



Emerging Contaminants in Soil and Water

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The global population increase puts tremendous pressure on the already dwindling natural resources such as soil and freshwater. Healthy and productive soils as well as the availability of freshwater resources are critical for agricultural productivity. On the other hand, climate change and variability make the water scarcity problem even worse. Agriculture, being the biggest consumer of fresh water, is expected to be affected significantly. Yet, agriculture is expected to play a significant role in achieving greater food, and fiber needs to meet the growing global population. In addition, soil and water quality are also becoming a bigger threat to soil productivity and freshwater availability. Some portion of nutrients applied to agriculture and urban landscapes end up in runoff and leaching water that feeds streams, rivers, lakes, groundwater, etc. These excess nutrient loadings are causing soil and water quality deterioration, which could have severe impacts on human health, aquatic ecosystems, and environmental sustainability. In addition to nutrient and chemical pollutions, emerging contaminants such as heavy metals are showing an increasing trend in soil and freshwater bodies. These emerging contaminants not only impair soil quality and freshwater sources but could also get into the food chain and affect human and animal health. While growing evidence is becoming available on the increasing threats from emerging contaminants, research and understanding are still limited. This mini-review paper summarizes available research on types of emerging contaminants and their impacts on soil and water quality.

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INTRODUCTION

In 2050, demands for water and energy are projected to significantly increase (McDonald et al., 2011; Alexandratos, 2012; Ray et al., 2013; Ittersum et al., 2016; Boretti and Rosa, 2019). According to a report by FAO (FAO, 2009), 90% of the required global increase in crop production is expected to be achieved through greater yields and increased cropping intensity as an expansion of agricultural lands is impractical (Cassman, 1999; Guilpart et al., 2017; Wu et al., 2018). This is because land availability is limited, and agricultural land use is facing competition with urbanization and other land uses. Soil quality degradation is also putting lands out of production. In addition, the combined effects of more frequent droughts, climate change, variability, and competing needs from different sectors put greater pressure on natural resources (Elliott et al., 2014; Iizumi and Ramankutty, 2015). These would significantly impact agriculture since it relies on productive soils and the availability of water resources (McDonald et al., 2011; Yigzaw and Hossain, 2016; Kullberg et al., 2017).

With population growth and dwindling freshwater resources, the use of reclaimed water for irrigation has increased (Lavrnić et al., 2017). Despite the advantages of using reclaimed wastewater, safety concerns have been raised regarding the use of this supply for irrigation water (Sato et al., 2013; Paltiel et al., 2016). The main issue with reclaimed water is that it contains various organic contaminants that have been identified as emerging threats (Calderón-Preciado et al., 2011; Bueno et al., 2012). Effluent from these treatment facilities can contain various organic chemicals. Some of these could cause cancer and contaminate the surrounding soil and water sources (US EPA, 2014). Very little attention is paid to date on the status of these contaminants in treated wastewater at various levels of the treatment processes (Bolong et al., 2009). Lack of routine measurements of emerging contaminants in the influent water into the wastewater treatment plants or effluent water at various levels of wastewater treatments, i.e., secondary, or tertiary treatments, limits our understanding of removal of these contaminants, if any, at any level of the wastewater treatment process (von der Ohe et al., 2011). The effectiveness of water treatment steps in the removal of emerging contaminants is not conclusive. Bai et al. (2018) suggested that wastewater treatment plants were primary sources of emerging contaminants observed in surface water samples. Therefore, it is erroneous to assume that even tertiary treated wastewater is free of these emerging contaminants (Köck-Schulmeyer et al., 2011; Cabeza et al., 2012; López-Serna et al., 2012).

During recent years there has been an increased awareness and concern regarding the new group of contaminants in soil and water bodies (Bolong et al., 2009; Houtman, 2010; von der Ohe et al., 2011, US EPA., 2015; Bai et al., 2018, 201). These exist in trace concentrations but are highly toxic and often originate from the disposal of treated wastewater into the soil and surface and groundwater bodies (Bolong et al., 2009; Loos et al., 2013; Petrie et al., 2015). The most common contaminants are solids, dissolved or suspended particulates, nutrients, and heavy metals (Wuana and Okieimen, 2011; Gasser et al., 2014).

