and isolating organic compounds at trace levels from the soil matrix and, on the other hand, in the fact that analyzing this type of pollutants is relatively expensive. Figure 5 shows the sites where monitoring studies aimed at determining the occurrence of OPECs in wastewater irrigated soils have been performed. In this figure the number of sites monitored is contrasted with the 20 countries with the highest use of untreated wastewater for agricultural irrigation. Most of the monitoring studies are concentrated in China, the country using the highest volume of untreated wastewater in agriculture [17], followed by the United States and Mexico –the latter is the second placed country in terms of reuse of untreated wastewater for irrigation–.

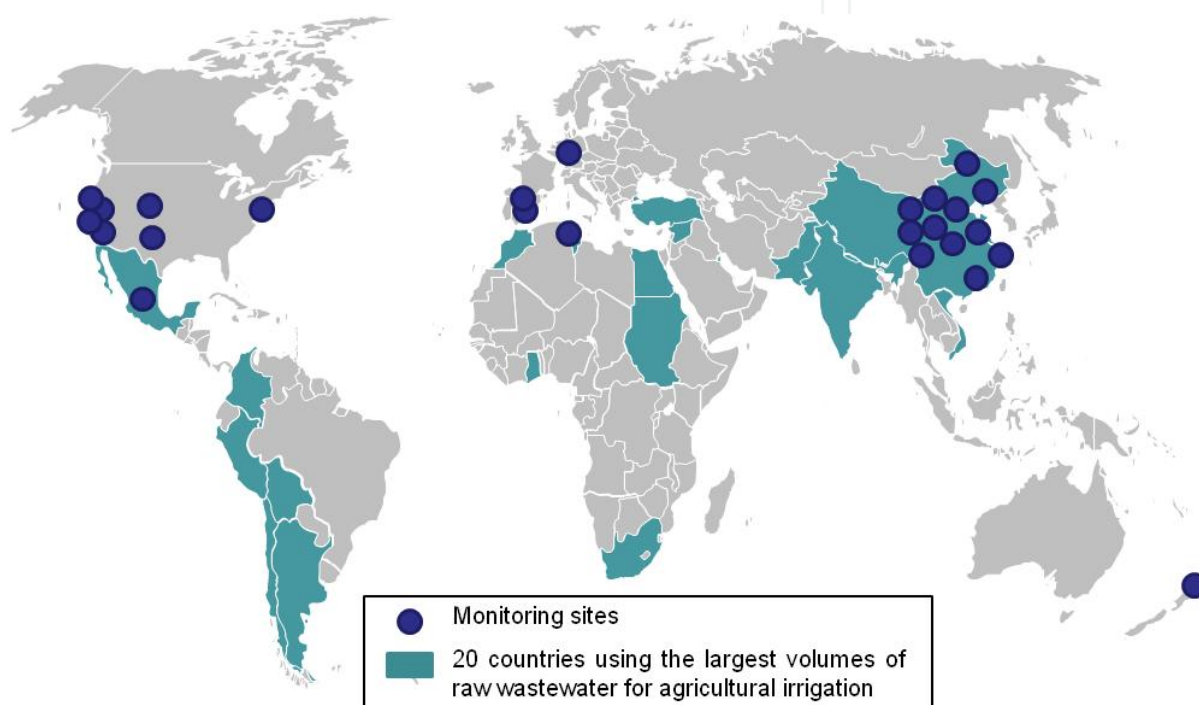


Figure 5. Monitoring studies for pollutants of emerging concern in wastewater irrigated soils throughout the world and comparison with the 20 countries using the largest volumes of raw wastewater for agricultural irrigation

Efforts in monitoring emerging pollutants in developing countries where the use of raw wastewater is widespread are of value; this requires cooperation with research centers where analytical techniques are currently validated to perform soil analyses or by sharing “know how” and technology with developing countries in order to perform analysis on site. Determination of OPECs in soil requires an exhaustive extraction step, which in most cases has to be carried out at a moderately high temperature, particularly in the case of analysis of thermolabile compounds (e.g. sulfonamide antibiotics). Extraction methods such as pressurized fluids extraction, microwave assisted extraction and ultrasonic assisted extraction are preferred over traditional Soxhlet extraction techniques, since they guarantee greater contact between the solvent and the soil particles, resulting in higher recoveries of analytes. Analysis of OPECs is commonly accomplished using either liquid or gas chromatography techniques; although liquid chromatography is preferred as it is more suitable for the analysis of polar

compounds, i.e. most PACs [164]. Monetary costs of these analyses are relatively high and analysis entails the use of potentially dangerous chemicals, which is in part the reason why monitoring studies for OPECs in soils are not carried out in poor countries. So far, the most reported emerging pollutants in wastewater irrigated soils are the pharmaceutically active substances (e.g. antibiotics, non-steroidal anti-inflammatory agents, anticonvulsants, anticoagulants and sex hormones), followed by plasticizers (e.g. phthalic acid esters and bisphenol A), metabolites of surfactants (e.g. nonylphenol, octylphenol) and antibacterial and antimycotic agents (e.g. triclosan and triclocarban). Table 10 shows the concentrations of some OPECs reported for wastewater irrigated areas.

