Plasticizers: distribution and impact in aquatic and terrestrial environments†

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The review highlights advanced removal strategies and their impacts on soil algae and nematodes, addressing plasticizer pollution comprehensively.

Abstract

Plasticizers, essential additives for enhancing plastic properties, have emerged as significant environmental and health concerns due to their persistence and widespread use. This study provides an in-depth exploration of plasticizers, focusing on their types, structures, properties, production methods, environmental distribution, and associated risks. The findings reveal that petroleum-based phthalates, particularly di-(2-ethylhexyl) phthalate (DEHP), are prevalent in aquatic and terrestrial environments, primarily due to the gradual degradation of plastic polymers. In the analysis of 39 studies on water contamination during the period of 2022–2023, only 22 works could be extracted due to insufficient details on the numerical value of ~~their~~plasticizer concentrations. Similarly, soil and sediment contamination studies were fewer, with only 11 studies focusing on sediments. These studies reveal that high plasticizer concentrations, notably in

industrial and urban areas, often exceed recommended environmental limits, posing risks to ecological integrity and human health through bioaccumulation. Bioaccumulation of these compounds in soil and water could negatively affect the microbial communities, nutrient cycling, and could destabilize the overall ecological integrity. Concerns about their direct uptake by plants and potential risks to human health and food safety are highlighted in this study due to the high concentrations exceeding the threshold values. The review evaluates current treatment technologies, including metal–organic frameworks, electrochemical systems, multi-walled carbon nanotubes, and microbial degradation, noting their potential and challenges related to cost and energy consumption. It underscores the need for improved detection protocols, cost-effective treatments, stricter regulations, public awareness, and collaborative research to mitigate the adverse impacts of plasticizers on ecosystems and human health.

Environmental significance

Plasticizers, notably petroleum-based phthalates like DEHP, pose significant environmental and health risks due to their widespread use and recalcitrant nature. This review highlights the ubiquity of these plasticizers in water and soil, their persistence, and their adverse effects, including bioaccumulation and endocrine disruption. Novel aspects include the comprehensive discussion of plasticizer impacts on soil algae and nematodes, and the emphasis on advanced removal strategies such as metal–organic frameworks, electrochemical systems, and biochar adsorption. The review's significance lies in its holistic approach to understanding plasticizer pollution and advocating for sustainable mitigation techniques, addressing a critical environmental issue with global implications.

1 Introduction

Ever since the mass production of plastic consumer goods started in the mid-20th century, to address the demands from various fields, plasticizers became one of the main choices in the plastic industry. Plasticizers are colorless, low molecular weight compounds of synthetic origin, that are majorly (≈90%) being utilized as additives for the production of polyvinyl chloride (PVC) based products such as food packaging, toys, flooring molds, paints, piping, rainwear, electronic insulation, cosmetic products, roofing systems medical appliances as well as in adhesives.[1] They are typically infused into polymers to increase flexibility, durability, and workability. Improving such properties will be crucial to make the plastics processable during manufacturing, to improve strength to withstand high tensile strength as well as elongation at break, to produce stretchable materials, to make them less brittle thereby aiding the lifespan of the materials. This will make the plastics ideally suited for various industries such as automotive, construction, packaging, and healthcare.[2,3]

It is anticipated that the annual production of PVC will expand up to 60 million metric tons by the year 2025, out of which about 40% contribution to the weight will be coming from plasticizers.[4] In addition to PVC, plasticizers are also an additive for polyvinyl acetate, poly(vinylidene chloride), polyamides, polyacrylates, cellulose derivatives, and polyurethane resins.[2,5] Regional analysis of the demand for plasticizers confirms that plasticizers and their products are much preferred by countries like China, Japan, and Korea in the Asian Pacific region.[1] The higher demand for plastic products in these countries mainly arises due to the impact coming from industrial growth, demand from essential sectors such as construction automotive, packaging materials, and electronics in addition to their favorable regulatory environments, economic expansion, and significant local manufacturing capabilities.[6]

Plasticizers are added to plastics with the intention of improving their flexibility, and distensibility, to avoid shrinking as well as the workability of the polymers.[7] They are typically not covalently bonded to PVC or to the polymer structure.[8] Plasticizers could weaken the intermolecular forces in between the polymeric chains and the primary role of a plasticizer is to reduce the glass transition temperature of the polymer and fine-tune the properties of the polymeric materials so that it is likely to be applied in various applications.[9] In this regard, plasticizers are known to affect the degree of crystallinity, optical clarity, electrical conductivity, fire resistance properties, and mechanical properties.[2] To date, there are many (about 30 000) odd plasticizer compounds available in the market out of which petroleum-based phthalates are the most popular among them.[3] Among the phthalates, di-(2-ethylhexyl) phthalate (DEHP) occurs to be the choice worldwide. In addition to DEHP, the use of diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), di(2-

propylheptyl) (DPHP) have also been used as plasticizers.[10] Other types of plasticizers include esters of aliphatic dicarboxylic acids, citrates, benzoates, tartrates, phosphates, epoxy vegetable oil, ethylene glycol, and esters of ethylene glycol.[2,7]

The current market would provide various plasticizers that match the specific requirements. However, as the plasticizers are not typically covalently bonded to the polymeric matrix and act as a lubricant, there is a high probability that these additives to leach from the polymeric matrix over the lifetime of the plastics. Plasticizers generally leach out rapidly at the beginning of a plastic product's life and then this rate gradually reduces. This phenomenon takes place due to several factors such as the initial high surface concentration of plasticizers, the mode of diffusion processes, the formation of a surface barrier, and various other environmental and material-specific factors.[11]

Furthermore, the overproduction of plasticizers and the worldwide omnipresent distribution of them has led to higher environmental and human exposure to these chemical compounds. More importantly, these plasticizers can get released to the environment during different stages such as production, processing, end use of the product or during waste disposal.[2] By these means, they could easily add up into rainfall, air, groundwater, and soil.[7] Furthermore, it has also been found that due to the lipophilic nature as well as the slow degradation, plasticizers could easily accumulate in soil.[12,13] However, significant concerns have been made about the use of phthalates in recent years, due to their possible health risks such as endocrine disruption and anti-androgenic effects.[12] Among various plasticizers, phthalates are known to create these effects by interfering with hormone-signaling pathways. They are known to interfere with hormone action, such as estrogen and testosterone, by binding to hormone receptors, thereby altering the expression of genes involved in hormone regulation. In addition, they are also known to disrupt the function of androgen receptors, leading to reduced androgenic activity. This could ultimately result in developmental and reproductive abnormalities in males leading to deformed reproductive organs and reduced sperm production.[14]

[Instruction: Please add this paragraph at the end of the previous paragraph]Therefore, over the years attempts have been made to seek alternative compounds with less harmful effects especially to manufacture childhood products such as toys and baby care products.[15,16] In this regard, the development of environmentally friendly, biodegradable, less toxic, green plasticizers has become an ongoing research hotspot.[9]

This review stands out itself by offering a uniquely comprehensive and interdisciplinary approach on the study of plasticizers. While many reported work focus on specific aspects such as chemical properties, environmental impact, or health effects, this work integrates these diverse areas into one cohesive narrative. It not only summarizes the current knowledge on plasticizers concerning production, environmental distribution, human exposure, and ecological implications but also identifies the critical gaps and suggests actionable recommendations for future research. The detailed regional consumption patterns of plasticizers, particularly giving more emphasis on the Asian Pacific region, predict global usage trends. Additionally, this review provides a significant emphasis on the environmental accumulation of plasticizers, highlighting the specific mechanisms through which these compounds leach into the anthropocene. More importantly, the ecotoxicity and threats of plasticizers on soil and water are poorly discussed in the literature and need to gain a fuller understanding. By revealing the emerging field of bio-based plasticizers, it highlights the urgent need for sustainable alternatives. This holistic perspective makes this review a valuable resource for a broad audience to understand the adverse impacts of plasticizers and advocate sustainable plastic usage.