Soil is considered as one of the final destinations of chemical wastes (Sakshi et al., 2019). Prolonged soil pollution with chemical wastes can harm living organisms within the food chain (Jaishankar et al., 2014). The increasing levels of emerging contaminants in the soil and aquatic environments pose a threat to human health and ecosystems (Srikanth, 2019). Anthropogenic activities such as mining and industrial waste disposal, as well as the use of chemicals and chemical fertilizers such as arsenic (As)-based fertilizers have been identified as contributing to the increasing emerging contaminants in ecosystems (Bali et al., 2021). Wastewater is also reported as a source for emerging contaminants since traditional methods of treating wastewater are not efficient and costly to completely remove emerging contaminants (Divyapriya et al., 2021). Petrie et al. (2015) confirmed that wastewater treatment procedures used in the treatment plants were not effective in completely removing emerging contaminants.

Up until recently, very little attention was given to these new group of contaminants which could exist in very low concentrations but are quite harmful to marine life and humans if they enter the food chain (Houtman, 2010; von der Ohe et al., 2011; Petousi et al., 2019). Furthermore, there is no full understanding of how these emerging contaminants accumulate in the soil, especially after several years of use of treated wastewater for irrigation and uptake and bioaccumulation of these contaminants by the plants. This mini-review mainly focuses on the major types of emerging contaminants that are reported to impair soil and water quality.

POLYCYCLIC AROMATIC HYDROCARBONS

Polycyclic aromatic hydrocarbons (PAHs) are abundant chemicals found naturally in fossil fuels (Cao et al., 2017). Incomplete combustion of coal, gas, wood, and oil also produces PAHs (Hsu et al., 2016; Cao et al., 2017). Soil is one of the ultimate ecological destinations of PAHs (Agarwal et al., 2009). PAHs are known for their high rate of bioconcentration and quickly entering the food chain (Yang et al., 2022). The United States Environmental Protection Agency (US EPA) has identified 16 PAHs as top contaminants (Cao et al., 2017; Li et al., 2019). Due to their lipophilic and hydrophobic properties, PAHs are persistent; they can stay in the soil for long periods (Agarwal et al., 2009; Košnář et al., 2018; Li et al., 2019). They do not burn very easily or break down in the water (Li et al., 2019). The increasing molecular mass can logarithmically decrease the solubility PAHs in an aqueous solution (Johnsen et al., 2005). Due to less solubility and low volatility of PAHs with five or more rings, they are abundantly found in a granular type, attached to contaminated air, soil, or sediment particulates (Choi et al., 2010). In contrast, PAHs with low rings are readily available for biological uptake and degradation due to their easy solubility in water (Mackay and Callcott, 1998). In general, PAHs with higher rings are more persistent in the environment than the lower rings (Johnsen et al., 2005).

The International Agency for Research on Cancer (IARC) Monographs Programme studied carcinogenic properties of 60 PAHs (IARC, 2010). Among 60 PAHs examined, benzo [a] pyrene was categorized as carcinogenic to humans. Cyclopenta [cd]pyrene, dibenz [a,h] anthracene, and dibenzo [a,l] pyrene were categorized as probably carcinogenic to humans. A total of 11 other studied PAHs were categorized as possibly carcinogenic to humans (Poucke et al., 2012; Jameson, 2019).

Regarding the effects of PAHs on plants, however, there were mixed reports. Several studies have reported that PAHs had adverse effects on the development of plants (Alkio et al., 2005; Liu et al., 2009; An et al., 2018). Studies also reported that PAHs have either no effect or promoted plant growth (Maliszewska-Kordybach and Smreczak, 2000; Ling and Gao, 2004; Meng and Chi, 2015).

