Possible influence of microplastic on the partitioning and bioavailability of 17α-ethinylestradiol in agricultural soil; a literature review using mass balance equations

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Abstract

Global concern regarding microplastic (MP) pollution increases. MPs may function as a novel compartment for the partitioning of chemical pollutants, thereby altering their bioavailability. 17α-ethinylestradiol (EE2), a potent endocrine disruptor compound, enters soil via biosolid application. Limited literature about influenced partition of EE2 in soil due to the presence of MPs is available. This research aims to assess the distribution of EE2 in soil in the presence of MPs for the plastic types of polyethylene (PE), polyamide (PA) and thermoplastic polyurethane (TPU) in different environmental compartments using mass balance modelling, based on recent literature.

Generally, EE2 was found to be majorly bound to soil, except for low values of partitioning of EE2 in soil, while high amounts PA MPs were present. Concluding, specific polymers in high concentrations present, may influence the distribution of EE2 in soils co-contaminated with MPs. The observed sorption order (PA> PE > TPU) differed from expectations based on literature. Combined effects of differences in crystallinity and strength of hydrogen bonds of PA possibly outweighs the difference in hydrophobic capacities between PA and PE. The observed concentrations of EE2 distributed in various compartments are not expected to show any adverse effects, based on the $PNEC_{water}$. Also, less EE2 was taken up by biota in the presence of a higher plastic mass, so the presence of MPs may reduce bioavailability of EE2.

However, this model does not adequately reflect real-life scenarios due to assumption made and the nature of the parameters. Nevertheless, it provides a rough estimate of EE2 partitioning in soil in the presence of MPs and highlights the lack of knowledge about toxicity of EE2 on soil organisms and the complexity of this matter. Follow-up research should focus on identifying partition values for EE2, for the variety of MPs and their degree of weathering found in soil. Additionally, trustworthy toxicity data is needed for accurate risk assessment.

Layman's Summary

Plastic usage has transformed daily life and brought societal benefits, but concerns increase because 79% of all plastic waste ends up in the environment with soil being an important sink. In the environment, plastic breaks down to microplastic (MP), which may function as an additional compartment to which chemicals can bind, thus possibly altering the environmental fate of chemical contaminants. After sewage sludge application on agricultural fields, a highly potent endocrine disruptor compound (EDC), EE2, may up in the soil. Proper analysis of specific interactions between EDC and MPs, however, is lacking.

This study used mass balance modelling based on recent literature to assess the distribution of EE2 in soil under the influence of MPs from three plastic types (polyethylene (PE), polyamide (PA), and thermoplastic polyurethan (TPU)) expected to show sorption: PE> PA > TPU (based on their hydrophobic properties). Due to the large variation of soil sorption values for EE2, the highest and lowest values were used to represent a range. Also, a worst- and best-case scenario of plastic pollution in agricultural fields was considered. The mass balance model calculated the distribution of EE2 over the soil solid phase, MPS, soil pore water, and biota.

The larger proportion of EE2 was sorbed to the soil in all scenarios, except for low soil sorption with worst-case pollution of PA. This result suggests that specific polymers in high concentrations present, may influence the distribution of EE2 in soils co-contaminated with MPs. Less EE2 was taken up by biota in the presence of a higher plastic mass, so the presence of MPs may reduce bioavailability of EE2. Reduced sorption concentrations, however, were very low. The observed EE2 sorption order was: PA > PE > TPU. This deviation from expected may be explained from differences in the molecular structure of the surfaces of PA and PE particles. EE2 leaching from ingested MPs could lead to a novel way of internal exposure, however, no literature is available on EE2 desorption from PE, PA or TPU. Only limited literature on EE2 toxicity and bioaccumulation in soil organisms is presents, hampering comparison result to literature data. The mass balance model does not adequately reflect a real-life scenario because of the assumptions made and the nature of the parameters.

Nevertheless, this study provides a rough estimate of EE2 distribution in soil in the presence of MPs and highlights the lack of knowledge on toxicity of EE2 to soil organisms and its complexity. Identifying the variety of MPs present in soil, their degree of weathering, and the sorption affinity of EE2 for all plastic types present in soil are suggestion for further research that enhance the model's prediction capabilities. Furthermore, trustworthy toxicity data are needed for accurate risk assessment.

Introduction

Plastic usage has transformed daily life and brought numerous societal benefits. The consumption of plastic continues to rise, with global production increasing from 335 million tons in 2016 to 368 million tons in 2019 (Plastics Europe, 2021). However, plastic waste has emerged as a significant global challenge (Thompson et al., 2009). After use, the vast majority of plastic ends up in the environment. Between 1950 and 2015, an estimated 5,000 billion tons of plastic waste were discarded in the environment, accounting for 79% of all plastic waste. This volume is anticipated to exceed 12,000 billion tons by 2050 if no action is taken (Geyer et al., 2017).

Once in the environment, plastic waste breaks down into smaller particles, known as microplastics (MPs) (Wright et al., 2013). Waste fragments ranging from 0.1μm to 5mm are classified as MPs, whereas particles smaller than 0.1μm are classified as nanoplastics (NPs) (Agboola & Benson, 2021). The degradation process underlying the embrittlement from plastic waste to MPs is caused by factors such as UV light (photo-oxidation), reactive oxygen species (ROS), and mechanical forces, resulting in physical abrasion.

Based on their source, MPs found in the environment can be classified as primary and secondary MPs. Primary MPs are purposefully produced for usage in a variety of products, such as cosmetics and nurdles. Secondary MPs are formed unintentionally from the degradation of larger plastic items (Galafassi et al., 2019). The majority of MPs are secondary, resulting from the breakdown of larger items. These larger items result in a wide variety of MPs due to their enormous diversity in polymer types, density, sizes, and shapes (Koelmans et al., 2022).

Although scientific and public concerns have mainly focussed on marine and aquatic systems, there is a growing interest among researchers in studying the fate and effects of MPS in soil and terrestrial ecosystems (Ng et al., 2018). Because the amount of plastic waste accumulating on land is expected to be 4 to 24 times higher than in marine environments, further research is needed to acquire a better understanding of the potential impacts of MP pollution on soilecosystems (Horton et al., 2017).

However, presumed toxicological effects and accumulation are not the only concerns related to MP pollution. MPs may function as an additional compartment for chemical partitioning, potentially affecting the transport and fate of chemical contaminants (Tourinho et al., 2019). Because of their hydrophobicity and large specific surface area, MPs are potential absorbents (Peña et al., 2023). Knowing the sorption mechanisms and interactions between MPs and soil contaminants is critical for acquiring a better understanding of the partitioning of soil contaminants, as well as their bioavailability and toxicity. Interactions between MPs

and chemical pollutants are complex, with many factors influencing sorption processes. The physicochemical properties of both the sorbate and the sorbent are of relevant, as are the properties of the medium in which they interact with each other (Tourinho et al., 2019).

The first few research articles on the interaction of MPs and pollutants date back to the 1970s and 1980s (Tourinho et al., 2019). However, in the last four years, this topic has received significant attention (*Figure 1).* Much research has focused on the interaction between MPs and pesticides. Other environmental contaminants of concern, such as endocrine disruptor compounds (EDCs), are frequently mentioned, but in-depth analyses of the implications of these interactions for bioavailability and toxicity in soil for specific hormones and plastic types are still lacking. EDCs enter agricultural soils through the application of sewage sludge. One such EDC is 17α-ethinylestradiol (EE2), a synthetic estriadiol analogue that is highly potent as an estrogen receptor agonist. This chemical was added to the European Watch List in 2018 due to its environmental occurrence (The European Commision, 2018). The compound can adversely affect organisms at concentrations as low as one nanogram per litre (Adeel et al., 2017). Interactions between EE2 and various types of MP may possibly result in variable partitioning and distribution in the environment, which may change its bioavailability and toxicity.