2 Plasticizers in the anthropocene

Human impacts on the geological time scale have been leaving their mark for decades now. A not-yet-official term, anthropocene, is used by several scientific and non-scientific publications to describe this emerging human epoch. Anthropocene, a word derived from the Greek words *Anthropos* (human) and *Kainos* (new), simply means “the human era”. Anthropocene mainly includes its key features in the human impacts on the Earth that are significant considering the age of the Earth and how these impacts or changes are planetary in scale. While the impact on the environment is the focus in scientific fields, this concept is being debated on social science and humanities and political platforms under the concern of the future impacts and challenges of a human-domineering world.[17] This section briefly highlights the plasticizers in the anthropocene discussing their categories, uses, and sources.

2.1 Different classes of plasticizers

Plasticizers can be categorized considering several characteristics such as molecular weight, the concentrations in which they are used in plasticizer blends, primary function, chemical structure, and bio-based or petro-based. Among them, classifying the plasticizers according to their molecular weight is one of the simplest and highly accepted classification types. It categorizes plasticizers into two groups; monomeric plasticizers and polymeric plasticizers.[18] Monomeric plasticizers are low molecular-weight plasticizers consisting of single molecular structures that are not polymerizable. They are often thin liquids at room temperature with high boiling points. They usually have their molecular weights in the range of 300–600 g mol^{-1}. A higher proportion of all the plasticizers can be categorized as monomeric plasticizers since almost all of them are esters. Polymeric plasticizers, on the other hand, have polymer molecular structures built with many repeating monomer units. Many polymeric plasticizers are polyesters and as any polymer, these do not have a specific molecular weight but average molecular weights in the range of 1000–10 000 g mol^{-1}.[18]

Since plasticizers are often used in combinations, they can be categorized according to the concentrations in which they are used in the blends. Primary plasticizers are the major plasticizers in blends or the only plasticizers in a formula while secondary plasticizers are the plasticizers used in low concentrations in plasticizer blends. However, a plasticizer cannot be strictly classified as primary or secondary since one plasticizer can be primary in one formula and secondary in another. As an example, di-2-ethylhexyl adipate (DEHA) is often used in PVC as a primary plasticizer as well as a secondary plasticizer in producing shoe soles.[18] Categorizing plasticizers depending on their primary function is more useful when developing new plasticizer formulae. A few of the most commonly used categories are; general purpose plasticizers, strong solvating plasticizers, low volatility plasticizers, low-temperature plasticizers, fast fusing plasticizers, specialty plasticizers, stain-resistant plasticizers, and flame retardant plasticizers.

Plasticizers, as any other chemical compound, can be classified according to their chemical type. Table S1† summarizes the chemical classification of plasticizers, their category according to the primary function and examples along with their applications. The functional groups of plasticizers (Fig. S1 †) can interact with polymer chains, reducing intermolecular forces and consequently increasing mobility. Due to this lack of chemical bonding between the plasticizers and the polymers, plasticizers can leach out of plastics when exposed to environmental factors like sunlight and heat, resulting in the widespread dispersion of plasticizers in the environment.[19]

Classifying plasticizers based on their origin is also an important categorizing method. All of the plasticizers used in earlier days were bio-based plasticizers such as camphor and castor oils. They were directly extracted from plants without the requirement of complex techniques for the extraction process. Since the beginning of the industrial revolution, petro-based plasticizers have been extracted and synthesized using complex industrial techniques. Recently, as industries take a turn back towards greener technologies, bio-based plasticizers are being studied for extraction and modification to use industrially.[9,20] Bio-based plasticizers can be extracted from epoxidized, acetylated and esterified vegetable oils, glycerol, cardanol, starch, cellulose, citric acid and bio-waste.[21] The chemical structures of plasticizers from each chemical category are included in Fig. S1,† whereas the physicochemical properties of the plasticizers are included in Table S2.†

2.2 Use of plasticizers

Plasticizers are mainly used to improve the flexibility of PVC products in several industries such as medical, food, domestic equipment, and toys. Depending on the performance requirements of the end product, the type and the concentration of plasticizers differ greatly. The properties of plasticizers are balanced, using a proper plasticizer formula to achieve this goal. Phthalate plasticizers have been the dominant type among all plasticizers since the beginning of plasticizers.[22] However, in some parts of the world, some phthalate esters such as DEHP are restricted its use as a plasticizer in cosmetics, toys, and food-grade plastics due to their potential toxicity.[23] The largest plasticizer market in the world is for the film, sheet, and garment industry. Medical plastics, toys, food coatings, wires and cables, automobile and aircraft interiors, adhesives, sealants, and shoe soles are a few other applications of plasticizer mixed end products. The uses of some selected plasticizers are summarized in Table S1.†

2.3 Different sources of plasticizers

Based on the origin of plasticizers, their classification describes the main two forms of sources of plasticizers as; bio-based and petro-based. Almost all plasticizers can be included in the petro-based category. DEHP, the most used petro-based plasticizer, representing a half of the global phthalate plasticizer production.[21] However, the world has moved towards alternative phthalate plasticizer formulae due to the toxicity of some phthalate esters. Therefore, high molecular weight plasticizers including di-(2-ethylhexyl) terephthalate, di-isononyl, di-isodecyl, di-*n*-octyl phthalates (DOPs) and low molecular weight phthalates such as butylbenzyl phthalates have been produced in plasticizer industry.[21] Other than phthalate esters, the chemical categories described above are petro-based plasticizers which can be synthesized in laboratories. Epoxidized soybean oil (ESO) does not fall in this category. Nonetheless, plasticizer migration has become a major concern since the migrated plasticizer molecules can contaminate soil and water subsequently generating health concerns in humans and livestock. Therefore bio-based plasticizers have become the novel trend in the plasticizer industry.[20]

Due to the novel green concepts in technology, industries are researching more about bio-based plasticizers. Bio-based plasticizers can be divided based on their origin including vegetable oils, cellulose, starch, and citric acid. Vegetable oils can be modified by epoxidation, acetylation, hydrogenation, amidation, alkali fusion, splitting, ozonation, or esterification to produce plasticizers.[24] The ESO has been existing for a longer period in the plasticizer industry as a secondary plasticizer. Recently scientists have studied its' expanded functionalities as a primary plasticizer in plasticizer blends for PVC.[25,26] Some other vegetable oils such as sunflower seed oil, castor bean oil, rapeseed oil, and palm oil also have been studied recently for their use as plasticizers.[27–30] Glycerol is another type of chemical compound that can be extracted from vegetable oil by transesterification to use as a plasticizer.[31] Glycerol is considered as a widely used, non-toxic plasticizer that is used in several industrial applications such as flexible PVC[32] and edible films.[33,34] It is often used in starch and other biopolymer-based films because the three hydroxyl groups of glycerol can form strong hydrogen bonds with biopolymers. Glycerol derivatives such as triacetin have also investigated for their plasticizing property in PVC recently.[35] Cardanol, a liquid extracted from cashew nut shell oils, is a novel interest in epoxy curing and plasticizing techniques. Cardanol and its derivatives are used to reduce volatility, enhance the flexibility and thermal stability of PVC.[36]