PHARMACEUTICAL AND PERSONAL CARE PRODUCTS

Pharmaceutical and personal care products (PPCPs) are products such as toothpaste, skincare products, fragrances, antibiotics,

pharmaceutical medicines used by consumers for their health and cosmetic purposes, or veterinary drugs that are used by agroindustry to enhance the growth or health of livestock (Wang and Huang, 2019; Bishnoi et al., 2022). PPCPs are becoming very common in environments where the traditional wastewater treatment plants are not able to effectively remove them (Wang and Wang, 2016). Waste from animal farms and sewage treatment plants can also lead to the release of emerging contaminants into the aquatic and soil environments (Ebele et al., 2017). Sewage sludge from wastewater treatment plants is commonly used as a fertilizer for agriculture (Corradini, 2014). It contains various nutrients such as potassium, nitrogen, manganese, and iron (Mtshali et al., 2014). However, treated sewage sludge can also contain various emerging contaminants such as antibiotics, chemicals, and engineering nanomaterials (Koumaki et al., 2021). PPCPs are among the emerging contaminants found in sewage sludge that have potential adverse ecological impacts or human health risks if they are released into ecosystems (Van et al., 2021).

Due to little understanding of the possible environmental impacts of PPCPs, they are considered contaminants of emerging concern (CECs) (Vasilachi et al., 2021). The other source of PPCPs in the soil is treated wastewater or contaminated river water, which is used for irrigation (Gallego et al., 2021). Soils are often contaminated with CECs that have low hydrophobicity. These can then be accumulated in the soil through organic material interactions (Beltrán et al., 2020).

A study in Spain on 166 emerging contaminants and heavy metals (e.g., Cd, Ni, Pb, and Hg) found that 38 pharmaceuticals, albeit low concentrations, were detected in tertiary treated wastewater (Cabeza et al., 2012). This supports similar findings from other studies (Bolong et al., 2009; Ziylan and Ince, 2011; Cabeza et al., 2012) suggesting that wastewater treatment processes are not effective in removing some of the emerging contaminants. Incomplete removal of these contaminants, particularly pharmaceuticals, during the treatment process is the main reason for recent findings of these contaminants in the water bodies used for disposal of treated wastewater (Kasprzyk-Hordern et al., 2008a, 2008b; Cabeza et al., 2012). Bai et al. (2018) conducted a detailed study on the status of emerging contaminants in surface water sources in Denver, Colorado, where the surface water flow is influenced by snowmelt during spring and discharge from several wastewater treatment plants distributed across that region. Their findings showed that 76% (109 of 144) analyzed pharmaceutical compounds were found in water samples (Bai et al., 2018). Such high percent detection of emerging contaminants in water samples, despite the substantial dilution of treated wastewater by the natural water flow, suggests that discharge of treated wastewater from several wastewater treatment plants could be a major source of emerging contaminants (Bai et al., 2018). Similarly, Petrie et al. (2015) summarized the concentrations of several pharmaceuticals in influent and effluent water from the wastewater treatment plant as well as surface water samples in the United Kingdom. There was a clear trend of detection of emerging contaminants in the surface water samples that were

exposed to treated wastewater with the effluent that has high concentrations.

PESTICIDES

A pesticide is a substance that works by killing pests or keeping them from damaging the environment (Aktar et al., 2009). Some examples of known pesticides are those used against insects, plant pathogens, and microorganisms. Although they are useful for keeping pests and diseases at bay, they can also cause toxicities to humans and other organisms (USGS, 2017). Over 95% of the chemicals used for pest control reach other places beyond their intended destinations such as air, water, and soils. A study conducted by the US Geological Survey (USGS) on the surface water of 38 streams in the US found top 10 most frequently detected anthropogenic contaminants were: eight pesticides (CIAT, chlorpyrifos, AMPA, metolachlor, dieldrin, atrazine, de-sulfinyl fipronil, and glyphosate) and two pharmaceutical drugs (caffeine, metformin) with 66-84% detection rates (Bradley et al., 2017). Pesticides are among the highly persistent chemicals in soil. The excessive use of these chemicals can lead to the formation of soil contaminants (Pullagurala et al., 2018). It has been revealed that the use of pesticides is increasing in some areas despite being banned (Pan et al., 2019). Organochlorine pesticides, also known as OCPs, are among the persistent organic pollutants. OCPs are known to have high toxicity, bioaccumulation, and biomagnification in the environment (Sparling, 2016). Bai et al. (2018) reported that surface water samples contained 39 of 72 (54%) of analyzed pesticides.