Hence, this study aims to assess the distribution of EE2 in soil for different compartments using mass balance modelling for different plastic kinds based on recent literature. EE2 is expected to be strongly bound to soil; nevertheless, since hydrophobic interactions are the expected main sorption mechanism for MPs, the expectation is that MPs will be the second compartment with the highest concentration of EE2 being sorbed. Given the properties of PE, PA, and TPU and the general conclusion in the literature about interactions between MPs and pollutants, PE is expected to exert the most hydrophobic interaction with EE2, followed by PA and TPU.
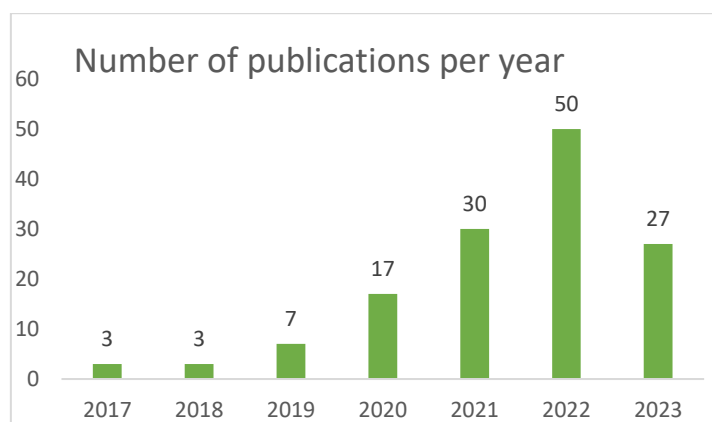
Figure 1: Publications per year in the database PubMed
for the key words "interactions", "contaminant", "microplastics" and "soil".

Literature search

To achieve the objective of this study, a literature search was conducted between April and June 2023 using PubMed, Scopus, and Google Scholar for the keywords "microplastic" in conjunction with "soil", "interactions", "pesticides", "EE2", "sorption" "toxicity", "sewage sludge", "biosolids", "concentration" to identify relevant studies. Other keywords used were "EE2" in conjunction with "soil", "partition coefficients", "sorption isotherms", "toxicity", "biosolids", "sewage sludge" and "microplastics". The reference lists of the initial relevant articles were viewed, resulting in additional papers that were included in the literature overview.

Factors influencing sorption properties of organic pollutants on MPs

Plastic properties
The physico-chemical characteristics of polymers influence the sorption of chemical contaminants. These characteristics include molecular chain arrangement, size, surface area, and acid-base ratios. Polymers can vary in structure, based on different configurations in their molecular chains. Crystalline, semi-crystalline, and amorphous are the structural variation types of polymers. A high degree of crystallinity hinders the affinity of pollutants, resulting in lower sorption capacity due to a more ordered and fixed carbon chain (Agboola & Benson, 2021). For instance, semi-crystalline polyethylene (PE) and polyamide (PA) are expected to have a lower sorption capacity based on this property compared to amorphous thermoplastic polyurethane (TPU) (Li et al., 2019; Djukic et al., 2020; Lin et al., 2019). Due to its linear arrangement, PE, has a higher degree of crystallinity compared to PA. Therefore, based purely on the crystalline properties, the expected sorption capacity for organic contaminants would be TPU > PA > PE.

Furthermore, sorption processes are influenced by the MP particle size. An increased adsorption capacity for three triazole fungicides on polystyrene (PS) was found by Fang et al. (2019). A significant difference in sorption capacity was observed between 10 μm particles and 100 μm particles, and between 10 μm particles and 2 μm particles. Surprisingly, 10 μm particles showed the highest increase in sorption in both comparisons, although smaller particles are expected with higher sorption capacity, due to their surface area-mass ratio. This result is explained by probable agglomeration of 2 μm PS particles in aqueous solution. Sorption capacities per size were also investigated by Munoz et al. (2021), who studied the sorption of diclofenac and metronidazole on PS, polyethylene terephthalate (PET), polypropylene (PP), and high-density polyethylene (HDPE). They found an increase in

sorption capacity, with a decrease in MPs size, for the range of 20-1000 μm particles. This is explained by the increasing surface area ratio present for sorption. These results suggest an increase in sorption at an increased surface area ratio, however, there might be a limit to this increase due to agglomeration.

Hydrophobic interactions

MPs and hydrophobic contaminants have an affinity for one another because of their poor solubility in water. Hydrophobic interactions are characterized by the aggregation of non-polar molecules on non-polar surfaces in an aqueous medium (Tourinho et al., 2019). These interactions are considered to be the main sorption mechanisms affecting the binding of contaminants to MPs. Due to the hydrophobic nature of the MP surface, hydrophobic interactions are likely to be stronger when the pollutant's hydrophobicity, indicated with its octanol-water partitioning coefficients, increase (Agboola & Benson, 2021). Aliphatic polymers, such as PE and PA, are indicated to have an increased sorption capacity attributed to hydrophobic interactions (Prajapati et al., 2022). PE is a non-polar polymer composed of repeating units of ethylene monomers. Because polar groups are absent from the molecular structure of PE ($(C_2H_4)n$), it has a high hydrophobic capacity.

The contact angle (CA) is a qualitative way to evaluate whether the surface of a polymer has hydrophobic or hydrophilic characteristics. Hydrophobic characteristics are expected at an angle higher than 90°. The CA of PE is 126°, indicating high hydrophobicity (Lock et al., 2008). PA is a polymer that has an amide (-CONH-) as a functional group. Based on the CA, PA is determined to have slightly hydrophobic behaviour with a contact angle of 107.7° (Lara et al., 2021). TPU is a co-polymer consisting of alternating hard and soft segments. The production procedures determine the specific makeup. An example of a difference in makeup is shown by polyether TPU and polyester TPU. Here, the functional groups found in the soft segments of TPU are ester groups (-COO-) and ether groups (-O-), while urethane linkages (-NH-CO-O-) are typically present in the hard segments of TPU (Huntsman, 2016). TPU shows slightly hydrophobic behaviour as well, with a contact angle of 98° (Jasmee et al., 2018). The soft segments are more polar than the hard segments. Given that the strength of hydrophobic interactions depends on the kind of plastic, PE is predicted to have the greatest sorption capacity for hydrophobic contaminants when comparing PE, PA, and TPU. Based on the hydrophobic properties, the expected sorption capacity for hydrophobic compounds will be PE > PA > TPU.

Electrostatic interactions

When a plastic polymer interacts with a pollutant, it attracts molecules with an electric charge opposite that of its own. Both the medium's pH and the pH_{pzc} (the point of zero charge) of the polymer are important factors to take into account for electrostatic interactions. When the medium's pH exceeds the pH_{pz}, the MP generally becomes negatively

charged (Agboola & Benson, 2021). The pH$_{pz}$ of PA is 3.6 (Asadi Miankafshe et al., 2020), for TPU 8.2. (Y. Li et al., 2020), and that of PE 7.12 (C. Wu et al., 2016a). A negatively charged surface develops on the MP with a higher pH of the medium compared to the pH$_{pz,}$ increasing the attraction of positively charged pollutants. This results in an increased sorption capacity compared to the sorption capacity of positively charged pollutants in a lower medium pH. For agricultural crops in soil, the optimum range of pH is 5.5 -7.5 (Odutola Oshunsanya, 2019). Considering this range, PA will have a negatively charged surface area in soil, TPU a positively charged surface area, and PE a non-charged surface area. Therefore, a non-charged plastic such as PE is expected to have the largest sorption capacity for a non-charged pollutant such as EE2.

The π-π interactions

Benzene rings can interact with one another via a noncovalent attraction. The study of Elizalde-Velázquez et al. (2020) showed that π-π interactions are important in the sorption of pharmaceuticals by PS MPs. Looking at PE, a simple polymer composed of repeated ethylene monomers that lack a benzene ring, and PA, which lacks a benzene ring as well, TPU would be expected to have the highest sorption affinity for hydrophobic contaminants based on only the π-π interactions. TPU can be aromatic for applications that require toughness, strength, and flexibility, or aliphatic for optical clarity (Huntsman, 2016).

Hydrogen bonds

Hydrogen bonds are another mechanism that contributes to the sorption of contaminants to MPs. They participate in sorption processes when a proton donor and proton acceptor are present in the contaminant and the MPs, respectively, or reversely. Hydrogen bonding interactions are less strong than hydrophobic and electrostatic interactions but stronger than van der Waals forces (Prajapati et al., 2022). Hydrogen bonds are expected to occur between EE2 and PA due to the functional amide group and its polar properties. PE is not expected to have any significant hydrogen bonding due to the absence of polar groups. TPU has, compared to PA, a lower density of donor and acceptor sites in its polymer structure; therefore, PA is expected to have the highest sorption capacity based on hydrogen bonds.