Overall, higher concentrations of OPECs are found in the first 30 cm of the soil profile. Such behavior suggests that these compounds are retained by the organic matter accumulated over time of irrigation; which is consistent with the organic nature of these contaminants, although several of them display some polarity. Concentration levels reported for the monitored PACs range from below the detection limits of the analytical techniques to tens of $\mu\text{g/kg}$ of soil (dry mass). Monitoring studies referred to in [165] report concentration levels of the pharmaceuticals ibuprofen, naproxen and carbamazepine in the range of 0.25 to 6.48 $\mu\text{g/kg}$ of soil (dry weight) in Phaeozem and Leptosol soils that have been irrigated using untreated wastewater for eight decades. Other studies [168] found average concentrations of 1.8 $\mu\text{g/kg}$ for triclosan and 2.5 $\mu\text{g/kg}$ for estrone. In contrast to PACs, concentrations reported for plasticizers and surfactants are of the order hundreds of $\mu\text{g/kg}$ of soil (dry mass). For example, in the study referenced in [170] concentrations of 14–80 $\mu\text{g/kg}$ are reported for nonylphenols, while concentrations of 140–2610 $\mu\text{g/kg}$ were observed for some plasticizers. Concentrations of up to 7110 $\mu\text{g/kg}$ of the plasticizer di-(2(ethylhexyl)phthalate, have been reported elsewhere [175]. High concentrations of plasticizers in soils are explained by the ubiquity of these compounds in environment. Phthalic acid esters are contained in almost all plastic products and can easily leach from the solid matrix (i.e. the plastic articles). Once phthalates are released from the solid matrix, they can get into environment not only via wastewater but by aerial deposition, using dust particles as carriers [176]. Nonylphenols, the major by-products of the anaerobic biodegradation of surfactants [177], are commonly found in wastewater irrigated soils due to the significant presence of detergents in municipal wastewater in combination with the anaerobic conditions prevailing in sewerage systems. In contrast to PACs, plasticizers and surfactant metabolites are non-polar in nature and for this reason, higher adsorption can occur for these compounds in soil, causing not only their build up in the surface layer of soil but the potential decrease in their bioavailability to soil microorganisms. Most monitoring studies of OPECs in environmental solid matrices are focused on determining these contaminants in biosolids amended soils rather than in wastewater irrigated soils. This is necessary since: a) biosolids in wastewater treatment plants concentrate organic pollutants during water depuration, hence a greater concentrations of contaminants are expected in biosolids amended soils than in treated/untreated wastewater irrigated soils; b) the use of biosolids as agricultural soil amendment is a more socially acceptable practice than reusing wastewater, thus it tends to be more practiced (or at least more reported) than wastewater irrigation, and it therefore becomes necessary to determine the pollutant load reaching the soil in this manner; c) since analysis of

Compound	Concentration (µg/kg)	Comments	Reference
Carbamazepine	0.28–0.94	Concentration range observed in the surface layer (0–10 cm depth) of a treated wastewater irrigated soil during an irrigation cycle (May to October). The lowest concentration was observed before irrigation started while the highest concentration was determined in soil at the end of the irrigation cycle. Irrigation at the site has been occurring for the last 30 years.	[165–167]
	5.14 and 6.48	Concentrations found in the surface layer (0–10 cm depth) of Leptosol and Phaeozem soils, respectively that has been irrigated using untreated wastewater for 85 years.	
	4.92, 2.9 and 1.92	Concentrations found in forested, grass-covered and cultivated soil irrigated with treated wastewater for more than 25 years. Carbamazepine was found mainly in the first 30 cm of the soil profile.	
Ibuprofen	<LOD–3; <LOD–3	Concentration ranges observed in loamy sand and sandy loam turf soils (0–30 cm depth) irrigated with treated wastewater at an irrigation rate of 1.1–1.2 and 1.5–1.6-fold the evapotranspiration rate, respectively. Wastewater irrigation has been occurring at the site for almost 20 years.	[168]
Naproxen	<LOD–12.5; <LOD–9.5		
Triclosan	<LOD–6; <LOD–2.8		
Bisphenol A	<LOD–1.25; <LOD–1		
Estrone	<LOD; <LOD–5.3		
Ibuprofen	<LOD and 0.25	Concentrations found in the surface layer (0–10 cm depth) of Leptosol and Phaeozem soils that have been irrigated using untreated wastewater for 85 years.	[165]
Naproxen	0.73 and 0.55		
Nonylphenols	123 and 41		
Triclosan	18.6 and 4.4		
Bisphenol A	14.8 and <LOD		
Di- <i>n</i> -butylphthalate	552 and 244		
Butylbenzylphthalate	346 and 171		
Di-2-(ethylhexyl)phthalate	2079 and 820		
Clofibric acid	<LOD–9	Concentration range observed in soil from a golf course irrigated with reclaimed wastewater	[169]
Triclocarban	<LOD –105	Concentration ranges for pharmaceuticals and endocrine disrupting chemicals in agricultural soils of Hebei province, north China, which have been irrigated using treated wastewater for more than 50 years.	[170]
4-nonylphenol	14.2–60.3		
Salicylic acid	1.4–10.7		
Tetracycline	<LOQ –19.9		
Oxytetracycline	1.1 –16, maximum 212		
Trimethoprim	<LOQ –2.6		
Primidone	<LOQ –3.3		
Omeprazole	6.5–24.3	Ranges of concentration found in two agricultural soils irrigated with treated wastewater in Spain. Pollutants were found at higher concentrations in the surface layer of the soils.	[171]
Spironolactone	0.6		
Diazepam	4.65	Concentration found in an agricultural soil irrigated with treated wastewater.	[172]
Carbamazepine	5.77	Pollutants were accumulated in the surface layer of the studied soil (0–30 cm).	
Butylbenzylphthalate	59–1580	Ranges of concentration of phthalate esters in agricultural soils irrigated with untreated wastewater in the peri-urban area of Guangzhou city	[173]
Di-2-(ethylhexyl)phthalate	107–29370		
Di- <i>n</i> -butylphthalate	9–2740		
Di- <i>n</i> -amylphthalate	1–80		
Caffeine	14	Concentrations reported for volcanic soils (Vitric, Orthic, Allophanic soils) irrigated using treated wastewater for more than 15 years (at rates of 70 mm/weak) in Rotorua, New Zealand.	[174]
Amitriptyline	<5		
Carbamazepine	217		
Chlorpromazine	<5		
17 α ethynilestradiol	<5		
Diltiazem	<248		
Thioridazine	<259		

<LOD: concentrations below the limit of detection of the analytical method used for determination.