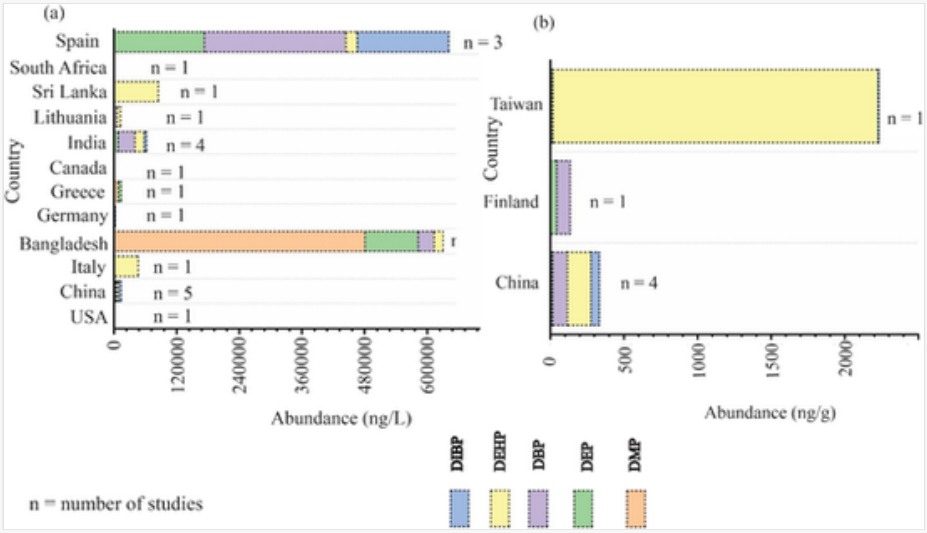
Sugar alcohols and isosorbide ester plasticizers are extracted from starches and cellulose taken from potatoes, rice, wheat, and other grains. Sugar alcohols are polyols which are mainly used as plasticizers for starch. Xylitol and sorbitol are two examples of sugar alcohol plasticizers. Isosorbide esters are heterocyclic sugar derivatives that have plasticizing properties. Isosorbide ester can be produced by double dehydration of sorbitol which is the hydrogenation product of glucose.[37] Isosorbide esters are usually used for pharmaceutical and cosmetic grade plastics due to their non-toxic nature. Oligo-(isosorbide adipate) (OSA), oligo-(isosorbide suberate) (OSS), and isosorbide dihexanoate (SDH) are a few examples of isosorbide ester plasticizers developed by scientists.[38,39] Esterification product of citric acid, which is extracted from citric fruits, beetroot, and sugarcane is used for plasticizing PVC used in medical equipment, toys, and food packaging and coating. These molecules are usually tri or tetra-esters with great variations arising due to the three carboxylic acid groups of citric acid.[40] Fig. S2† depicts the plant and biowaste-based plasticizer classification.

3 Plasticizers in water and sediment

Plasticizers have emerged as a significant environmental issue due to their widespread presence in the ecosystem, as well as their durability and negative impact on soil and water quality. Dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), DEHP, di-iso-butyl phthalate (DIBP), dioctyl phthalate (DnOP), triphenyl phosphate (TPhP), and benzyl butyl phthalate (BBP) are the extensively recognized plasticizers contaminated in environments while DEHP stands as the most spread plasticizer, showcasing its pervasive nature. DEP can be recognized as the second most prevalent entity of overall distribution. The maximum concentrations reported of widely recognized plasticizers reported in respectivevarious countries during 2023 and 2024 wereas graphically illustrated in Fig. 1. Dihexyl phthalate (DHP), DIDP, bisphenol AF (BPAF), bisphenol B (BPB), bisphenol A diglycidyl ether (BADGE), 1,2,4,5-tetrachlorobenzene (TCB), triclosan (TCS), 2,4,4-trimethylpentane (TXIB), trimethyl phosphate (TMP), tributyl phosphate (TBP), ATBC, 4-NP (4-nonylphenol), and isodecyl diphenyl phosphate (IDPP) appear to have the lowest prevalence in the environment considering the overall distribution overview. Twenty-three studies revealed DEHP contamination, which showed a peak value of 85 μg L^{-1} in drinking water refilled in polyethylene terephthalate

(PET) bottles in Sri Lanka.[41] This amount is critical when compared with the WHO guidelines for the DEHP in drinking water (8 μg L^{-1}). A study of the impact of human exposure on commercially available bottled drinking water and six different packed beverages in the market expresses the ubiquitous invasion of plasticizers where triphenylphosphine oxide (TPPO) was detected in all packed beverages and bottled water. Among them, 2-ethylhexyl diphenyl phosphate (EHDPP) is found to be the most abundant organophosphate ester compared to the other plasticizers in regular cola, juice, and wine available in Barcelona Spain.[42]

Fig. 1



The r~~R~~espective maximum concentrations of frequent plasticizers in water (a) and sediments (b), reported ~~in~~across various countries during 2023~~,~~ and 2024 (See Tables S3 and S4† for more details).

The pollution of plasticizers in aquatic settings, particularly drinking water, is a key and significant issue instigating a global concern today (Table S3 †). Upon analyzing the prevalence of plasticizers in water and sediment matrices worldwide, it has been determined that phthalate esters are the most common plasticizers contributing to this problem. The pervasive discharge of plasticizers from plastics into waterways via wastewater runoff is the primary cause of plasticizers combined with drinking water. Wang *et al.*,[43] Lorre *et al.*,[44] and Vimalkumar *et al.*[45] are among several investigators who found that the municipal purification process is insufficient for removing certain endocrine-disrupting chemicals (EDCs) from drinking water. Jayaweera *et al.*[41] illustrated the importance of essential intervention for PET bottle reusability since it significantly increases plasticizer intake with drinking water. The notable distribution pattern for predominantly spread contaminants in global water matrices was identified as DEHP > DEP, DBP > DMP, DIBP > BBP while BPAF, BPB, BADGE, TCB, TCS, tris(2-ethylhexyl) phosphate (TEHP), TXIB, triethyl phosphate (TEP), TMP, TBP, 4-NP and IDPP from a few studies (Table S3†).

Furthermore, plasticizers coming from consumer products will leach and accumulate in soil and sediments over time, affecting not only the terrestrial ecosystem but also the aquatic. It will generate harmful effects for soil-dwelling organisms like microorganisms, worms, and aquatic organisms like fishes. Predators at the top of the food chain like humans experience a high risk of bioaccumulation of plasticizers in their bodies as an indirect adverse effect of this. The most ubiquitous plasticizers found in sediment and soil environments were tri-*n*-butyl phosphate (TnBP), TPhP, and TBEP. The highest value for the reported plasticizers in sediments was 2207 ng ~~per~~ g^{-1} (dry weight), ~~which is responsible for~~attributed to DEHP contamination in sediments~~ in have reported DEHP in sediments~~. DEHA, DINP, Salt River in Taiwan even though two instances diphenyl phthalate (DPhP), dinonyl phthalate (DNP), dimethoxyethyl phthalate (DMEP), bis-2-ethoxyethyl ester (DEEP), dipentyl phthalate (DPP), di-*n*-hexyl phthalate (DnHP), di-*n*-butyl phthalate (DnBP), DHP, DIDP, bisphenol S (BPS), TEHP, tricresyl phosphate (TCP), TEP, ATBC were the notable infrequently encountered plasticizers found in soil and sediment.[46,47]

The geographical distribution of contaminated water, soil, and sediment resources has clustered to the Asian and the European countries. The major reason for this observation may be due to population density, industrial impacts, waste management practices, and the lack of reported studies in other countries. Industrial zones and highly urbanized areas

showed higher concentrations of plasticizers in their consumable water, surface water, and sediments. Rural and remote areas have also been discovered to have trace quantities of plasticizers, indicating the global scope of contamination.[48] Tables S3 and S4[†] depict the most recent research studies (in 2022 and 2023) on plasticizers found in worldwide water matrices and sediment samples. Even though thirty-nine studies had been conducted to investigate the contaminated plasticizers in various water resources, only twenty-two works could be extracted due to insufficient details on the numerical value of their concentrations. Out of this data pool, two studies were the illustration of water-contaminated plasticizers based on peak area (%) using GC-MS instrumentation. During each year comparatively, an equal number of studies have been done on water-contaminated plasticizers. A few studies have been directed at plasticizer contamination with soil or sediment, when compared with the water, in 2022 and 2023. Only eleven studies were ~~in the pool of plasticizers in sediments~~included in the pool of research on plasticizers in sediments. The most probable reason for this study gap may be complexity of extraction and analysis procedures which are both time-consuming and ~~expensive~~costly. Out of these studies, only six contained detailed numerical values for concentrations of detected respective plasticizers in sediment. The rest of the publications produced total phthalate esters (PAEs) concentrations while two studies present short- and medium-chain chlorinated paraffin distribution in sediments. Hence, it was hard to extract the required information of plasticizers from the~~m~~se studies. Studies on plasticizers in wastewater and sludge treatment units in municipal wastewater treatment plants can be seen as an outstanding and extensively focused topic in this period. Moreover, a comparatively equal number of studies have been done on investigating plastic additives in sediments each year. The difference in extraction method will lead to discrepancies in data for the comparison due to the variation of analytical sensitivity, detection limits, and standards.[49] Establishing standardized protocols for sampling and extraction will reduce significant variation of data and can enhance the reliability of these results. The lack of adequate studies has been noticed for long-term monitoring as well as for analyzing temporal trends.