Van der Waals Force

When electrostatic or hydrophobic interactions fail to explain sorption processes, they are attributed to van der Waals forces. Because of the relatively weak, non-specific interactions between the plastic polymer and the pollutant, they can adhere to each other (Agboola & Benson, 2021). Since PEs are non-polar aliphatic polymers with no specific functional groups, hydrophobic contaminants can interact with PE due to van der Waals Forces (Prajapati et al., 2022).

Aged microplastic

MP sorption capacity is additionally influenced by the degree of weathering. Weathering increases the surface area by expanding the pore area, implying larger sorption capabilities. MPs, on the other hand, develop due to the weathering of polar oxygen-containing groups such as -OH, -C=O, and C-O. This causes the formation of a negative charge on the surface, which leads to the sorption of hydrophilic and polar contaminants. As a result, their hydrophobic surface qualities are changed (Prajapati et al., 2022). Furthermore, hydrogen bond interactions may impair the sorption capability of aged MPs by limiting the accessibility of the sorption sites through preferential sorption of water molecules on their surface (Hüffer et al., 2018). Xue et al. (2021) found that due to UV aging conditions, the C-N and C-O bonds of the urethane of TPU are broken, forming an amino radical and an alkyl radical, releasing CO_2, thus altering the functional groups on the polymer surface. They observed an increased sorption of CU(II) on aged TPU, possibly explained by a rougher surface area, with more pit structures favourable for adsorption. In addition, the dissociated functional groups may lead to a negative charge on the surface, attracting more positive pollutants. These finding suggest that the aging of MPs influences their sorption properties.

Modelling of chemical and physical adsorption to MPs

Kinetic and sorption isotherm data can be used to analyse the mechanisms influencing the sorption behaviour of pollutants on MPs. The review of Peña et al. (2023) found for kinetic data of pesticides, that the majority fit the pseudo-second-order and intraparticle diffusion well. Pesticides are generally within a few hours sorbed to MPs, reaching equilibrium. Sorption of carbendazim, trichlorfon, malathion, diflubenzuron, and difenoconazole on PE, reached equilibrium with in two hours of contact with PE particles. However, time needed to reach equilibrium, depends on the properties of the organic pollutant, the plastic type, and degree of weathering. 48 hours was needed to reach a sorption equilibrium for α-endosulfan on low-density PE. For aged PE, equilibrium times shortened. In addition, fipronil sorption rates were faster for biodegradable MPs compared to conventional MPs.

Peña et al. (2023) reviewed that wide variety of sorption isotherm data were mainly fitted to the Freundlich equation. This model explains non-linear sorption processes, where saturation or multilayer sorption on the MP surface can occur. For neutral organic pollutants the slopes of the Freundlich model are generally close to linearity, indicating that adsorption should occur through hydrophobic partition on the plastic surface. However, for charged particles, the log K_{ow} does not accurately predict adsorption. Other factors, such as electrostatic interactions, are probably preferred.

EE2

Usage and sources of EE2

The synthetic estrogen EE2 is very potent endocrine disrupter and therefore widely used in hormone therapies. Consequently, human urine is considered the main source of EE2 entering wastewater treatment plants (WWTPs) (Tang et al., 2021). The removal is incomplete, so with the application of sewage sludge (biosolids) to agricultural fields, EE2 ends up in the soil. Consequently, EE2 has been detected in different environments, such as waste, surface, groundwater, and drinking waters, as well as soils and sediments. To estimate the partitioning of EE2 in soil, it is important to know its properties.

EE2 has an ethynyl-group, and due to this C≡C bond, the synthetic hormone is quite resistant to oxidation in the environment. The half time of EE2 was determined to be 2.1 days in loam soil. Key properties of the loam soil were ratio of sand, silt, clay: 40,45,15, pH 7.4, field capacity 40%, 3.2% organic matter (OM). The loam soil was incubated with 1 mg/kg EE2 substrate at 30°, with a moisture percentage of 15% (Moschet, 2009). At lower temperatures and dryer soil EE2 showed to be more persistent. Specific bacteria can enhance the degradation; for example, bacteria *Sphingobacterium spiritivorum*, isolated from WWTPs, was able to degrade EE2 by converting it to E1 (Haiyan et al., 2007). Quicker degradation (2-4 hours) in the WTTPs compared to natural systems are attributed to the higher bacteria density (Moschet, 2009).

The water solubility of EE2 is 4.8 mg/L, implying the compound is not easily dissolved. Its octanol-water partition coefficients (log K_{ow}) varies between 3.67 and 4.2, meaning it is considered a hydrophobic compound (Scientific Committee on Health and Environmental Risks (SCHER), 2011). Therefore, EE2 is expected to be strongly bound to the soil and accumulate in the topsoil layer, although the binding strength depends on the specific physical and chemical properties of the receiving soils (Szabó et al., 2020). EE2 has a pK_A of approximately 10 (Wang et al., 2014). As for most agricultural crops, the ideal pH of the soil is between 5.5 and 7.5 (Odutola Oshunsanya, 2019). EE2 will be mostly present in soil it is non-ionized form.

Toxicity of EE2

Since the 1990s, EDC have received attention due to their potential adverse health effects on wildlife. These adverse health effects are mainly observed in aquatic organisms; several studies have shown that exposure to EE2 causes a reduction in biomass and interrupts the aquatic food chain. At concentration as low as 10 ng/L, EE2 negatively affected, the heart function of bullfrog tadpoles (Adeel et al., 2017). Remarkably, given that low concentrations show adverse effects in amphibians and aquatic organisms, very little research is done in EE2 toxicity for soil organisms. Kuo et al., (2023) determined the no observed adverse effect

levels (NOAELs) for *Caenorhabditis elegans,* a nematode living in soil, and reported a no observed effect concentration (NOEC) of 0.75 mg/L EE2 for cumulative offspring and 5.1 mg/L for body length. The nematodes were, however, exposed in aqueous medium not in soil. Since limited toxicity data is present for soil organisms, a predicted no effect concentration (PNEC) for soil can be derived from the PNEC for water. Caldwell et al. (2012) proposed a $PNEC_{water}$ of 0.1 ng/L for EE2. The $PNEC_{soil}$ can be calculated via:

$$PNEC_{soil} = Kd * PNEC_{water}$$

Where $PNEC_{water}$ is the predicted no-effect concentration for water (mg/L), $PNEC_{soil}$ is the predicted no effect concentration for soil (mg/kg), and Kd is the partition coefficient soil-water. Using the partition coefficients found in the literature (*Table 1),* the $PNEC_{water}$, of 0.1 ng/L, results in a $PNEC_{soil}$ range of 0.01- 15.97 mg/kg. However, it must be noted that this value needs to be carefully interpreted. The effects on aquatic species can only be considered as effects on soil organisms that are exposed exclusively to the soil pore water and may only be appropriate for organisms with a water-permeable epidermis.

Mass balance model

Use of the mass balance model to estimate EE2 partitioning

Using a mass balance model contributes to the understanding of the partitioning of chemicals in a multi-compartment medium like soil, allowing a holistic assessment over different environmental compartments. In addition, when information is available on the input of a chemical into an environment, it allows for the estimation of concentrations present in each compartment, providing valuable information for risk assessment and management strategies.

In this study, a mass balance model was used to predict various scenarios of EE2 partitioning in soils co-contaminated with MPS and assessing its potential impact. For the application of this mass balance model, PE, TPU, and PA were the polymers of focus. PE is one of the most common polymer types found in soil and is linked to agricultural sources (You et al., 2022). In addition, the presence of PE MPs in soil is found to influence the transport of hydrophobic organic pollutants. The sorption of two pesticides was reduced in the presence of PE, suggesting that PE contamination may reduce the soil's natural sorption capacity (Hüffer et al., 2019). Another plastic type that has been commonly found in the environment is TPU (Jiang et al., 2023). PA, known as nylon 6, is also commonly found in soil (J. Li et al., 2023). One major route by which MPs ends up in soils is via the application of biosolids. The sludge

from WWTPs is a recipient of microplastics from wastewater (Alavian Petroody et al., 2021). Therefore, investigating the interaction between MPs and EE2 present in biosolids in soils is necessary for assessing a possibly altered bioavailability in the soil due to the presence of MPs.