<LOQ: below the limit of quantification of the analytical technique.

Table 10. Concentrations of organic pollutants of emerging concern in treated/untreated wastewater irrigated soils

OPECs in soil is expensive, these types of monitoring studies are conducted mainly in developed countries, where the use of biosolids as soil amendment is practiced more intensively than the reuse of treated/untreated wastewater in agricultural irrigation. At present there are no regulations that establish maximum permissible concentrations for organic pollutants of emerging concern in soils. The development of such regulations relies on the results obtained in both acute/chronic toxicity tests and in health risk assessments.

Environmental fate of organic pollutants of emerging concern (OPECs) in wastewater irrigated soils. The environmental fate of OPECs in the soil is governed by the physical and chemical properties of both the compounds and the soil as well as by the climatic conditions of the site where reuse is taking place. The chemical properties of the organic pollutants significantly impacting the environmental fate of OPECs are polarity, hydrophobicity and volatility. Table 11 shows some OPECs found in municipal wastewater which serve as examples of the differences in the chemical properties affecting the environmental fate of OPECs in soil. Due to the organic nature of OPECs, soil organic matter, mainly its non-polar fraction, plays a determinant role in the retention of these pollutants in soil [178]. However, sorption onto soil organic matter does not occur equally for all contaminants, since polar molecules tend to remain soluble in water rather than be retained in the soil organic matter; conversely, non-polar molecules are instantaneously adsorbed by soil organic matter [179]. The polarity of organic compounds is determined by the presence of ionizable radicals within the molecules; carboxyl, phenol, amine and amide moieties may gain or lose protons, depending on soil pH values, acquiring a positive or negative charge, respectively. The compounds for which functional groups lose protons may be poorly retained by soil due to repulsion forces between the deprotonated radical and the negatively charged soil particles (i.e. organic matter and clay); this results in the facilitated leaching of organic pollutants into the aquifer [180]. However, when functional groups within organic molecules gain positive charge, they may be retained onto the soil particles by cation exchange –as occurs for some tetracycline antibiotics– [181]. In both cases, the organic moiety within OPEC molecules may be held in the soil organic domain by hydrophobic affinity. In general, the pH of wastewater irrigated soils tends to be neutral to basic [81], which results in low retention of negatively charged compounds compared to neutral or positively charged organic compounds [180]. Studies referenced in [182] found that non-steroidal anti-inflammatory drugs (NSAIDs) such as naproxen, which can produce negatively charged molecules after the ionization of the carboxyl functional group, are adsorbed to a lower extent than other compounds displaying higher hydrophobicity, such as carbamazepine or triclosan, in organic soils with high clay content. Organic compounds lacking of ionizable functional groups or displaying non-ionizable functional groups express their hydrophobicity by spontaneously migrating from water to the soil organic domain [183]. In wastewater irrigation systems, dissolved and particulate organic matter contained in wastewater tends to accumulate in the surface soil horizons, significantly favoring the build up of these compounds in topsoil. In studies referred to in [184] a greater accumulation of hydrophobic compounds, such as carbamazepine and esters of phthalic acid, was found in surface horizons of the irrigated soils, whereas hydrophilic compounds, namely ibuprofen, naproxen and diclofenac, were found in subsurface horizons. This behavior is explained, on the one hand, because hydrophilic compounds remain dissolved in water rather

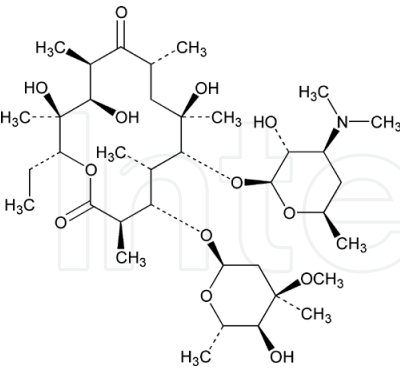
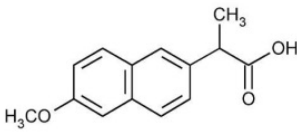
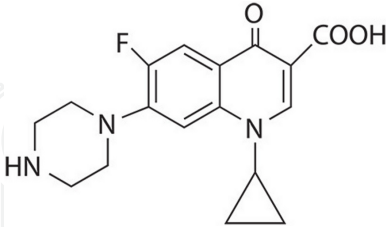
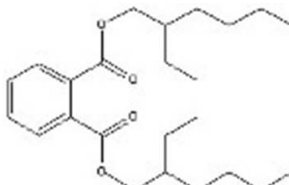
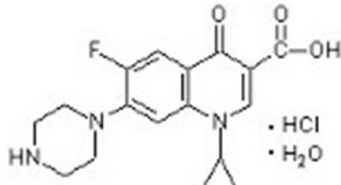
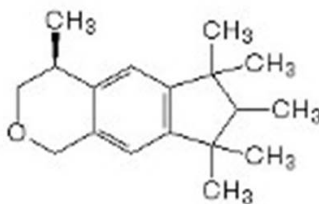
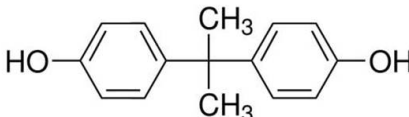
Polarity (ionization state at commonly found soil pH values)		
Positive	Negative	Positive/Negative (zwitterions)
Erythromycin (antibiotic)	Naproxen (non-steroidal analgesic drug)	Ofloxacin (antibiotic)
		
pK _a 8.91	pK _a 4.15	pK _a 6.27 (COOH); pK _a 8.87 (NH ₂ ⁺)
Hydrophobicity		
Hydrophobic	Hydrophilic	
Di-2-(ethylhexyl)phthalate (plasticizer)	Ciprofloxacin hydrochloride (antibiotic)	
		
pK _{ow} 7.5	pK _{ow} - 0.82	
Solubility in water at 25°C: 4.1x10 ⁻² g/L	Solubility in water at 25°C: 30 g/L	
Volatility		
Volatile	Non-volatile	
Galaxolide (fragrance used in detergents)	Bisphenol A (plasticizer precursor)	
		