4 Plant uptake

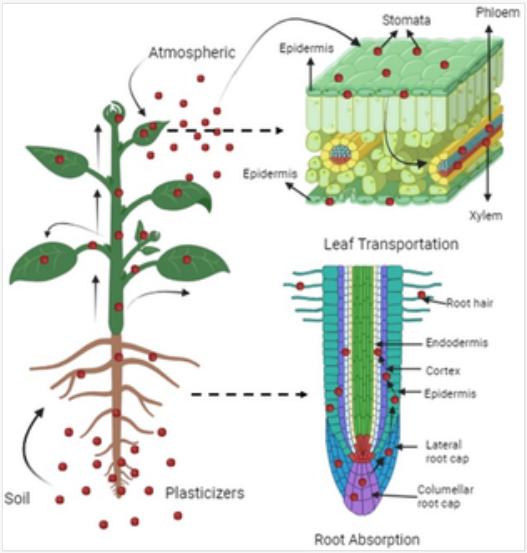
The primary focus on the environmental fate of plasticizers is mainly on their leaching from plastic products into the surrounding environment, either soil or water. There is evidence of plasticizers entering into the environment through different methods, for instance, runoff from treated surfaces and leaching from landfills.[48,50,51] However, the direct uptake by plants is not as well-studied as them.[50] Several factors could influence the potential for plants to take up plasticizers, including the type of plasticizer, soil conditions, plant species, and environmental conditions. Some plasticizers are identified to be persistent in the environment, and their breakdown products might have the potential and possibility to interact with the plants.[52] The degradation rates of plasticizers are controlled by several factors including environmental conditions (*e.g.* temperature, moisture, and UV light), soil properties, and the microbial communities present in soils, sludges, and waste amendments.[50]

4.1 Plant uptake mechanisms

Many plants have been known to be contaminated and accumulate plasticizers from the environment, including water sources, soil, and atmosphere.[53] Several studies have investigated the uptake of plasticizers by plants and have identified multiple pathways through which these chemicals could enter plant tissues. One significant route is through the soil, where plasticizers may leach from plastic-containing materials and subsequently be absorbed by plant roots.[50,52] Additionally, plasticizers can be present in water sources, either directly or through the runoff from plastic-containing products, leading to waterborne uptake by plants. Once inside the plant, plasticizers can translocate to various tissues, including leaves and fruits.[52]

Plants play a crucial role in absorbing and accumulating organic compounds within the terrestrial food web.[54–57] As illustrated in Fig. 2, apart from being absorbed from the soil, the entry of organic compounds into plants is also facilitated by the uptake of airborne pollutants through processes such as gaseous deposition, particle deposition, or a combination of both.[54,58,59~~54,59,60~~] Additionally, the resuspension of soil particles on the soil surface, followed by their settling on leaves, is a contributing factor to the occurrence of organic compounds in low-height plants.[~~61~~60] The uptake of substances by plants through these routes can result in higher concentrations within the plants compared to the surrounding environment, thereby elevating the risk of human exposure through the consumption of food.[54]

Fig. 2



The absorption mechanism of plasticizers by soil involves root uptake, with subsequent translocation *via* transportation pathways from the roots to the stems and further movement from the stems to the leaves and fruits. Exposure to the atmosphere highlights the entry of plastic into the leaf stomata, leading to its subsequent transfer to various parts of the plant.[58,61]

4.2 Evidence on plant uptake of plasticizers

Given below are some of the examples of experiments conducted to identify the uptake of plasticizers by plants. The research on the uptake of DBP and organophosphate esters (OPEs); tris(2-chloroisopropyl) phosphate and tris(2-butoxyethyl) phosphate by rice and wheat roots has found out that, these compounds were transported to aboveground plant parts and evidence of translocation in fruits.[62,63] A study conducted by Kumari and colleagues explored the uptake of a plasticizer DBP and how that impacts on the biochemical and physiological responses of barley.[64] DBP is one of the most commonly used plasticizers. Even though many studies have been steered to investigate the toxicities of phthalate in animals,[65] plants have not been much explored. It was evident that DBP caused morpho–physiological perturbations in barley plants, abnormalities or disturbances in both the physical structure (morphology) and functional processes (physiology). Accumulation and translocation of DBP in the roots and shoots of barley plants were observed. Further decline in all the morphological indices (*i.e.*, dry weight, net primary productivity, seed number per spike, and seed weight) of barley plants was also significant. Therefore, it proved that phthalates' uptake and translocation are involved in mediating phytotoxic responses in barley plants.[64] Accumulation and translocation of traditional and novel OPEs and PAEs in plants during the whole life cycle was much evident in another study that investigated the presence of OPEs and PAEs in peanut and corn plants throughout their life cycle under field conditions.[54] OPEs exhibited an enrichment effect in rhizosphere soil, while PAEs showed a depletion effect. Significant differences in PAE concentrations were observed between peanut and corn, but not in OPE concentrations. OPE metabolites were detected in plants, with lower concentrations. Temporal variations in OPEs, novel OPEs, and PAE concentrations were species and tissue-dependent. Leaves were identified as the primary reservoir for OPEs and PAEs. The low translocation potential into kernels suggested reduced risks through food consumption. Root concentration factors were higher for less hydrophobic compounds, in contrast to the hydroponic experiment findings. A study was conducted to investigate whether plastic film mulching increases the accumulation and human health risks of phthalate esters in wheat grains.[66] In this study, DBP and DEHP were detected in all soil and grain samples, and DEHP was found to be the dominant PAE compound in grains. Two plasticizers, bis(2-ethylhexyl) terephthalate (DEHTP) and DEHP, have been isolated from the leaves of *Capparis spinosa* L. (the caper bush), a plant that is widely used in food seasonings and traditional medicine.[53] Likewise, the detection of plasticizers in plants and food that are intended for consumption raises concerns about their potential adverse effects on human health.

5 Impact of plasticizers on soil and water

There are over 30 000 plasticizers currently being employed worldwide. Among those, phthalates are the most extensively used plasticizers and contribute up to 85% of the total plasticizers in the global market.[3] Plasticizers have

received significant attention due to their potential ecotoxicological and health concerns, including bioaccumulation, carcinogenicity, development defects, and endocrine disruption.[3,67–69] However, the ecotoxicity and threats of plasticizers on soil and water are yet to be revealed and needed to gain a fuller understanding.[50]

Recently, micro-and nano-plastics (MNPs) have emerged as persistent contaminants that are lavishly detected in aquatic, soil, and terrestrial ecosystems, with plasticizers regularly leaching out from these MNPs thereby further contributing to environmental contamination.[70,71] MNPs are defined as plastics of less than 5 mm or 100 nm and are found in numerous morphologies, including fragments, films, fibers, and beads.[70,72] There are two types of micro and nanoplastic, namely primary and secondary MNPs. The primary MNPs are produced and directly released into the environment. In contrast, the secondary MNPs are degraded products from the larger plastic wastes due to water, sunlight, wind, and other environmental factors.[72,73]

When the larger plastics break down into smaller fragments through processes like mechanical degradation, UV radiation, and chemical interactions, the structural integrity of the plastic matrix is generally weakened. The fragmentation of plastics can result in the release of chemical additives, including plasticizers, which were initially added to the plastic to make it more flexible or durable. The accumulation of these leached plasticizers, as well as MNPs in soil and water, continuously increases as a result of various anthropogenic activities and environmental factors. The main sources of plasticizers and MNPs in soil and water include irrigation, agricultural compost, littering, flooding, street runoff, plastic mulches, industrial waste, sewage sludge, and atmospheric deposition.[72–74] The relationship between the exposure of the derivatives of plastics, including MNPs, plasticizers, and potential carcinogenic effects has been extensively summarized by Baj and coworkers. Based on the previous literature, the authors reported that these could potentially induce DNA damage leading to numerous cancers, including hepatocellular carcinoma, pancreatic cancer, pancreatic ductal adenocarcinoma, biliary tract cancer, and some endocrine-related cancers.[75] However, there is scarce information on the health and environmental concerns posed by plasticizers in soil and water. The limited availability of studies is partly due to the analytical challenges associated with the complex extraction, detection, and identification of MNPs from water and heterogeneous soil systems.[76] The following section discusses several recent studies reported on the impact of plasticizers on soil and water.