The study of Tourinho et al. (2019) used a mass balance model for estimating the partitioning of PCBs and phenanthrene in soil in the presence of MPs. For this research, their model was used and adapted. The environmental compartments used are porewater, air, soil, dissolved organic carbon, biota, and plastic. The distribution of EE2 (mg) in soil (Qt) when assuming a linear partitioning constant can be described as:

$$Q_t = C_w * V_w + C_w * V_a * K_{air} + C_w * M_s * K_d + C_w * M_{doc} * K_{doc} + C_w * M_{bio} * K_{bio} + C_w * M_{mp} * K_{mp}$$

In which C_w is the concentration in porewater (mg/L), V_w is the volume of porewater (L), V_a is the volume of air (L), and M_s, M_{doc}, M_b and M_{mp} are the masses of soil, dissolved organic carbon, biota, and microplastic, respectively. K_{air}, K_d, K_{doc}, K_{bio}, and K_{mp} are the partitioning coefficients between the compartment-porewater and air, soil, DOC, biota, and microplastics, respectively. To calculate the mass of EE2 in a compartment, the amount of chemical in the compartment x can be calculated by dividing the amount (Mx Kx) by the total amount, cancelling out C_w. For example, to get the total amount of EE2 in the MP compartment, the equation can be adapted to:

$$Q_{tmp} = \frac{M_{mp} * K_{mp}}{(V_w + V_a * K_{air} + M_s * K_d + M_{doc} * K_{doc} + M_{bio} * K_{bio} + M_{mp} * K_{mp})}$$

For PA and TPU, no linear partitioning isotherm could be found in the literature. Therefore, values with a Freundlich isotherm were used. It is important to note that linearity is assumed because the concentrations of EE2 are low, and therefore saturation is not expected.

Partition values included in the model
The Scientific Committee on Health and Environmental Risks (SCHER) summarized environmental distribution coefficients from numerous studies (SCHER), 2011). Only parameters derived from experimental research were used for the model; calculated values were not.

For deriving the $K_{air-water}$, the following calculations were made. The solubility in water (9.2 mg/L) at 25°C divided by the molecular weight (296.41 g/mol) resulted in $3.1*10^{-5}$ mol/L. The Henry constant (K_h) can be calculated by dividing the vapour pressure at 25°C ($6.0 * 10^{-9}$) by the solubility in water (Environmental Toxicology, an Open Online Textbook - Wikiwijs Maken, n.d.). This results in a $K_{air-water}$ of $7.80*10^{-13}$, following the equation $K_{air-water}= K_h/RT$.

The log K_{oc} values ranged from 2.92 to 5.44. These values were derived from multiple studies, using soil, sediments, bed sediments, and sewage sludge. The diversity of sorbates is a likely explanation for the wide range of the K_{oc}. The K_p (sediment-water) values were calculated by SCHER from the K_{oc}. According toSeth et al. (1999) the K_{om} can be calculated as $K_{om}= 0.58* K_{oc}$.

According to Jager (1998) the bioaccumulation factor (BCF) for the uptake of chemicals from pore water into earthworms can be calculated as $BCF= 0.93 * K_{ow} – 3.01$. The Log K_{ow} values ranged from 3.67 to 4.2.

C. Wu et al. (2016b) Investigated the sorption of EE2 on PE debris (250 to 280 μm) and found a linear sorption coefficient of 312 L/kg with a standard error of 21.5. Jiang et al. (2023) found a K_f (L/kg) of 6.2 for the adsorption of EE2 on TPU microplastics (70-74 μm). Their data fitted the Freundlich model with a correlation coefficient (R^2) of 0.9845. Lara et al. (2021) investigated the sorption of chemicals, including EE2 to PA (< 350 μm), under different conditions. One of the conditions was ultra pure water, and the resulting Freundlich value for the sorption of EE2 on PA ($K_f= 1490$, $R^2= 0.94$) was used in my calculations.

Table 1
Lowest and highest values for the partitioning of EE2 over different compartments found in the literature. The calculations are explained in the text.

	Lowest values	Highest values	Source
$K_{air-water}$	$7.81 * 10^{-13}$	$7.81 * 10^{-13}$	
Kp (sediment-water) (L/kg)	25	34429	(SCHER), 2011)
K_d (DOM-water) L/kg	111	159745	Calculated with values from SCHER, (2011)
BCF (L/kg)	4346	14736	Calculated with values from SCHER, (2011)
K_{mp} PE (L/kg) linear	312	312	(C. Wu et al., 2016b)
K_{mp} TPU (L/kg) Freundlich	$K_f= 6.24$ n= 0.82	$K_f= 6.24$ n= 0.82	(Jiang et al., 2023)
K_{mp} PA (L/kg) Freundlich	$K_f= 1490$ 1/n= 0.9	$K_f= 1490$ 1/n= 0.9	(Lara et al., 2021)

Scaling of the environmental compartments

The model used represents 1 ha of agricultural soil. In agricultural settings, during mechanical cultivation, a mixing depth of 5 cm is assumed for permanent crops. EE2, which is present in sewage sludge, is expected to stay in the topsoil layer because of its strong binding to organic matter. Therefore, EE2 is expected to be present in the top 5 cm soil layer ("EFSA Guidance Document for Predicting Environmental Concentrations of Active Substances of Plant Protection Products and Transformation Products of These Active Substances in Soil," 2017). The maximal allowed amount of sewage sludge applied on the field depends on local regulations, mainly to regulate the occurrence of heavy metals in soil. Within the EU, the maximal allowed application reported ranged greatly from 1.6 to 7 tons/ha/year of dry solids (Directorate-General for Environment (European Commission) et al., 2022). For this model, the average of these values was chosen (4.3 tons/ha). Cantarero et al. (2017) found a concentration of 0.54 mg/kg EE2 in biosolids from an anaerobic digestion WWTP. This value was taken as a representative of the concentration of EE2 in applied sludge. The concentration of EE2 per kg of soil was calculated as follows:

The sludge application rate was 4330 kg/10,000 m^2. It is assumed that EE2 stays in the 5 cm topsoil layer. The topsoil layer multiplied by the hectare results in m^3 of the soil compartment. The kg of the soil compartment is the m^3 multiplied by the average bulk density, which is assumed to be 1400 kg/m3. The concentration of EE2 (2.34 g/ha) divided by the kg soil in 1 ha results in the concentration of EE2 per kg soil.

The volume of water is calculated as 25% of the soil's dry weight, corresponding to 175,000 L. An average dissolved organic carbon (DOC) level of 33mg/L was used to calculate the amount of DOC present in the soil pore water (De Troyer et al., 2014).

For the compartment biota, the earthworm (*Eisenia fetida* or *Eisenia Andrei*) was chosen to represent the amount of lipid in the compartment biota. Earthworms have semi-permeable body walls and are well known for their ability to bioaccumulate pollutants from the environment, both via ingestion of contaminated organic matter (OC) and as well from the pore water as via their body surface. Therefore, they are commonly used as bioindicators and in toxicity tests for evaluating pollution. For the amount of biota, the guidelines of OECD test guidelines of OECD 220 were used. Ten earthworms (*Eisenia fetida* or *Eisenia Andrei)* are used in 500 g dry weight of soil, each weighing 300-600mg, assuming an average of 450 mg/worm. This gives 9 g fresh mass of earthworm per kg of soil. Assuming a dry weight of 20%, this results in 1,8 g dry mass per kg of soil for the biota compartment (*Test No. 222: Earthworm Reproduction Test (Eisenia Fetida/Eisenia Andrei)*, 2016).

The air compartment was calculated as follows: assuming a height of the atmosphere of 15 km (the troposphere), above 1 ha there is $1.5*10^5$ m3 air, resulting in $1.5*10^8$ L air.