Vapor pressure: 7.27x10 ⁻² Pa	Vapor pressure: 9.33x10 ⁻⁶ Pa	

Table 11. Relevant physical and chemical properties in terms of the environmental fate of emerging pollutants in soil

than being retained in soil and, on the other hand, because of hydrophilic compounds are more susceptible to desorption from soil either during further irrigation or heavy rain events, and thus tend to rapidly reach subsoil and the aquifer [180, 182].

The chemical structure also affects the environmental fate of OPECs in soil. Molecules displaying aromatic moieties, such as carbamazepine and naproxen, have been shown to be

strongly retained by soil organic matter –both to the aliphatic and aromatic fractions of soil organic matter– compared with compounds that have no resonance structures [182, 185–186]. This behavior is explained by the formation of bonds between aromatic rings within the solute molecules and the soil organic matter [185]. Nonylphenols and octylphenol compounds have surfactant properties as they possess an aliphatic chain and a phenol moiety at the edge of the molecule [177]. Due to this structure, these compounds can promote resolubilization of organic contaminants retained in soil, although the estimated risk of this occurrence is considerably low [187]. The presence of heteroatoms in organic molecules can impact upon their environmental fate in soil. For example, oxygen atoms within the ciprofloxacin molecule can form covalent bonds with aluminum and iron oxides in soil, resulting in irreversible adsorption of the compound onto the solid matrix [188]. With respect to volatile OPECs, artificial fragrances represent the best example of this feature; these compounds are contained both in personal care products and detergents. Typically, the more volatile compounds are also hydrophobic, so they can be spontaneously retained in topsoil and then volatilize when temperature increases [189]. Since irrigation using untreated wastewater, which contains large amounts of fragrances, is carried out in arid areas, it is expected that a significant fraction or all of the fragrance molecules are rapidly volatilized upon their input to soil via wastewater. Volatilization of OPECs in wastewater irrigated soils is still an unexplored issue; studies aimed at determining the fraction of organic contaminants that can be volatilized in soil enriched with organic matter via wastewater irrigation are still needed.

Natural attenuation processes leading to the removal and dissipation of OPECs in soil are shown in Figure 6. Contaminants may either dissipate in soil by photodegradation, biodegradation or chemical degradation (hydrolysis, oxidation or reduction) mechanisms; they may be accumulated in soil by adsorption or removed from soil by volatilization. There is a significant lack of information in the literature with regard to the natural photodegradation (i.e. photolysis of compounds by sunlight) of emerging pollutants in soil. The information available on the photodegradation of pesticides in agricultural soils is useful in elucidating, to some extent, the potential for photodegradation of OPECs in soil. Studies on natural photodegradation of the pesticide quinalphos showed that photodegradation takes place only in the first 2–5 mm of soil (photic layer); this photolysis takes place in two stages, each one at a different depth [190]. In the uppermost soil layer (the first 2 mm) direct photodegradation of the organic compounds (i.e. the transformation of compounds due to the direct incidence of photons) occurs; in this same layer, the production of free radicals (e.g. hydroxyl radicals and excited dissolved organic matter) occurs due to the breakdown of the soil organic matter. In the second stage, the free radicals migrate to the lower photic layer through facilitated transport by soil moisture; subsequently, photolytic transformation occurs below by the action of free radicals generated in the upper layer of soil (indirect photodegradation) [191]. As a result of the aforementioned aspects, soil moisture content as well as organic matter are determinant factors in the photodegradation of organic contaminants retained in the soil surface [191]. The physical structure of the soil can also significantly impact upon the photodegradation of organic pollutants, as it defines the depth to which solar radiation can penetrate the soil. In the study referenced in [192], sunlight photolysis of 4–nonylphenol in biosolids amended soils was studied. Photolysis resulted in 40% conversion of the compound within 30 days, with photodegradation observed

in the first 5 mm of the soil. Since natural photodegradation occurs only in the soil surface layers, the organic compounds retained in the topsoil will be the most exposed to direct sunlight, although this does not necessarily imply increased rates of photodegradation. An example of this is the anticonvulsant agent carbamazepine, which is prominently retained in topsoil but has demonstrated poor photodegradation in water studies. Conversely, the anti-inflammatory drug diclofenac has been shown to present significant photoactivity [193], but it is less well retained in the topsoil. Due to this, photodegradation is unlikely to occur in soil by direct or indirect means. In spite of almost all of the studies evaluating the natural photodegradation of OPECs have been carried out in aqueous matrices [194], the results obtained in these experiments provide valuable information concerning the photoactivity of such compounds; which can be useful for studying the photolysis of organic pollutants in soil. For example, it is known that the NSAID ibuprofen and the anticonvulsants drugs carbamazepine and primidone are poorly photodegraded in water whereas the antibacterial agent triclosan, the antibiotic drug sulfamethoxazole and the NSAIDs diclofenac and naproxen are readily photodegraded [194]. These results can be the basis to establish experiments aimed at determining or modeling the photodegradation of organics in soil. In general terms, the natural sunlight reaching the troposphere (i.e. the surface of earth) does not possess enough energy to mineralize most photodegradable compounds [195]; therefore a wide variety of by-products occurs when organic contaminants in water and soil are photodegraded. It is known that, in some cases, more harmful compounds can be produced by photodegradation of some organic pollutants. For example, 2,8-dichlorodibenzo-*p*-dioxin is produced by the natural photodegradation of the antibacterial agent triclosan [196]. Differently to triclosan, its breakdown product has the potential to cause cancer in mammals. Another example is the antiepileptic drug carbamazepine, which photodegrades to acridone [197], a compound related to the occurrence of cancer in aquatic species.