5.1 Impact of plasticizers on soil

Soil has the natural tendency to adsorb hydrophobic organic pollutants, including plasticizers. The adsorption–desorption process plays a significant role in the migration and transformation of these contaminants in soil.[77] Over the past few years, numerous studies have been reported on soil contamination by plasticizers. For instance, Chakraborty and coworkers examined the high levels of plasticizers generated from electronic waste (e-waste), including PAEs, BPA, polycyclic aromatic hydrocarbons (PAHs) along with heavy metals (HMs) in major metropolitan areas in India.[78] They investigated the amounts of these contaminants in the surface soil of e-waste recycling workshops and nearby open dumpsites in four quadrilateral cities, namely, New Delhi (north), Kolkata (east), Mumbai (west) and Chennai (south). These studies reported the average concentrations of 445 ng g^{-1} for seven different PEAs, 1029 ng g^{-1} for sixteen different PAHs, 140 ng g^{-1} of BPA and 1286 mg kg^{-1} of eight HMs in the e-waste recycling sites, respectively. The authors also mentioned the presence of 150 ng g^{-1} for PEAs (07), 1029 ng g^{-1} for PAHs (16), 121 ng g^{-1} of BPA and 675 mg kg^{-1} for HMs (08) in nearby open dumpsites.[78]

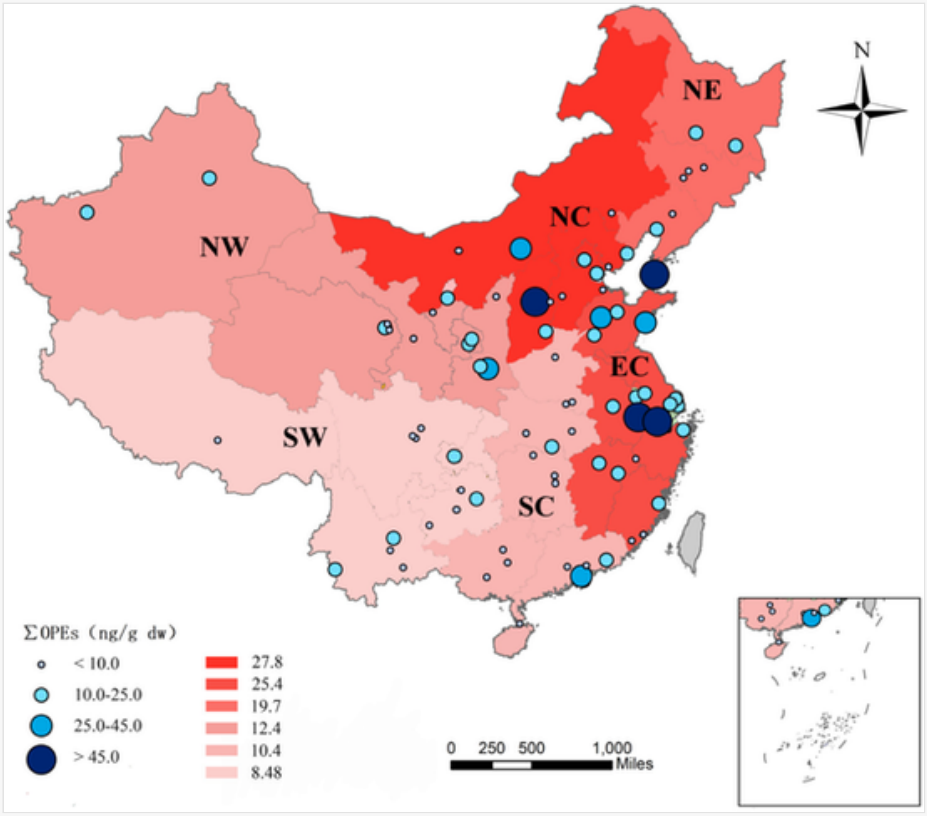
Zhu and his colleagues examined the role of plasticizers derived from PVC microplastics on microbiome and nitrogen cycling in soil ecosystems. The study discussed the direct involvement of phthalate plasticizers in microbial taxonomy and nitrogen metabolism.[79] Further, the effect of PVC microplastics on soil microbiome and available nitrogen (N) and phosphorus (P) content in acidic and neutral agricultural soils in China have also been explored.[80] The study reported that PVC microplastic levels below 1% did not induce significant changes in overall bacterial community diversity and nutrient content in soil over 35 days.[80] It has been also evident that the soil type, plasticizer presence, and microplastic concentration would impact the interaction of microplastics with soil and communities.[81] In their study, microplastic addition exhibited a positive effect on soil available P content in the acidic red soil, whereas a negative effect was detected in the neutral paddy soil. However, several changes in soil nutrients and the relative proportion of specific bacterial taxa such as genera *Lysobacter*, *Streptomyces* and P-solubilizing species were distinguishable, indicating the

importance of further investigations to monitor the toxicity of microplastics at environmentally relevant concentrations.[80]

~~In the work of~~ Luo *et al.* studied the occurrence of thirteen OPE plasticizers in seventy-four soil samples collected from the road greenbelts, residential areas, drylands, waste grasslands, education lands, industrial areas, city parks, and rural homesteads of Shenyang city, China.[82] The authors reported that the OBEs were ubiquitously found in the city environment, and concentrations ranged from 0.039 to 0.95 mg ~~per~~ kg^{-1} (dry weight) ~~(DW)~~. Most abundant OBEs reported in Shenyang city include tri-iso-butyl phosphate (TiBP), tris-(1-chloro-2-propyl) phosphate (TCPP), tri-butoxyethyl phosphate (TBEP), and tris[2-chloro-1-(chloromethyl) ethyl] phosphate (TDCP). The principal component analysis (PCA) and absolute principal component score-multiple linear regression (APCSMLR) suggested that OPE pollution in soils may be caused by road runoff, vehicular traffic emission, wastewater/reclaimed water irrigation, sludge application, and atmospheric deposition. The authors further reported that the pollution levels of OPEs in the urban soils of Shenyang are significant.[82]

He and coworkers studied the presence and health risks of OPE plasticizers in the soil of residential areas covering eighty-nine (89) cities in China.[83] Twelve (12) OPEs with a relatively low contamination level of 1.70–179 ng ~~per~~ g^{-1} (dry weight) of OPEs in the residential soil of China were detected as compared with point source soils and urban soils. The common OBEs found were tris(1-chloro-2-propyl) phosphate (TCIPP), tris(2-butoxyethyl) phosphate (TBOEP), tris(2-chloroethyl) phosphate (TCEP) and triphenyl phosphate (TPHP). Out of all, tris(1-chloro-2-propyl) phosphate (TCIPP) was the most abundant OPE. The authors also revealed significant correlations between OPE concentration and socioeconomic parameters in underdeveloped regions/cities without point sources. Fig. 3 shows the geographical distribution of OPEs in the residential soil of China based on our nationwide baseline survey. According to their study, the health risk assessment is minimal for residents. However, the generation and usage of chlorinated OPEs may not be disregarded.[83]

Fig. 3



Spatial distribution of OPEs (2018) in residential soil across China. Reprinted with permission from He *et al.*, 2019.[83] Blue dots indicate the studied cities with relative OPE concentrations, and red solid lines indicate different regions.