For the mass of plastic in the model, the assumption was made that the compartment consists of one single plastic type. Across the globe, the concentration of MPs varies greatly; in heavily polluted areas, the concentration of MPs in soil can reach up to 6.7% (Fuller & Gautam, 2016). Due to the wide dispersion, MPs are found even in natural areas. Scheurer & Bigalke (2018) established a mean concentration of MPs in Swiss floodplain nature reserves of 5 mg/kg. For the model, this value was taken as a base line to represent an agricultural field without the record of mulching and/or applying biosolids. Ng et al. (2018) found that for a lifetime input of biosolids in Europe, between 2.3 and 15.8 tons of MPs end up in an agricultural topsoil of 10 cm. Berg et al. (2020) found in agricultural fields in topsoil (0-30 cm) with intense ploughing no significant depth-dependence in the MP, due to homogenization of the distribution of MPs, which avoids vertical gradient formation. Therefore, the M_{pl} was divided into a best-case scenario (2300kg/ha + baseline MP level) and a worst-case scenario (15800kg/ha + baseline MP level).
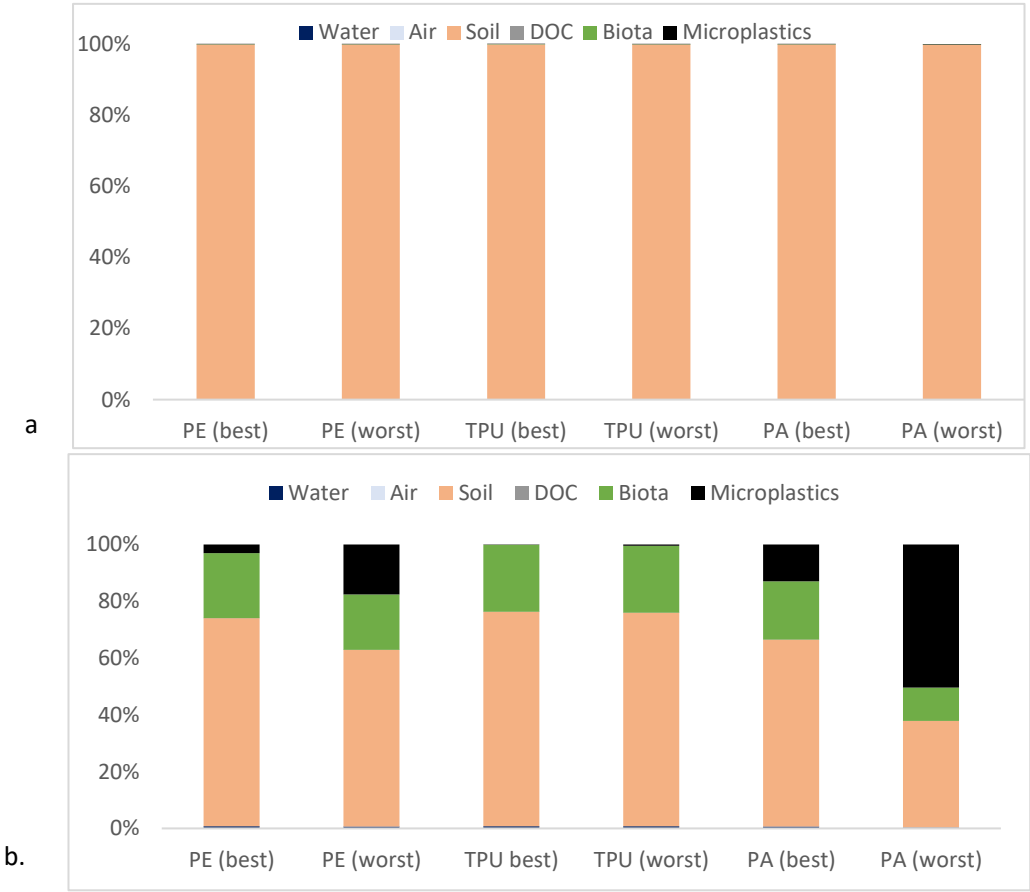
Figure 2: Distribution of 17α-ethinylestradiol (EE2) over different environmental compartments in a soil co-contaminated with different types of microplastics, estimated for best- (2300 kg microplastics/ha soil) and worst (15800 kg microplastics/ ha soil) case microplastic pollution present, using an environmental partitioning model with high (A) and low (B) soil sorption coefficients. PE = polyethylene , TPU = thermoplastic polyurethane , PA = polyamide . See text for further explanation.

Results from the mass-balance model

Figure 2 and *Table 2* shows the distribution of EE2 in the different environmental compartments as a result of the mass balance equation with the proposed parameters. For both the highest and lowest partition values (situations a and b) in *Figure 2, Table 2*, the major portion of the EE2 was found to be bound to the soil compartment, except for the plastic type PA in situation b. Here, the major proportion (50.4%) was found bound to PA MPs.

For situation a, biota was the second compartment with highest proportions of EE2 sorbed in both worst- and best-case scenarios, with 0.08% of EE2 being taken up by biota, except for PA, with 0.1% being sorbed to MPs in the worst-case scenario. Upon increasing the plastic mass in situation, a, small changes in the proportional distribution of EE2 are observed for PE (from 0.0% to 0.02%) and PA (from 0.01% to 0.10%). For TPU no increase in proportional distribution was observed.

For situation b, the second compartment with the highest proportions also was biota containing 19-24% of total amount of EE2 present in the system, except for PA (containing 11%-20%, depending on MP mass present).

For situation a, the proportion of EE2 bound to MPs ranged from 0.0% to 0.1%. Contrasting to situation b, where 0.06%-50.42% of EE2 concentration was bound to MPs. When looking at the range of expected sorption concentrations for EE2 per plastic type, derived from the mass balance model (*Table 3),* PA had the highest sorption, followed by PE, and TPU.

In situation b, upon increasing the MP mass, the amount of EE2 taken up by biota became less (*Table 2)*, indicating with an increased amount of MP mass present, less EE2 is sorbed into the biota compartment.

Since K_{oc} varies greatly, the partitioning was expected to vary depending on soil type. The sorbed concentrations in the compartments are quite low, ranging in the scale of nanograms (*Table 3)*. The sorbed ranges of EE2 on MPs or the soil in this model for the microfauna species *C. elegans* are not expected to exert an adverse observed effect regarding reproduction and body length since a NOAEL of 0.75 mg/L EE2 for cumulative offspring and 5.1 mg/L for body length was found.

When comparing the ranges of expected sorption concentrations of EE2 in soil to the calculated $PNEC_{soil}$, which ranged between 0.01- 15.97 mg/L, no adverse effects within this model are expected. Ranges of expected concentration of EE2 in pore water in the presence of MPs did not exceed the $PNEC_{water}$, suggesting no adverse effects are expected.

Table 2, proportions of concentrations 17α-ethinylestradiol (EE2) distributed over different environmental compartments in a soil co-contaminated, with different types of microplastics and for best- (2300 kg microplastics/ha soil) and worst (15800 kg microplastics/ ha soil) case microplastic pollution present, estimated using an environmental partitioning model with high (A) and low (B) soil sorption coefficients.

Situation A	Polyethylene best-case scenario	Polyethylene worst-case scenario	Thermoplastic polyurethane best-case scenario	Thermoplastic polyurethane worst-case scenario	Polyamide best-case scenario	Polyamide best-case scenario
Water	0%	0,00%	0%	0%	0%	0%
Air	0%	0,00%	0%	0%	0%	0%
Soil	99,92%	99,90%	99,92%	99,92%	99,91%	99,82%
Dissolved organic carbon	0%	0,00%	0%	0%	0%	0%
Biota	0,08%	0,08%	0,08%	0,08%	0,08%	0,08%
Microplastics	0%	0,02%	0%	0,0%	0,01%	0,10%
Situation B						
Water	0,73%	0,62%	0,76%	0,75%	0,66%	0,37%
Air	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%
Soil	73,31%	62,32%	75,54%	75,27%	65,83%	37,47%
Dissolved organic carbon	0,00%	0,00%	0,00%	0,00%	0,00%	0,00%
Biota	22,94%	19,50%	23,64%	23,56%	20,60%	11,73%
Microplastics	3,01%	17,56%	0,06%	0,42%	12,91%	50,42%

Table 3, range of expected sorption concentration of EE2 (µg/L) over different environmental compartments in a soil-co-contaminated with different types of microplastic estimated using an environmental partitioning model with high and low soil sorption coefficients. See text for further explanation.