Most photodegradation studies of OPECs (in water matrices) have been carried out in developed countries at latitudes higher than 30°N [194]. It is therefore necessary to investigate the intensity of photodegradation processes occurring at lower latitudes, in zones where higher incidence of sunlight occurs and treated/ untreated wastewater irrigation is more intensively practiced.

Biodegradation of OPECs in soil has been studied in greater detail than photodegradation. Laboratory studies have found that biodegradation of emerging pollutants occurs optimally under aerobic conditions, while negligible transformations have been observed under anaerobic conditions [198]. This implies that biodegradation of this kind of contaminants is more likely to occur in well-structured soils, where tillage activities are frequently carried out, which allows better gas exchange through the soil matrix. The opposite behavior may be observed in anoxic/anaerobic soils, for instance in paddy fields. The antiepileptic drug carbamazepine is reported as one of the most refractory organic pollutants in soil, which has led researchers to consider this antiepileptic agent as a marker for anthropogenic contamination of surface and groundwater bodies [199]. In the study referenced in [200], mineralization of carbamazepine in soil was found to be less than 2%, after 120 days of incubation under aerobic conditions, while the reported in [201] show half-life times of 472 days in aerobic

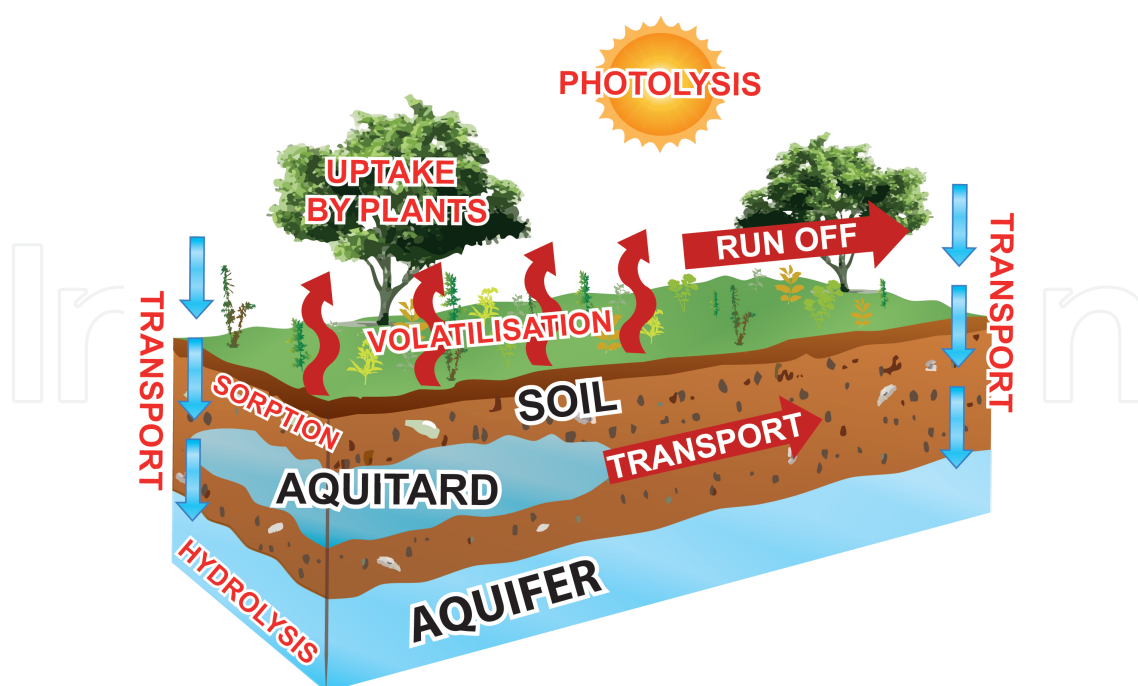


Figure 6. Processes involved in the environmental fate of emerging pollutants in soil

biosolids amended soils. Other compounds listed as recalcitrant in soil are the X-ray contrast media iopaminol, iomeprol and iohexol, whose biodegradation kinetic rate constants range from 0.29 to 0.46 $\mu\text{M}/\text{day}$ [202]. Pharmaceuticals, such as the antiepileptic drug primidone and the psychoactive diazepam have shown recalcitrance in water [203]; further studies are necessary in order to elucidate whether such behavior may also occur in soil. Substances designed to exert an effect on microorganisms have been shown to be rapidly biodegraded in soil. Examples of these are antibacterial agents such as triclosan, triclocarban and antibiotic substances [204–205]. Triclosan and triclocarban have been shown to be biodegraded in aerobic soils after 18 and 108 days, respectively [198], whereas the antibiotic compounds erythromycin, oleandomycin, tylosin, tiamulin and salinomycin displayed half-lives in aerobic soil of 20, 27, 8, 16 and 5 days, respectively [205]. Endocrine disrupting compounds, such as phthalate esters have been shown to efficiently biodegrade in agricultural soils, displaying half-lives of 7.8 to 8.3 days for di-butyl phthalate and 26–30 days for di-2-(ethylhexyl)phthalate [206]. Currently, few soil microorganisms have been identified as degraders of emerging pollutants. For example, the fungi *Trametes versicolor* has been demonstrated to degrade naproxen [207], while *Rhodococcus rhodochorus* bacteria [208] have been shown to degrade carbamazepine down to levels of 15% of its initial concentration in soil. In the case of phthalates (plasticizers) bacteria belonging to groups of *Corynebacterium*, *Mycobacterium* and *Nocardia* were demonstrated to degrade up to 90% of di-butyl phthalate within 48 hours in biodegradation experiments using isolated bacteria cultivated in saline solution [209]. Knowing the species of microorganisms that perform the biodegradation of OPECs in soil is useful in order to design engineered systems to treat wastewater and polluted soils based on the increased ability of degraders to degrade specific compounds by acclimatization and bioaugmentation. Such systems were