PHTHALATE ESTERS

Phthalate esters (PAEs) are often used as an additive to improve the flexibility of certain polyvinyl chloride (PVC) resins. They are also used in various other resins such as cellulose, vinyl acetate, and polyurethanes. The stability, fluidity, and low volatility of Phthalate esters make them ideal for plasticizers (Peijnenburg, 2008). These derivatives are produced by phthalic anhydride and are mixed with plastics to increase their properties, such as resilience, plasticity, and pellucidity (Thomas and Brogat, 2017). PAEs can also be used as enteric coating agents for various applications (Kapoor et al., 2020). End-user applications of these derivatives include resin houses, agricultural adjuvants, cosmetic products, soap and laundry detergents, toys, and various other applications. PAEs are poorly water-soluble chemicals. The water solubility of a chemical is also a vital factor that influences the biodegradability and aquatic toxicity of a chemical. It also affects the distribution of these chemicals. Although PAEs are known to have low aqueous solubility, they can be quickly absorbed by organic residue and solid surfaces in the environmental systems (John Autian, 1973). Slow and steady accumulation and release of these chemicals could affect the ecological conditions of water systems. Sludge-amended soils and wastewater treatment facilities are also affected by this condition (Staples et al., 1997). Due to the widespread use of PAEs, their ubiquity has led to the accumulation of these chemicals in several ecosystems' compartments. The accumulation of PAEs in agricultural soils could lead to the contamination of food chains and vegetables. It could also cause indirect or direct human exposure (Zeng et al., 2008).

HORMONES

Due to the industrial growth of the world, steroidal estrogen has been considered an emergent issue. It has been known to severely affect aquatic life and soil fertility (Singh et al., 2021). Steroidal hormones are either synthetic or naturally occurring forms of estrogen that are released from the adrenal cortex and other parts of the animal and human body (Biga et al., 2019). Many of these emerging contaminants, such as synthetic or natural hormones, are known as hormone disrupters (Preisendanz et al., 2021). The human population discharges about 30,000 kg of natural steroidal estrogens and 700 kg of synthetic estrogens solely from birth control pill practices each year. The release of estrogens from livestock can be quite high. In the US and European Union, for instance, it is estimated that about 83,000 kg of estrogens are released annually (Adeel et al., 2017). Natural estrogens discharged from animal and human waste have been considered a serious threat to the environment (Arnon et al., 2008). This environmental issue is especially alarming since the use of bio-solids such as animal manure for organic farming has been widely adopted in the field (Xuan et al., 2008). A study conducted by USGS and EPA in 1999 and 2000 revealed that out of the 139 streams analyzed, 82 chemicals were found in 80 percent of them. The most common types of chemicals were steroids hormones, antibiotics, and insect repellent (USGS, 2002).

PERFLUORINATED COMPOUNDS

Perfluorinated compounds (PFCs) are known to have various functional groups, such as perfluoroalkyl and perfluoro carboxylic acids (Corsini et al., 2014). Due to their high surface activities and chemical and thermal resistance, PFCs are commonly used as industrial chemicals in various industries such as textile, pesticides, and refrigeration (Prevedouros et al., 2006; US EPA, 2014; Liu et al., 2020). Perfluoroalkyl acids (PFAAs) are a type of perfluoroalkyl carboxylic acid. PFAAs are known to have widespread distribution and high abundance (Sha et al., 2022). Due to their persistence in the environment, PFAAs have been considered as an emerging contaminant of concern and a threat to human health and the environment (Kurtz et al., 2019). The PFAAs contaminate the soil in many ways, such as when the reclaimed wastewater is used for irrigation (Jürling, 2021)or biosolids are added as a fertilizer for crop production (Blaine et al., 2013). Biosolids are the organic materials produced by the treatment of sewage sludge. They are typically treated according to the regulations of their respective governments (Lu

et al., 2012). In the US, around 60% of the land used for farming is devoted to the application of these materials (Blaine et al., 2013). Currently, the US Environmental Protection Agency enforces various regulations regarding the land use of biosolids (US EPA, 2013b). However, there is no regulation for PFAAs in biosolids. This means that repeated applications of biosolids could cause potential contamination of the environment including soil, surface, and groundwater (Müller et al., 2011).