The occurrence, distribution and risk assessment of eleven (11) organophosphate flame retardant (OPFR) plasticizers in nationwide farmland soils of mainland China was investigated by Han *et al.*.[84] The authors estimated the total

concentration of OPFRs ranged from 2.41–35.8 ng per g^{-1} (dryweight). Their PCA showed that the main sources of OPRFs in farmland soils were irrigation, plastic mulching, and atmospheric deposition. They also reported that direct exposure to farmland soils had no high risks to humans and ecological environments.[84] The soil ecotoxicity of the plasticizer, DEHP has been examined using five taxonomic soil species, namely, plants, earthworms, soil algae, Collembola, and soil nematodes and reported that there is no soil toxicity of DEHP against plants and earthworms at high concentrations.[85] However, the authors noted adverse effects on soil algae, *Collembola*, and soil nematodes, primarily by inhibiting their reproduction. Despite this, no significant toxicity from plasticizers on soil species at environmentally relevant concentrations was observed in these studies.[85]

Plasticizers can affect soil microorganisms *via* two main mechanisms: direct biotoxicity and indirect hindrance to nutrient availability and microhabitats. The oxidative stress mediated by plasticizers directly contributes to the biotoxicity of soil microorganisms. Plasticizers indirectly regulate microbial diversity by influencing soil physicochemical and microbiological characteristics such as pH, nutrients, porosity, biofilm formation, bulk density, and organic matter content. For instance, small pH changes due to plasticizers in soil may affect microbial membrane-bound proton pump and protein stability, subsequently imposing physiological constraints such as inhibiting enzyme activities, cell metabolism, and limiting nutrient availability. Moreover, the adsorption of nutrients by plasticizers present in soil could increase nutrient demand for soil microorganisms, causing an imbalance in nutrients, including nitrogen. Thus plasticizers could alter ing the microbial habitats and their functions.[86]

5.2 Impact of plasticizers on water

Water is essential for humans and other living beings, and water pollution significantly influences human health. Water pollution could lead to numerous diseases, contamination of drinking water and food chains, and destruction of biodiversity. Recently, plasticizers in water bodies have gained special consideration worldwide as significant fractions of plasticizers released into the environment could subsequently accumulate in drinking water.[87] The drinking water has also been regarded as one of the main exposure pathways for plasticizers, to humans.[88,89] However, only limited literature reported on plasticizers in water. For example, Li *et al.* investigated the presence of common plasticizers (phthalates and metabolites) and new alternatives (bisphenol analogs, *t*-butylphenyl diphenyl phosphate (BPDP), and BPA-bis(diphenyl phosphate) (BDP)) in urine, hair, drinking water including both tap water and bottled water, and airborne particle samples from seventeen (17) kindergartens in Hong Kong.[89] The authors reported high concentrations of BPDP and BDP in urine, hair, tap water, bottled water, and air particulate samples. The estimated median daily intake values for phthalates in tap water were 10.7–115 ng per kg^{-1} (body weight) per day^{-1} and showed the geometric mean concentration of bisphenol analogs in tap water as 0.90–3.70 ng L^{-1}. Even though the doses of plasticizers tested impose no risk, the authors reported that the estimated urine excretion values of bisphenol analogs were due the exposure *via* tap water, and airborne particulate inhalation may not be ignored in Hong Kong.[89]

Chakraborty and coworkers examined the occurrence, sources, estrogenicity screening and ecotoxicity of seven (07) plasticizers, BPA, steroids, and caffeine in the surface water of River Ganga and Sunderban wetland along the Bay of Bengal.[78] Concentrations of BPA and plasticizers were in the range of (0.04–4.46 μg L^{-1}), (0.43–7.63 μg L^{-1}) and (0.21–2.82 μg L^{-1}), (0.85–2 μg L^{-1}) in the river and the Sunderban wetland, respectively. The authors reported that even though the environmental concentrations of BPA and plasticizers were detectable, these substances posed no risk to wildlife or humans at the reported concentrations.[78]

The occurrence and concentrations of thirty-nine contaminants, including legacy and replacement plasticizers, bisphenols, and flame retardants, were investigated in potable water samples from Montreal (five bottled water brands and three drinking water treatment plants (DWTPs)) and South Africa (one urban DWTP in Pretoria and one rural DWTP in Vhembe).[90] According to their reports, a higher concentration of plasticizers was evident in Montreal than in South Africa whereas legacy and replacement plasticizers were detected in all samples at similar frequencies and concentrations.[90] However, replacement plasticizers such as DINCH, DINP, DIDA, and DEHA and legacy plasticizers, including DEHP, DEP, DBP, and MEHP, are not currently regulated in drinking water. Therefore, analyzing the prevalence and toxicity effects of these compounds is extremely important.[90] Moreover, the presence of thirteen (13) OPEs (chlorinated and alkyl) have been investigated in main water sources in Northeast and Southeast

China.[91] The reported mean concentration of OPEs in drinking water was 380.8 ng L^{-1}, and the average concentration of OPE in southeast cities was greater than in northern cities. Thus, it was estimated that chlorinated OPEs accounted for about 65% of the total concentration. The most widely reported OPEs in water samples were triethyl phosphate (TEP), tri (2-chloroethyl) phosphate (TCEP), and tri (chloropropyl) phosphate (TCPP) ~~(K. Zhu et al., 2022)~~. The authors also reported that the lesser rainfall areas exhibit higher OPE concentrations in water. Their ecotoxicological assessments revealed that the majority of OPE have either no or less risk to organisms, including fish, crustacea, and algae.[91]

Jebara and coworkers investigated the occurrence of six PAEs and two non-phthalate plasticizers (NPPs) (from April 2018–May 2019) in seawater, sediment, seagrass, and fish from different sites along the coast of Mahdia in Tunisia.[92] In that study, a lower plasticizer contamination in seawater was identified as compared to sediments. The authors reported that tourism also preferentially contributed to the distribution of plasticizers in coastal regions. For instance, tourism activities generate and release plasticizers into the coastal seawater. PAE and NPP congeners are found in diving, swimming, and surfing items, along with plastic bags, food packaging, and sunscreen containers discarded accidently on beaches. Besides tourism, urban stormwater runoff, seasonal rainfall, and atmospheric deposition also synergistically contributed to the spatial distribution of the plasticizers in the aquatic environment.[92]

6 Approaches to reducing the impact of plasticizers on the environment

Plasticizers are intercalated into plastics through non-covalent bonds and therefore they can easily leach into the environment from plastic waste and industrial effluents. Later on, freed plasticizers have a greater tendency to accumulate in anoxic water, soil, and sediments.[93] The ubiquitous presence of plasticizers in surface water, soil, and food has become a hot spot worldwide due to its bad impacts on the health of biota including human.[77,94,95] The removal of plasticizers has been studied and performed through conventional as well as recently invented wastewater treatment methods over the years.[96,97] Removal efficiency or capacity and mechanism behind the removal followed by the recently investigated novel approaches for plasticizer removal are documented in Table S5.†

6.1 Removal of plasticizers in water

Since the presence of plasticizers in water systems has been reported immensely, recent studies tended to discover the removal techniques of plasticizers.[95] Metal–organic frameworks, metal alloys, multi-wall carbon nanotubes, supercritical water degradation, supercritical water partial oxidation, electrocatalytic oxidation, advanced peroxymonosulfate systems, electrochemical systems, dielectric barrier discharge plasma, *etc.* have been successfully used to remove different plasticizers efficiently. Moreover, char-fortified beds, activated seaweed carbon, activated sludge, hybrid graphene oxide, magnetically activated biochar, acid-leached carbon black waste, and modified membrane filters were introduced as the adsorbents which have effective filtration for the contaminated water with plasticizers. Without limiting to a single technique, hybrid removal systems of sewage sludge biochar and microorganisms have been optimized to have an efficient removal of plasticizers (Table S5†).