	Polyethylene	Thermoplastic polyurethane	Polyamide
Water	$1.38*10^{-13}$ - $1.19*10^{-10}$	$1.38*10^{-13}$ - $1,44*10^{-10}$	$1.38*10^{-13}$ - $7.15*10^{-11}$
Air	$1.08*10^{-25}$ - $9.28*10^{-23}$	$1.08*10^{-25}$ - $1.12*10^{-22}$	$1.08*10^{-25}$ - $5.58*10^{-23}$
Soil	$4.77*10^{-9}$ - $2.97*10^{-9}$	$4.76*10^{-9}$ - $3.59*10^{-9}$	$4.76*10^{-9}$ - $1.79*10^{-9}$
Dissolved organic carbon	$2.21*10^{-9}$ - $1.32*10^{-8}$	$2.21*10^{-8}$ - $1.60*10^{-8}$	$2.21*10^{-8}$ - $7.97*10^{-9}$
Biota	$2.04*10^{-9}$ - $5.17*10^{-7}$	$2.04*10^{-9}$ - $6.24*10^{-7}$	$2.04*10^{-9}$ - $3.11*10^{-7}$
Microplastics	$4.32*10^{-11}$ - $3.17*10^{-7}$	$8.64*10^{-13}$ - $8.96*10^{-10}$	$2.06*10^{-10}$ - $1.07*10^{-7}$

Implication for toxicity for to organisms

A novel route of exposure to EE2 is via the ingestion of MPs with absorbed EE2. EE2 could possibly leach from the MPs directly into these organisms, causing internal exposure. Although no literature is available for desorption of EE2 on PE, PA, and TPU, some literature focused on other MPs is available. For example, J. Wu et al. (2022) found that hydrophobic properties of PVC were reduced in the presence of gastric acid. Thus, leaching of EE2 from MPs may be expected in the presence of gastric acid for example, after ingestion. However, the leaching properties probably depend on the plastic type, and research about the leaching properties of EE2 from PE, TPU, and PA has not yet been conducted.

There is very limited toxicological data available on the exposure of EE2 to soil organisms, indicating a big knowledge gap on adverse effects attributed to the possible leaching of EE2 from microplastics. Internal exposure to EE2 leaching from MPs is not investigated at all. Given the potency of EE2 and this novel exposure route, the importance of additional research is highlighted by this study. Although the sorbed ranges of EE2 on MPs or the soil in this model for the microfauna species *C. elegans* are not expected to exert an adverse observed effect regarding reproduction and body length, the NOEC is dependent on specific exposure routes. A higher sensitivity could be observed after ingesting MPs with sorbed EE2.

Markman et al. (2007) found that EDC accumulates in *Eisenia fetida.* Also, the aquatic oligochaete *Lumbriculus* accumulated EE2 from artificially spiked sediment. Their results highlighted the possibility of food chain effects involving invertebrates accumulating EE2. From the mass balance model, the assumption can be made that with lower partition values of soil, less EE2 is sorbed to biota due to the presence of MPs. Following this, less bioaccumulation is expected, which would be beneficial for the ecosystem. However, the reduction in bioaccumulation in biota was so small, that it is questionable what the effect will be in terms of risk reduction. In addition, there is limited literature about the biomagnification of EE2, which poses a problem when comparing the results of uptake in biota from this model to existing literature.

The calculated $PNEC_{soil}$ and the $PNEC_{water}$ were compared with the concentrations sorbed to soil and porewater, respectively, resulting from the mass balance model to the calculated. No adverse effects were expected. However, as mentioned before, this value needs to be carefully interpreted since the effects on aquatic species can only be considered as effects on soil organisms that are exposed exclusively to the soil pore water and may only be applicable for organisms with a water-permeable epidermis. These implications highlight the lack of knowledge for soil organism toxicity.

Applicability of the mass balance model

A few critical notes have to be made on the proposed model. Firstly, a linear sorption may overestimate the partitioning to solid phases and not be fully representative of the partitioning processes happening in field soils. Although saturation is expected only at higher concentrations, a linear model might not be the most accurate. Nevertheless, for a rough estimation of partition behaviour, this model is useful. In addition, the mass balance model is static and does not include the dynamics of a varying concentration of EE2 over time, due to degradation, this may lead to a possible overestimation of the concentration EE2 present in the system.

Another critical note is the assumption that the microplastics consist of only one plastic type. This may result in either underestimation or overestimation. In soil, there might be a complex mixture of different types of MPs, with different partition coefficients. Assuming that the mass of plastic consists of one plastic type with a high partition coefficient may lead to an overestimation of EE2 sorbed to the plastics. PA has a higher partition compared to TPU, so assuming the plastic compartment to be PA might be an overestimate. Reversely, it may lead to an underestimation. To solve this problem, research is needed on the composition of MPs in the field. This research should not only focus on the MP types, but also on their properties, e.g., size and shape, as this may also affect the specific surface area and consequently sorption capacity for hydrophobic contaminants. Complicating matters, the concentrations, types, and properties of MPs present may be very location dependent.

Another assumption made was a 'clean' field. Beside atmospheric distribution and the application of biosolids, there are more sources of MP contamination. For example, the agricultural practice of mulching may result over time in the accumulation of MPs in soil. Sajjad et al. (2022), reviewing the literature, found a concentration of 50-260 kg/ha of plastic fragments in topsoil after long-term mulching. Since this is not included in the model, it may lead to an underestimation of sorbed EE2 concentration is the plastic compartment for the soils with lower partitioning values. Also, the location of the field is important since heavily urban or industrial areas contain a higher concentration of MPs in the soil. Adding to this, monitoring data about MPs in soil is limited, especially for South America, Africa, and Oceania.

The model used assumed that EE2 is the only pollutant present, however, in agricultural fields there might be a complex mixture of different pollutants competing for adsorption sites on MPs. This model assumed a top layer of 5cm for permanent crops, however, annual crops have a mechanical cultivation depth of 20 cm ("EFSA Guidance Document for Predicting Environmental Concentrations of Active Substances of Plant Protection Products and Transformation Products of These Active Substances in Soil," 2017). For annual crops, the model therefore leads to an overestimation since the concentration of EE2 would be

distributed in a larger volume of soil, leading to lower concentrations and possibly to more sorption into the soil. In addition, the parameters used in the model were all from research with pristine MPs. As mentioned before, it is expected that due to weathering, the hydrophobic groups on the surface will lose their function, probably resulting in less sorption of hydrophobic compounds. Another critical point is that the used parameters are partition coefficients limited to a specific size range of MPs. MP sizes underlying the used partition coefficients differ greatly, with particles ranging from 70 μm to 350 μm. However, since sorption is influenced by MP size and greater sorption is shown by smaller particles (till 2 μm) the presented sorption may be an underestimation. To summarize, it can be concluded that this model is no representation of the real field situation, however, it might provide valuable insights into the partition process of EE2 under the influence of MPs.

Conclusion

This study aimed to assess the distribution of EE2 in soil over different compartments using mass balance modelling for the plastic types of PE, PA, and TPU based on recent literature. EE2 was expected to be most strongly bound to soil, however, due to hydrophobic interactions, MPs were expected to be the second compartment with the highest concentration of EE2 being sorbed. Given the properties of PE, PA, and TPU, the following sorption was expected: PE > PA > TPU.

Generally, EE2 is majorly bound to soil, except for low partition coefficients of EE2-soil while high amounts PA MPs are present. Changes in the proportional distribution of EE2 upon increasing the plastic mass for the polymer types of PE and PA, indicates that EE2 sorption on MPs increase with an increase in MPs. However, for TPU binding of EE2 to the soil compartment seems strongly dominating. The difference in range of concentrations of sorbed EE2 on MPs, indicates an observable difference in sorption to different plastic types and mass of plastic present. Concluding, although the majority of EE2 is expected to bound to the soil, specific polymers in high concentrations present, may influence this distribution.

The observed sorption order (PA> PE > TPU) is different from what was expected from the literature. One possible explanation might be the degree of crystallinity. PA shows a lower degree of crystallinity compared to PE, possibly allowing more space and less hindrance for EE2 to be absorbed to the MP. Another factor playing a role in the sorption process are hydrogen bonds. Because of the presence of the amine groups in PA, this polymer may have more hydrophobic interactions compared to PE. Even though PE is more hydrophobic compared to PA, the degree of crystallinity and the hydrogen bonds together may outweigh the difference in hydrophobic behaviours, resulting in more sorption in PA.