tested in [210] using the fungus *Trametes versicolor* to degrade up to 94% of carbamazepine in wastewater after 6 days in an air pulsed bed bioreactor. Biodegradation of OPECs in soil is influenced by the sorption phenomenon, therefore soil characteristics such as the content of organic matter, soil texture and soil pH are crucial for this process to occur. Adsorption of the organic contaminants onto the surface of the soil particles may favor biodegradation when the sorbed compounds are still bioavailable; conversely, when strong adsorption occurs (chemisorption on soil organic matter, clay or soil micropores) it can result in decreased bioavailability of the compounds and thus in the confinement of the pollutants within the soil matrix. Other properties of soil involved in the biodegradation of OPECs are: a) the climatic conditions of the site; b) the physical structure of soil; c) the soil moisture; and, d) the adaptation of soil organisms to biodegrade the target pollutants. It is possible that microorganisms in long-term wastewater irrigated soils more efficiently biodegrade OPECs than those living in non-irrigated soils or soils irrigated for a shorter time. This is due to the ability of soil microorganisms to adapt to using emerging pollutants as a carbon source. In this sense, studies comparing the degradation efficiency of OPECs in long-term wastewater irrigated soils with that observed in non-irrigated soils or newly irrigated soils are needed in order to establish appropriate strategies to prevent contamination of groundwater. Very few efforts have been made to determine the nature and quantity of by-products generated in soil by the biodegradation of OPECs. As shown in [200], biodegradation of emerging pollutants can generate by-products that can be more harmful than the original substance [196–197], thus the presence of these by-products as well as their environmental fate should be priority for further research.

Those emerging pollutants that are not degraded by soil microorganisms may either accumulate in soil, be assimilated by plants (if they are bioavailable) or be degraded by other mechanisms (e.g. photodegradation or hydrolysis). In the case of carbamazepine, studies referred to in [184] explain that this compound is one of the most highly accumulated in wastewater irrigated soils. Moreover, carbamazepine can be assimilated by plants in wastewater irrigation systems at environmentally relevant concentrations (i.e. within the range 1–3 µg/L). The study referenced in [211] shows that cucumber (*Cucumis sativus* L.) can accumulate carbamazepine in different parts of the plant: 4.5 µg/kg in roots, 1.9 µg/kg in stem, 39.9 µg/kg in leaves and 2.1 µg/kg in fruit. According to the authors, phytotoxic effects were observed when carbamazepine was supplied to soil by irrigation at concentrations as high as 10,000 µg/L. Results of this study show that consumption of carbamazepine polluted cucumber results in doses of 1 ng of carbamazepine per gram of fruit. Other studies show that soybean (*Glycine max* L.) can take up carbamazepine, triclosan and triclocarban in roots, stems and leaves at concentrations of 1.3–3.4 µg/kg for carbamazepine and 2.4–13.7 µg/kg for the antibacterial agents triclosan and triclocarban. Concentrations of antibacterial agents in plants at a second harvesting were found to be higher than those obtained in the first one; this may be due to the accumulation of contaminants in the soil, as a bioavailable pool, between each irrigation events [212]. To date, the study of the assimilation of OPECs by plants in wastewater irrigated soils is still limited; moreover, priority should be given to develop health risk assessment studies related to the consumption of contaminated crops.

Adsorption (i.e. retention of solutes on the surface of the soil particles) of OPECs in the soil is a decisive process in their environmental fate, since through this process contaminants may either be retained or migrate into the aquifer. In cases where organic pollutants are retained in topsoil, photodegradation or volatilization phenomena can easily take place. The strength of the bonds that pollutants establish with soil particles determines the bioavailability of molecules to plants and soil microorganisms. Adsorption of pollutants onto soil is measured by the distribution coefficient (K_d) which relates the amount of compound retained by soil to the mass remaining in the liquid phase [213]. Several models to determine the distribution coefficient of organic compounds have been developed; such models vary in complexity and the accuracy with which they represent the field conditions; yet simple adsorption models such as linear, Langmuir and Freundlich are the most used [213]. Due to their organic nature, OPECs tend to be rapidly and strongly adsorbed by soil organic matter; due to this effect, non-polar emerging pollutants, such as phthalates, have been shown to instantly adsorb onto organic soils [214]. On the other hand, OPECs displaying negative charge at the soil pH values, as occurs for NSAIDs, exhibit less adsorption by soil due to the repulsive forces between the negatively charged moiety within the molecule and the soil particles displaying negative charges (i.e. organic matter and clay) [182]. Accumulation of organic matter in wastewater irrigated soils increases the soil's ability to adsorb organic compounds. The proof of this can be found in the study referenced in [96], which reports greater adsorption of the antibiotics sulfamethoxazole and ciprofloxacin in long-term wastewater irrigated soils compared to non-irrigated ones from the same area. In addition to soil organic matter, OPECs may be retained by the inorganic domain of soil; for instance, ciprofloxacin showed strong and instantaneous adsorption by iron oxides and clay in agricultural soils, which was achieved by the formation of covalent bonds between metals in the soil and the oxygen atoms within ciprofloxacin molecules [188]. Furthermore, adsorption of carbamazepine by smectite type clays has been reported by [215]. According to studies referred to in [182, 185, 215], the adsorption of OPECs with multiple aromatic rings is more efficient in soils displaying a high content of humified organic matter –which displays higher aromaticity than labile organic matter–. Polyaromatic compounds can establish π – π bonds between the aromatic rings within the pollutant molecules and aromatic compounds contained in soil organic matter. The formation of such bonds should be studied in future research in order to determine the optimum chemical characteristics of soil organic matter which enable better retention of contaminants, hence preventing their mobilization into the aquifer and/or making them available for uptake by plants. OPECs may be adsorbed by dissolved organic matter to soil via wastewater. Adsorption of organic pollutants to dissolved organic matter increases the solubility of the compounds and hence facilitates the lixiviation through soil. Studies referenced in [216–217] report that compounds such as naproxen, carbamazepine and sex hormones can be adsorbed onto dissolved organic matter, notably to the hydrophobic and neutral hydrophilic fractions of dissolved organic matter. The speed of formation and strength of bonds between organic compounds and the dissolved organic matter varies depending on the quality of both wastewater and dissolved organic matter in soil [217]. The continuous occurrence of OPECs in wastewater irrigated soils can impact upon the adsorption of other organic pollutants; this is because at the time emerging pollutants enter to soil via wastewater, some of the active adsorption sites in soil are still