Fluids that are highly compressible at their critical point are used for the removal of plasticizers at higher temperatures and pressures. The supercritical technique has the potential to remove plasticizers consisting of long-chain alkenes and alkanes. For instance, supercritical water degradation and supercritical water partial oxidation treatments have been used to remove BPA and DEHP with a maximum conversion of 98.13%.[98] Moreover, with around 100% removal efficiency, phthalates in the spores of *Ganoderma lucidum* were removed using supercritical fluid extraction through the mechanisms of hydrolysis and oxidation. As ~~SCFE~~supercritical fluid extraction techniques have greater potential to remove plasticizers without disturbing the content of nutrition in the sample and therefore supercritical fluids can be successfully used to remove plasticizers in food and beverages.[99]

Oxidative species (free radicals) like $^{\cdot}OH$, $^{1}O_2$, and $^{\cdot}O_2^-$ have been largely occupied for the removal of plasticizers through various removal techniques such as dielectric barrier discharge, photoelectric catalytic process, ultrasonic oxidation, ozonation, and ozone micro-bubble oxidation. Further, degradation followed by the free radicals has achieved a remarkable removal efficiency (Table S5†). High-frequency electric plasma was used to remove DMP and tetrabromobisphenol A (TBBPA) from water and have been found that the removal efficiency (more than 95% at 18

kV and > pH 7) depends on the pH of the solution and the applied voltage.[8,100] Removal mechanism of plasticizers *via* photoelectrodes involved with the free radicals (˙OH and $\dot{O}_2^-$). A photoelectrocatalytic process with 3D (001) TiO_2/Ti photoelectrode was utilized to degrade DMP with a nearly 100% removal efficiency and about 90% of total organic carbon removal.[101] Superoxide radical anions ($O_2^{\cdot-}$) and ˙OH radicals have played a vital role in BPA decomposition under water radiolysis by irradiation with γ-rays.[102] Hydroxyl radicals (˙OH) were capable of removing DBP with a 90% removal efficiency reported from an electrocatalytic oxidation technique showing high performance with an Iro_2–Ta_2O_5/Ti electrocatalytic.[103] Electrochemical techniques can also be utilized to remove different plasticizers by preventing the use of conventional liquid electrolytes and advancing the features of the electrolytes. As an example, electroperoxone with a solid polymer electrolyte was used to remove several plasticizers namely *o*-chlorophenol (2-CP), phenol (PE), DMP, 1,3-dichlorobenzene (*m*-DCB), and DEP with a 50% removal efficiency within 10 minutes.[104]

Further, plasticizer degradation through reactive oxidizing species (O_3, ˙OH, and $O_2^{\cdot-}$) has been identified as the primary removal mechanism in this electroperoxone with a solid polymer electrolyte electrochemical system. A variety of polymers and metals have been applied to make effective membranes and filters for the removal of plasticizers from water in several studies (Table S5†). Cross-linked β-cyclodextrin polymers, $Fe_2O_3^-$ graphene oxide hybrid material, and indigenously developed CuO/TiO_2 coated ceramic can be introduced as novel membranes that have exhibited enhanced removal.[105,106] Small pores limit the penetration of plasticizers therefore, the pore sizes of some membrane materials can be reduced by doping with other micro or meso-sized polymers. For instance, macro-porous membranes doped with micro-mesoporous β-cyclodextrin polymers (β-CDP), named β-CDP membranes were able to remove BPA with >99% removal efficiency.[107] Recyclability of membranes and filters has been successfully performed with the use of ethanol.[108–110] Recovery of the membranes was excellent as more than 90% of removal efficiencies were obtained after several cycles.[111] Metal–organic frameworks and metal and metal alloys can also be applied to eliminate bisphenol plasticizers. Once the chromium terephthalate metal–organic framework (MIL-101) was utilized with or without $-NH_2$ functionality to remove BPS, MIL-101-NH_2 demonstrated the highest adsorption capacity for BPS (513 mg g^{-1} at pH 7), indicating that H-bonding between the $-S(=O)_2$ groups of BPS and the NH_2 groups of MIL-101-NH_2, as well as H-bonding between the $-NH_2$ groups of the metal–organic frameworks and the –OH groups of BPS. These interactions are likely to contribute as key mechanisms for the efficient removal of BPS.[110] BPA in water could be removed by β-scission and oxidation during the filtration through a membrane made of Ni metal and $Ni_3ZnC_{0.7}$ alloy nanoparticle catalyst encapsulated in N-doped graphite.[112] As plasticizers consist of various functional groups and the electronegativity in their polymer chains, they can successively undergo mono-layer adsorption processes with different adsorbents like biochar through hydrogen bonding, Lewis acid–base interaction, electrostatic interactions, functional group interaction, cation-π interaction, and surface complexation.[113]

Activated biochar and sludge prepared from different waste and biological sources and their composites showed enhanced adsorption in several studies (Table S5†).[96,114] Though some approaches did not perform as much as the novel advanced techniques, some bio-products such as acid-leached carbon black waste ~~(LCBW)~~, a carbonaceous residue from petroleum refineries and activated sludge could adsorb plasticizers with 90–99% and >50%, respectively.[114,115] Moreover, 222.32 mg g^{-1} of BPA adsorption capacity has been obtained from $FeCl_3$-activated seaweed carbon/MCM-41/alginate hydrogel composite ~~(ECAC/MCM-41/ALG)~~ cross-linked with ~~calcium chloride (~~2% $CaCl_2$~~)~~.[109] Moreover, through different types of removal mechanisms and designs, microorganisms have played an important role in the degradation of plasticizers such as BPA, and DOP. Strains of algal (high-rate algal ponds for BPA), bacterial (halotolerant bacterial consortium for DOP, *Mycobacterium* sp. DBP42 and *Halomonas* sp. for DBP, DEHP, acetyl tributyl citrate (ATBC)), and fungal (marine-, freshwater-, and terrestrial-derived fungal strains for DBP and DEP) were involved in the biodegradation of plasticizers.[116–119] In several hybrid approaches, microorganisms were consumed as process enhancers using their potency for plasticizer removal.[120,121] For instance, typical plasticizer degrading bacteria (*Burkholderia cepacia*, *Archaeoglobus fulgidus*, and *Pseudomonas aeruginosa*) and correction 3D-QSAR model have been applied to hydrolyze DEP.[121] Further, a hybrid system of luene + sewage sludge biochar + *Pseudomonas* sp. (*Acinetobacter*) was designed to biodegrade DEHP with 94.9 ± 0.2% removal efficiency.[120] Digestive enzymes of microorganisms have exhibited an enhanced removal process involving the hydrolysis of plasticizers.

Likewise, plasticizers in water systems have been removed through various traditional and novel approaches based on modified materials and techniques. Due to their great efficacy, adsorption using metal–organic frameworks and sophisticated oxidation techniques are among the best for removing plasticizers from water; nonetheless, they have issues with regeneration and cost. Although promising methods like electrochemical treatments show great efficiency, they still need to be improved in terms of energy consumption and electrode stability. In order to obtain the best plasticizer removal, future research should concentrate on improving long-term performance, controlling byproducts, creating affordable materials, and combining several cost-effective approaches.