Due to the limited research available and the nature of the parameters, no hard conclusions can be drawn from the mass balance model. Further research that leads to improvement of the predictive capacities of the model involves identifying the mixture of MP types present in soil, and their degree of weathering, investigating sorption isotherms of EE2 for all plastic types, pristine and aged, found in soil and reliable toxicity values for adverse effects on representable soil organisms. Nonetheless, this research provides a rough estimate of EE2 partitioning in soil under the presence of MPs and highlights the knowledge gap about the toxicity of EE2 on soil organisms and the complexity of this matter.

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References

Adeel, M., Song, X., Wang, Y., Francis, D., & Yang, Y. (2017). Environmental impact of estrogens on human, animal and plant life: A critical review. *Environment International*, *99*, 107–119. https://doi.org/10.1016/j.envint.2016.12.010

Agboola, O. D., & Benson, N. U. (2021). Physisorption and Chemisorption Mechanisms Influencing Micro (Nano) Plastics-Organic Chemical Contaminants Interactions: A Review. *Frontiers in Environmental Science*, *9*. https://doi.org/10.3389/fenvs.2021.678574

Alavian Petroody, S. S., Hashemi, S. H., & van Gestel, C. A. M. (2021). Transport and accumulation of microplastics through wastewater treatment sludge processes. *Chemosphere*, *278*, 130471. https://doi.org/10.1016/j.chemosphere.2021.130471

Asadi Miankafshe, M., Bashir, T., & Persson, N.-K. (2020). Electrostatic grafting of graphene onto polyamide 6,6 yarns for use as conductive elements in smart textile applications. *New Journal of Chemistry*, *44*(18), 7591–7601. https://doi.org/10.1039/C9NJ06437K

Caldwell, D. J., Mastrocco, F., Anderson, P. D., Länge, R., & Sumpter, J. P. (2012). Predicted-no-effect concentrations for the steroid estrogens estrone, 17β-estradiol, estriol, and 17α-ethinylestradiol. *Environmental Toxicology and Chemistry*, *31*(6), 1396–1406. https://doi.org/10.1002/etc.1825

Cantarero, R., Richter, P., Brown, S., Ascar, L., & Ahumada, I. (2017). Effects of applying biosolids to soils on the adsorption and bioavailability of 17α-ethinylestradiol and triclosan in wheat plants. *Environmental Science and Pollution Research*, *24*(14), 12847–12859. https://doi.org/10.1007/s11356-017-8836-5

De Troyer, I., Merckx, R., Amery, F., & Smolders, E. (2014). Factors Controlling the Dissolved Organic Matter Concentration in Pore Waters of Agricultural Soils. *Vadose Zone Journal*, *13*(7), vzj2013.09.0167. https://doi.org/10.2136/vzj2013.09.0167

Directorate-General for Envrionment (European Commission), IMDEA, Ricardo, Trinomics, Tyrsky, & Wood. (2022). *Support to the evaluation of the Sewage Sludge Directive - Exploratory study: final report, .*

Djukic, S., Bocahut, A., Bikard, J., & Long, D. R. (2020). Mechanical properties of amorphous and semi-crystalline semi-aromatic polyamides. *Heliyon*, *6*(4), e03857. https://doi.org/10.1016/j.heliyon.2020.e03857

EFSA Guidance Document for predicting environmental concentrations of active substances of plant protection products and transformation products of these active substances in soil. (2017). *EFSA Journal*, *15*(10). https://doi.org/10.2903/j.efsa.2017.4982

Elizalde-Velázquez, A., Subbiah, S., Anderson, T. A., Green, M. J., Zhao, X., & Cañas-Carrell, J. E. (2020). Sorption of three common nonsteroidal anti-inflammatory drugs (NSAIDs) to microplastics. *Science of The Total Environment*, *715*, 136974. https://doi.org/10.1016/j.scitotenv.2020.136974

Environmental Toxicology, an open online textbook - Wikiwijs Maken. (n.d.). Wikiwijs.
https://maken.wikiwijs.nl/147644/Environmental_Toxicology__an_open_online_textbook#!page-5658449

Fang, S., Yu, W., Li, C., Liu, Y., Qiu, J., & Kong, F. (2019). Adsorption behavior of three triazole fungicides on polystyrene microplastics. *Science of The Total Environment*, *691*, 1119–1126. https://doi.org/10.1016/j.scitotenv.2019.07.176

Fuller, S., & Gautam, A. (2016). A Procedure for Measuring Microplastics using Pressurized Fluid Extraction. *Environmental Science & Technology*, *50*(11), 5774–5780. https://doi.org/10.1021/acs.est.6b00816

Galafassi, S., Nizzetto, L., & Volta, P. (2019). Plastic sources: A survey across scientific and grey literature for their inventory and relative contribution to microplastics pollution in natural environments, with an emphasis on surface water. *Science of The Total Environment*, *693*, 133499. https://doi.org/10.1016/j.scitotenv.2019.07.305

Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics ever made. *Science Advances*, *3*(7). https://doi.org/10.1126/sciadv.1700782

Haiyan, R., Shulan, J., ud din Ahmad, N., Dao, W., & Chengwu, C. (2007). Degradation characteristics and metabolic pathway of 17α-ethynylestradiol by Sphingobacterium sp. JCR5. *Chemosphere*, *66*(2), 340–346. https://doi.org/10.1016/j.chemosphere.2006.04.064

Horton, A. A., Walton, A., Spurgeon, D. J., Lahive, E., & Svendsen, C. (2017). Microplastics in freshwater and terrestrial environments: Evaluating the current understanding to identify the knowledge gaps and future research priorities. *Science of The Total Environment*, *586*, 127–141. https://doi.org/10.1016/j.scitotenv.2017.01.190

Hüffer, T., Metzelder, F., Sigmund, G., Slawek, S., Schmidt, T. C., & Hofmann, T. (2019). Polyethylene microplastics influence the transport of organic contaminants in soil. *Science of The Total Environment*, *657*, 242–247. https://doi.org/10.1016/j.scitotenv.2018.12.047

Hüffer, T., Weniger, A.-K., & Hofmann, T. (2018). Sorption of organic compounds by aged polystyrene microplastic particles. *Environmental Pollution*, *236*, 218–225. https://doi.org/10.1016/j.envpol.2018.01.022

Huntsman. (2016). *A guide to thermoplastic polyurethanes (TPU)*.

Jager, T. (1998). Mechanistic approach for estimating bioconcentration of organic chemicals in earthworms (oligochaeta). *Environmental Toxicology and Chemistry*, *17*(10), 2080–2090. https://doi.org/10.1002/etc.5620171026

Jasmee, S., Omar, G., Nordin, M. N. A., Masripan, N. A. B., & Kamarolzaman, A. A. (2018). Hydrophobicity performance of thermoplastic polyurethane coated with TiO2 under thermal aging effect. *Advanced Material and Mechenical Engineering Research*.

Jiang, H., Li, Q., Sun, J., Huang, Y., Zhang, P., Mao, Y., Qu, Y., & Liu, X. (2023). Studies on competitive adsorption characteristics of bisphenol A and 17α-ethinylestradiol on thermoplastic

polyurethane by site energy distribution theory. *Environmental Geochemistry and Health*. https://doi.org/10.1007/s10653-023-01566-z

Koelmans, A. A., Redondo-Hasselerharm, P. E., Nor, N. H. M., de Ruijter, V. N., Mintenig, S. M., & Kooi, M. (2022). Risk assessment of microplastic particles. *Nature Reviews Materials*, *7*(2), 138–152. https://doi.org/10.1038/s41578-021-00411-y

Kuo, Y.-H., How, C. M., Huang, C.-W., Yen, P.-L., Yu, C.-W., Chang, C.-H., & Liao, V. H.-C. (2023). Co-contaminants of ethinylestradiol and sulfamethoxazole in groundwater exacerbate ecotoxicity and ecological risk and compromise the energy budget of C. elegans. *Aquatic Toxicology*, *257*, 106473. https://doi.org/10.1016/j.aquatox.2023.106473

Lara, L. Z., Bertoldi, C., Alves, N. M., & Fernandes, A. N. (2021). Sorption of endocrine disrupting compounds onto polyamide microplastics under different environmental conditions: Behaviour and mechanism. *Science of The Total Environment*, *796*, 148983. https://doi.org/10.1016/j.scitotenv.2021.148983

Li, D., Zhou, L., Wang, X., He, L., & Yang, X. (2019). Effect of Crystallinity of Polyethylene with Different Densities on Breakdown Strength and Conductance Property. *Materials*, *12*(11), 1746. https://doi.org/10.3390/ma12111746