occupied by previously adsorbed pollutants. In the study referred to in [182], the distribution coefficients of three OPECs, namely naproxen, carbamazepine and triclosan, were determined by an adsorption model which takes into account the previous presence of organic pollutants in the soil (the initial mass model [218]). The authors found modest differences between the values obtained in their study and those reported in the literature. However, it was observed that compounds previously adsorbed onto soil, i.e. naproxen and carbamazepine, were released from the solid matrix each time wastewater “washes” the soil in each irrigation event, resulting in a risk of contamination of the aquifer.

The transportation of OPECs through soil is closely related to their adsorption onto the solid matrix. Transport studies can be performed using different approaches, either packed soil columns or undisturbed soil columns tests. Transport of OPECs and pathogens is better described using the undisturbed soil column approach; through this approach, it is possible to evaluate the impact of both physical and chemical properties of soil on the transport of pollutants. In transport assays using undisturbed soil columns it is possible to assess the impact of preferential paths on the transport of solutes and particles, at the same time determining the effect of chemical properties of soil in the retention of solutes under dynamic flow conditions. The type of clays in soil significantly impacts on the transport of organic pollutants. The presence of expansive clays in soil results in the disappearance of preferential paths in the porous network of soil once clay becomes wet, which in turn provokes the decay in transport of contaminants contained in water. However, in such cases, soil conditions become anaerobic and thus organic pollutants are biodegraded with difficulty. The understanding of the environmental fate of OPECs in wastewater irrigated soil still has many gaps. It is therefore important to carry out studies on the laboratory scale and then in the field (plot level or landscape level) in order to determine the fate of these substances under real conditions. Results of these studies are of great importance, on the one hand, to allow more accurate and useful risk assessment studies and, on the other hand, to determine the characteristics of the sites suitable for irrigation with treated/untreated wastewater without posing a risk to the health of organisms and to the quality of crops and water sources. Lastly, regulations for OPECs in soil should be established in order to set maximum concentration limits for the accumulation of these compounds in terms not only of the effects caused to soil organisms, but also their potential to reach groundwater.

3. Perspectives for further studies

Reuse of wastewater in agricultural irrigation is a complex issue that requires the development of numerous studies in different disciplines; in this section some perspectives for further studies are presented.

1. Long-term studies aimed at determining the improvement of soil properties to produce food. Such studies should compare the rate of entry and conversion of carbon, nitrogen and phosphorus in irrigated soils in order to obtain a mass balance showing either the sustainability or the accumulation of organic matter in wastewater irrigated soils.

Moreover, studies demonstrating the long-term increase in the soil's ability to treat wastewater used for irrigation should be carried out for each of the properties addressed in this chapter, as well as those considered appropriate in each system.

2. The determination of OPECs and pathogens in soils irrigated with wastewater. Such monitoring studies can be used to establish an inventory of contaminated sites that reflects the level of pollution in developed and developing countries. This can help in proposing *ad hoc* solutions for each site.
3. Determining feasibility and the mechanisms that can lead to horizontal propagation of antibiotic resistance genes in soil microorganisms (either innocuous microorganisms or opportunistic pathogens).
4. Chronic toxicity studies of OPECs in wastewater irrigated soils covering either several crop cycles, several generations of organisms or several years. Toxicity studies should address the effects of the presence of mixed contaminants at trace levels (environmentally relevant concentrations) on soil organisms. Such studies should be conducted including new emerging contaminants, e.g. nanoparticles.
5. The study of the environmental fate of emerging contaminants using different model molecules in soil. Such environmental fate studies should be carried out at laboratory and field scale. In the case of environmental fate studies at laboratory scale, conditions used should be those that best emulate field conditions, e.g. sunlight lamp intensities similar to those observed in the field for testing photodegradation or undisturbed soil columns in transport assays through soil.
6. The determination and quantification of the by-products appearing in soil upon dissipation of OPEC. Harmful compounds such as dioxins, chlorophenols and polyaromatics may be produced in soil from substances such as triclosan and carbamazepine. Discerning the occurrence and fate of these substances in soil should be addressed in future studies
7. Determination of the environmental fate of organic, inorganic and microbial contaminants in agricultural soil remaining after irrigation with wastewater has ceased. Worldwide, notably in developed countries, there are several sites where irrigation with wastewater has been stopped after a considerable time; in such cases, it is necessary to know the fate of the pool of pollutants that accumulated in soil during continuous input via wastewater. Phenomena such as the release of heavy metals confined in soil organic matter can occur when soil organisms start to mineralize organic carbon accumulated in the soil. In addition, the soil microorganisms can lose the capacity to treat pollutants in wastewater, leaving the soil vulnerable in cases where wastewater irrigation is restarted.
8. Studies elucidating the conditioning methods for agricultural soils newly irrigated with wastewater. Since in arid regions a considerable increase in the area under irrigation is being observed, it is necessary to use current knowledge to implement regulations establishing the optimal conditions for soils candidate to receive treated/untreated wastewater. These are necessary to prevent soil degradation and contamination of water sources in the irrigated area.