6.2 Removal of plasticizers in soil

Removal of plasticizers in soil is still in its early stages as not many studies have been involved to date. Nevertheless, aside from looking into novel techniques, the biodegradation of plasticizers has been immensely investigated for the removal of plasticizers in soil. It has been recognized that microorganisms have a remarkable ability to degrade plasticizers in soil. In particular, soil microorganisms have the potential to partially degrade plasticizers.[122,123] Indigenous microorganisms in soil and their genes can readily be involved in the degradation of phthalates in both aerobic and anaerobic conditions hydrolyzing them into phthalic acid and then into benzoic acids. *Actinomycetales* have been identified as the dominant phthalate degraders where *Acidobacteria*, *Proteobacteria*, *Gemmatimonadetes*, and *Bacteroidetes* like phyla were best performers in the anaerobic conditions.[124] Without limiting to the individual degradation, a consortium of bacteria such as *Achromobacter* sp. strain DEPA3, *Pseudomonas* sp. strain DEPB3, and *Enterobacter* sp. strain DEPC1 has greater potential to degrade DEP completely converting them into CO_2 and H_2O.[125]

As well, DOPs in soil were removed through biodegradation by using Halotolerant bacterial consortium (LF) with 100 mg kg^{-1} of and 89.3% of removal capacity and removal efficiency, respectively.[118] ~~Further~~Nonetheless, the hydrolysis, indirect photolysis, and biodegradation of plasticizers in the soil environment may be affected by the soil pH, organic acid, and dissolved metals. Ubiquitously present phthalates in the environment such as DEHP and DEHA are partially biodegraded by soil microorganisms (*Rhodococcus rhodochrous*) emitting metabolites; 2-ethylhexanal and 2-ethylhexanol which can further degrade undergoing mineralization in the gas phase.[122,123] Nevertheless, removing volatile components during the remediation mechanism would cause the pollution in atmosphere. In the presence of hexadecane, *Rhodococcus rhodochrous* were able to eliminate dioctyl phthalate (DOP), bis 2-ethylhexyl adipate (BEHA), and dioctyl terephthalate (DOTP) from the soil undergoing hydrolysis followed by oxidation of the ester functional groups in the plasticizers.[126] Both DOP and DOTP were partially removed while BEHA were completely removed producing intermediates; 2-ethylhexanol and 2-ethylhexanoicacid eventually. The stimulation of functional genes and association with the soil microbial communities for the biodegradation of plasticizers in the soil environment was slightly studied.[124]

Accordingly, the biodegradation of plasticizers by soil microorganisms is a promising avenue for future research on soil plasticizer removal. There are still restrictions in place even if some progress has been achieved, especially with certain bacteria that can break down plasticizers completely or partially. Aswell, t~~T~~he rate at which biodegradation proceeds can be influenced by several factors such as the pH and organic content of the soil. Additionally, volatile byproducts may cause secondary soil pollution. To improve the efficiency of plasticizer removal from soil, future research should concentrate on comprehending the role that functional genes and microbial communities play in this process. It should also look at other environmental conditions that affect degradation.

7 Challenges and future outlook

The establishment of a proper meta-analysis approach that combines the research output of many studies, has been a key requirement nowadays to address many of the issues associated with the collection of reliable data on the environmental distribution of plasticizers, their fate, degradation in the soil, life cycle analysis, disposal, fate of them in soil organisms, possible interactions with chemical fertilizers, bioaccumulation, and the effect on fauna and flora as well as on the possible toxicities.[50] Concerning the possible toxicity, it is pertinent to take toxicity measures by relating to the molecular targets and the expression of some specific genes.[13] Nevertheless, it is identifiable that the data relating to

these traits are limited and poorly investigated.[65] This has made the identification of plasticizers as safer compounds extremely difficult, except for a few that are considered less toxic.[27,127]

This is an even true fact when plasticizers are replaced by substitutes, where proper analyses have not been conducted.[50] In such circumstances, it has ended up with various adverse repercussions related to both public health and the environment. One such example is the replacement of BPA with other bisphenols like BPS, BPP, BPZ, and BPF which have resulted in neuro and reproductive disorders making such substitutions extremely undesirable.[128] Therefore, the implementation of proper pollution control and emission supervision strategies is now a timely necessity. Among the pollution control biodegradation of plasticizers has shown to be promising and however, some research studies have indicated that the interaction of plasticizers with microbes would lead to the formation of metabolites such as 2-ethylhexanoic acid and 2-ethylhexanol, which have become resistant to further degradation.[122,123]

In addition, these bench scale results are not reflective to extrapolate into the real field. This has mainly arisen due to the heterogeneities resulting from mass transfer limitations, and the diverse nature of the soil and water.[5] As a way of addressing the demerits of plasticizers, the generation of plasticizers from renewable natural sources shows promise.[129,130] However, the drawbacks related to their cost of production, poor mechanical properties, poor mixing, excessive hydrophilicity as well as low processability remain to be significant.[131] Nevertheless, to mitigate the risk associated with both traditional plasticizers and alternative plasticizers, it is considered that the implementation of green chemistry practices in each of the steps from the production, and usage up to the end of the life cycle will be essential to avoid any future hazards.[3]

Moreover, it is essential to update and implement a stricter regulatory framework on plasticizer concentrations, conduct vigilant monitoring programs, and mandate industry reporting on discharge. Public awareness programs will be also crucial in advocating the adoption of safer alternatives. Allocation of necessary funding for research on the evaluation of plasticizer impacts and effective treatment technologies will help to develop favorable solutions. Besides, strengthening international collaboration will be useful in implementing successful strategies to reduce plasticizer pollution and safeguard ecosystems and human health.

8 Conclusions

Plasticizers once affirmed as essential additives for enhancing the properties of plastics, have emerged as a critical environmental concern. Their widespread use and persistence in the environment have made them ubiquitous in aquatic and terrestrial ecosystems. The key finding of this study highlights the details on various types of plasticizers, their mode of production as well as the subsequent distribution through different environmental compartments, their potential for bioaccumulation, and the consequent risks to ecosystems and potentially human health. It provides a comprehensive holistic perception of the silent emerging environmental challenge. Plasticizers are found to infiltrate ecosystems through a variety of channels, such as plastics' leaching into soil and water, impacting aquatic and terrestrial ecosystems and perhaps endangering fish, worms, and microbes. Plasticizers, especially phthalate esters, are ubiquitous and persistent in ecosystems, affecting the quality of water and soil. Thus, plasticizers build up in soil and water ecosystems, requiring additional study to comprehend their effects on microbial communities, nutrient cycling, and ecological integrity. Greater concentrations of plasticizers are found in industrial and urbanized areas according to geographic distribution, which may be attributed to factors including waste management techniques, industrial activity, and population density. This type of disproportionate geographical distribution of plasticizers emphasizes the immediate requirement for targeted mitigation strategies. Plasticizers may be absorbed by roots and then translocated to aboveground tissues, which could be dangerous for human health and food safety, ultimately. However, the direct uptake of plasticizers by plants is still poorly understood. The plasticizer concentrations observed to date, often exceed the recommended environmental guidelines. For instance, according to the specific limits set for certain phthalates in water by the European Union and the United States Environmental Protection Agency, it is clearly identifiable they should present in the low concentrations (ppb range). However, current reports suggest that concentrations of phthalates in surface water and groundwater exceed these recommended values, particularly in areas near to industrial zones and discharge sites.

To address these challenges it is imperative to move ahead with a multidisciplinary approach, which will include strict monitoring, development of effective removal strategies and promoting sustainable practices. Recent studies have concentrated on several creative strategies to lessen plasticizers' negative environmental effects, which include metal–organic frameworks, electrochemical systems, supercritical water degradation, biochar adsorption, and microbial degradation. However, to date, the practiced plasticizer treatment techniques have been ineffective in removing many plasticizer types and found to contain some research gaps. Many of these methods ~~like~~such as advanced oxidation processes and adsorption techniques, are associated with high cost and found to be energy-intensive. Moreover, well-proven comprehensive data on long-term efficiency is lacking thereby creating research gaps that necessities the requirement for improved detection and quantification methods for plasticizers prevalent in various environmental matrices. This will particularly emphasize the need to understand the interplay between plasticizers and other pollutants, as well as propose developing cost-effective and scalable treatment technologies. Furthermore, to minimize the negative impact of plasticizers, it will be essential to prioritize the research, thorough meta-analyses, toxicity evaluations, and pollution control measures. Moreover, the build-up of a proper regulatory framework and public awareness will help to safeguard the health of both ecosystems and the human population.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

■■■■

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Please change the reference type and add the following details:
Book name: Applied Plastics Engineering Handbook (Second Edition)- Processing, Materials, and Applications
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Footnotes

[†] Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d4em00317a

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