Li, J., Yu, S., & Cui, M. (2023). Aged polyamide microplastics enhance the adsorption of trimethoprim in soil environments. *Environmental Monitoring and Assessment*, *195*(6), 669. https://doi.org/10.1007/s10661-023-11350-2

Li, Y., Rehbock, C., Nachev, M., Stamm, J., Sures, B., Blaeser, A., & Barcikowski, S. (2020). Matrix-specific mechanism of Fe ion release from laser-generated 3D-printable nanoparticle-polymer composites and their protein adsorption properties. *Nanotechnology*, *31*(40), 405703. https://doi.org/10.1088/1361-6528/ab94da

Lin, T. A., Limin, B., Lin, M.-C., Lin, J.-Y., Lou, C.-W., & Lin, J.-H. (2019). Impact-resistant polypropylene/thermoplastic polyurethane blends: compatible effects of maleic anhydride on thermal degradation properties and crystallization behaviors. *Journal of Materials Research and Technology*, *8*(4), 3389–3398. https://doi.org/10.1016/j.jmrt.2019.03.015

Lock, E., Walton, S., & Fernsler, R. (2008). *Preperation of Ultra Thin Polystyrene, Propylene and Polyethylene Films on Si Substrate Using Spin Coating Technology*.

Markman, S., Guschina, I. A., Barnsley, S., Buchanan, K. L., Pascoe, D., & Müller, C. T. (2007). Endocrine disrupting chemicals accumulate in earthworms exposed to sewage effluent. *Chemosphere*, *70*(1), 119–125. https://doi.org/10.1016/j.chemosphere.2007.06.045

Moschet, C. (2009). *Microbial Degradation of Steroid Hormones in the Environment and Technical Systems*.

Munoz, M., Ortiz, D., Nieto-Sandoval, J., de Pedro, Z. M., & Casas, J. A. (2021). Adsorption of micropollutants onto realistic microplastics: Role of microplastic nature, size, age, and NOM fouling. *Chemosphere*, *283*, 131085. https://doi.org/10.1016/j.chemosphere.2021.131085

Ng, E.-L., Huerta Lwanga, E., Eldridge, S. M., Johnston, P., Hu, H.-W., Geissen, V., & Chen, D. (2018). An overview of microplastic and nanoplastic pollution in agroecosystems. *Science of The Total Environment*, *627*, 1377–1388. https://doi.org/10.1016/j.scitotenv.2018.01.341

Odutola Oshunsanya, S. (2019). Introductory Chapter: Relevance of Soil pH to Agriculture. In *Soil pH for Nutrient Availability and Crop Performance*. IntechOpen. https://doi.org/10.5772/intechopen.82551

Peña, A., Rodríguez-Liébana, J. A., & Delgado-Moreno, L. (2023). Interactions of Microplastics with Pesticides in Soils and Their Ecotoxicological Implications. *Agronomy*, *13*(3), 701. https://doi.org/10.3390/agronomy13030701

Prajapati, A., Narayan Vaidya, A., & Kumar, A. R. (2022). Microplastic properties and their interaction with hydrophobic organic contaminants: a review. *Environmental Science and Pollution Research*, *29*(33), 49490–49512. https://doi.org/10.1007/s11356-022-20723-y

Sajjad, M., Huang, Q., Khan, S., Khan, M. A., Liu, Y., Wang, J., Lian, F., Wang, Q., & Guo, G. (2022). Microplastics in the soil environment: A critical review. *Environmental Technology & Innovation*, *27*, 102408. https://doi.org/10.1016/j.eti.2022.102408

Scheurer, M., & Bigalke, M. (2018). Microplastics in Swiss Floodplain Soils. *Environmental Science & Technology*, *52*(6), 3591–3598. https://doi.org/10.1021/acs.est.7b06003

Scientific Committee on Health and Environmental Risks (SCHER). (2011). *Alpha-ethinylestradiol EQS dossier 2011.*

Seth, R., Mackay, D., & Muncke, J. (1999). Estimating the Organic Carbon Partition Coefficient and Its Variability for Hydrophobic Chemicals. *Environmental Science & Technology*, *33*(14), 2390–2394. https://doi.org/10.1021/es980893j

Szabó, L., Vancsik, A., Király, C., Ringer, M., Kondor, A., Jakab, G., Szalai, Z., & Filep, T. (2020). Investigation of the sorption of 17α-ethynylestradiol (EE2) on soils formed under aerobic and anaerobic conditions. *Chemosphere*, *240*, 124817. https://doi.org/10.1016/j.chemosphere.2019.124817

Tang, Z., Liu, Z., Wang, H., Dang, Z., & Liu, Y. (2021). Occurrence and removal of 17α-ethynylestradiol (EE2) in municipal wastewater treatment plants: Current status and challenges. *Chemosphere*, *271*, 129551. https://doi.org/10.1016/j.chemosphere.2021.129551

Test No. 222: Earthworm Reproduction Test (Eisenia fetida/Eisenia andrei). (2016). OECD. https://doi.org/10.1787/9789264264496-en

The European Commision. (2018). *Commission Implementing Decision (EU) 2018/840 of 5 June 2018 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council and repealing Commission Implementing Decision (EU) 2015/495 (notified under document C (2018) 3362)*. Offical Journal of the European Union.

Thompson, R. C., Moore, C. J., vom Saal, F. S., & Swan, S. H. (2009). Plastics, the environment and human health: current consensus and future trends. *Philosophical Transactions of the Royal Society B: Biological Sciences*, *364*(1526), 2153–2166. https://doi.org/10.1098/rstb.2009.0053

Tourinho, P. S., Kočí, V., Loureiro, S., & van Gestel, C. A. M. (2019). Partitioning of chemical contaminants to microplastics: Sorption mechanisms, environmental distribution and effects on toxicity and bioaccumulation. *Environmental Pollution*, *252*, 1246–1256. https://doi.org/10.1016/j.envpol.2019.06.030

van den Berg, P., Huerta-Lwanga, E., Corradini, F., & Geissen, V. (2020). Sewage sludge application as a vehicle for microplastics in eastern Spanish agricultural soils. *Environmental Pollution*, *261*, 114198. https://doi.org/10.1016/j.envpol.2020.114198

Wang, Y., Hu, L., Wang, Q., Lu, G., & Li, Y. (2014). Adsorption Behaviors of 17 α -Ethinylestradiol in Sediment-Water System in Northern Taihu Lake, China. *The Scientific World Journal*, *2014*, 1–6. https://doi.org/10.1155/2014/371075

Wright, S. L., Thompson, R. C., & Galloway, T. S. (2013). The physical impacts of microplastics on marine organisms: A review. *Environmental Pollution*, *178*, 483–492. https://doi.org/10.1016/j.envpol.2013.02.031

Wu, C., Zhang, K., Huang, X., & Liu, J. (2016a). Sorption of pharmaceuticals and personal care products to polyethylene debris. *Environmental Science and Pollution Research*, *23*(9), 8819–8826. https://doi.org/10.1007/s11356-016-6121-7

Wu, C., Zhang, K., Huang, X., & Liu, J. (2016b). Sorption of pharmaceuticals and personal care products to polyethylene debris. *Environmental Science and Pollution Research*, *23*(9), 8819–8826. https://doi.org/10.1007/s11356-016-6121-7

Wu, J., Lu, J., & Wu, J. (2022). Effect of gastric fluid on adsorption and desorption of endocrine disrupting chemicals on microplastics. *Frontiers of Environmental Science & Engineering*, *16*(8), 104. https://doi.org/10.1007/s11783-022-1525-8

Xue, X.-D., Fang, C.-R., & Zhuang, H.-F. (2021). Adsorption behaviors of the pristine and aged thermoplastic polyurethane microplastics in Cu(II)-OTC coexisting system. *Journal of Hazardous Materials*, *407*, 124835. https://doi.org/10.1016/j.jhazmat.2020.124835

You, X., Wang, S., Li, G., Du, L., & Dong, X. (2022). Microplastics in the soil: A review of distribution, anthropogenic impact, and interaction with soil microorganisms based on meta-analysis. *Science of The Total Environment*, *832*, 154975. https://doi.org/10.1016/j.scitotenv.2022.154975