9. Studies on the migration of contaminants in soil due to extreme events caused by climate change. Extreme rainfall events can cause an incremental increase in the mobilization of organic contaminants retained in the surface layers of soil into aquifers or to non-irrigated soils affected by runoff. However, increases in temperature can decrease the biodegradation of organic pollutants in the soil due to excessive drying of the solid matrix.
10. The development and implementation of wastewater treatment systems to remove organic, inorganic and biological pollution without reducing the content of organic matter in the water. These systems must be inexpensive for dissemination in developing countries. Advanced primary treatment systems may represent a plausible strategy in such cases.
11. The development and validation of environmentally-friendly analytical techniques for the determination of OPECs in soils..

4. Conclusions

The reuse of treated/untreated municipal wastewater for agricultural irrigation definitely has positive impacts on soil as a medium for the development of plants and animals; additionally, this practice results in positive impacts on the welfare of farmers due to the monetary savings and profits that they obtain by the use of wastewater as a fertilizer and water source for crops. Similarly, the soil's ability to self-cleanse and treat the wastewater supplied at each irrigation event increases with the reuse of wastewater. The accumulation of organic matter in the soil surface results in changes in soil pH to neutral and basic values, an improvement of soil physical structure and an increase in the soil microbial activity. Together with this, soil organisms become acclimatized to the presence of contaminants and thus their resilience to the harmful effects caused by pollutants increase. These phenomena lead to an improvement in the ability of the soil to act as a filter and transforming medium for contaminants and thereby to an increase in its capacity to treat wastewater. Such an improvement in soil functions can be capitalized by the State and the conventional treatment regime can be changed to a cheaper one driven by natural attenuation mechanisms. This in turn improves the quality of life of people living in the area by increasing food production and the possibility of obtaining profit by sales of produce. The responsible reuse of municipal wastewater for agricultural irrigation can help to mitigate three problems which are a priority in developing countries: a) water stress in arid areas where rain-fed agriculture makes development uncertain. In such areas freshwater sources are used for agriculture rather than human consumption, and therefore the reuse of municipal wastewater not only results in savings of freshwater but also in the recharge of the aquifer in the irrigated area. Recharge is with good quality water produced by infiltration of wastewater through the soil; b) the food crisis and the lack of jobs in rural and peri-urban areas in developing countries. Reuse of wastewater represents a way of producing food for consumption and sale; and, c) the treatment of municipal wastewater generated in urban and rural areas through a low cost natural treatment systems which in turn generate profits for population.

In order to reuse wastewater responsibly and exploit its inherent benefits for soil and people living in the irrigated area, the occurrence of contaminants in wastewater—especially untreated wastewater— must be kept in mind. The presence of pathogenic microorganisms and the potential for antibiotic resistance dissipation via wastewater should be priority concerns in designing wastewater reuse schemes in agricultural areas, notably when using raw wastewater. Attention should be paid to the fate of emerging contaminants in wastewater irrigation schemes including its transportation through irrigation canals, storage in dams and deposition in agricultural soils and transport to aquifers. Another priority is the elucidation of the chronic toxic effects caused by the continuous presence of traces of emerging contaminants in irrigated soils. Since the group of OPECs is quite broad, model compounds should be selected to determine the rate at which they are dissipated or retained/transported through soil, as well the risk of these compounds reaching the aquifer or being assimilated by plants. Despite the spread of antibiotic resistance in the environment it has not been conclusively shown the role that irrigation with treated/untreated wastewater plays in this. To date, the concentrations of OPECs found in soil irrigated with wastewater are lower than the toxicity thresholds reported in literature. The precautionary principle states that wastewater must be minimally treated before irrigation in order to remove pathogenic microorganisms and trace of heavy metals, as well as to reduce as much as possible the concentration of emerging pollutants. Other areas of opportunity to be developed in order to reduce the risk of soil degradation and effects on soil organisms are: a) the development of environmentally friendly everyday-consumer products, containing organic compounds that have been proven to have no harmful effects on living organisms even at trace concentrations. Consumer products must follow strict risk assessments before release to the market; b) an improvement in health systems in cities in order to reduce the incidence of infectious diseases that ultimately generate biological contamination of soil, especially in irrigation systems using raw wastewater; c) the maintenance of wastewater irrigation schemes fed with municipal wastewater in order to avoid a high input of heavy metals and refractory organic compounds to soil and crops through irrigation; and, d) the *ad hoc* treatment of municipal wastewater to allow its reuse in agricultural activities. Low cost treatment systems aimed at removing microorganisms, suspended solids and trace heavy metals are recommended to treat wastewater without affecting its properties as a fertilizer and source of organic matter to improve physical, chemical and microbiological soil properties. Such an approach allows soil to fulfill its ecological functions as a generator of food and livelihoods and as a protective barrier to the aquifer.

Author details

Juan C. Durán-Álvarez¹ and Blanca Jiménez-Cisneros²

1 Centre of Applied Science and Technological Development, National Autonomous University of Mexico, Mexico D.F., Mexico

2 International Hydrological Programme (IHP), UNESCO, Paris, France

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