ENGINEERED NANOMATERIALS

Engineered Nanomaterials (ENMs) are generally defined as particles with a dimension of less than 100 nm (US EPA, 2017). ENMs can be made through various chemical processes and physical steps, such as self-assembly or milling. ENMs exhibit special properties such as physicochemical, electrical conductivity, and mechanical strength (Luoma, 2008; US EPA, 2008). Due to their unique properties, nanomaterials are becoming more prevalent in various industries. However, their safety and environmental concerns are still unknown (US EPA, 2017). The release of ENMs into the soil during the field applications of biosolids and wastewater has been identified as a major source of pollution (Pan and Xing, 2012). They may also be released into the environment through manufacturing and ecological applications or inappropriate handling (US EPA, 2013a). The increasing number of ENM being deposited in terrestrial environments is expected to make these areas the largest repository for harmful materials.

The structure of nanomaterials can absorb toxic heavy metals such as copper, lead, mercury, and cadmium in the soil, air, and water. Due to their toxic properties, these metals can cause various disorders (Kamal et al., 2021). ENMs can also transform their properties depending on the environment's biological, chemical and physical processes (Nowack et al., 2012). Researchers have been trying to determine if models or experiments are needed to predict the distribution of ENM pollutants in different environmental compartments such as soil, water, and atmosphere (Wiesner et al., 2009; Westerhoff and Nowack, 2013).

The factors that determine the exposure risks of engineered nanomaterials will also be affected by the processes involved in their transformation. Not only does this process affect the release of ENM into the environment, but it also affects the products that contain it. Depending on the properties of the material and the transformation they undergo, released ENM may have a lesser or greater environmental impact than the materials that were initially produced. Although the released and transformed materials are the ones that are actually in the environment, the effects of these are still unknown (Nowack et al., 2012).

The effects ENMs on plants depends on several factors including soil properties and physicochemical characteristics of ENMs. Although the presence of other co-existing contaminants can affect the bioavailability of ENMs. Studies have shown that soil amendment with substances such as biochar can help minimize the uptake of certain ENMs by plants (Reddy et al., 2016; Deng et al., 2017; Servin et al., 2017; Pullagurala et al., 2018).

CONCLUSION

Increasing trends in emerging contaminants have been documented in several places throughout the world. Several studies have documented considerable evidence of widespread concern on the emerging contaminants contamination of soils and surface water linked to the discharge of treated wastewater. However, there is a lack of full understanding about the fate of these contaminants in treated wastewater when used for irrigation, in terms of crop uptake, bioaccumulation, getting into the food chain, and eventually health risks to humans and other living organisms. In addition, the effectiveness of different wastewater treatment procedures to remove emerging contaminants and/or their metabolites from the influent water is not clearly understood. As such, there is a critical need to develop standards and policy guidelines regarding limits of these emerging contaminant concentrations contaminant in soil and water. Therefore, this mini-review calls for the need for assessing the environmental and potential human exposure risks of emerging contaminants originating from the discharge of treated wastewater into natural water bodies. Specifically, there is a compelling need to investigate: 1) temporal variation in concentrations of various emerging contaminants in secondary and tertiary treated wastewater from wastewater treatment plants, depending on the level of wastewater treatment before it is disposed to surface or groundwater bodies or marine environment or used for irrigation of crops; 2) potential risks

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of these contaminants, if exist in treated wastewater in high concentrations, entry into the food chain by agricultural products which are irrigated by treated wastewater directly or surface water which receive treated wastewater discharge as disposal mechanism. The availability of such information will help to guide policy towards developing critically needed standards on threshold limits of such contaminants in discharge water from wastewater treatment plants and other point sources of pollution.

AUTHOR CONTRIBUTIONS

HB prepared the draft manuscript, FT conducted an additional literature review, HB, FT, and YL contributed to manuscript revision, proofreading. All authors have approved the submitted version of the manuscript.

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