REVIEW PAPER

A review on morpho-physiological traits of plants under phthalates stress and insights into their uptake and translocation

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Abstract

Phthalates are synthetic chemical compounds that are primarily used as plasticizers in various plastics and polymers to improve their physical properties. They are reported as ubiquitous pollutants in diferent spheres of the environment due to the presence of physical bonding with the polymeric matrix. In animals, including humans, they are known to cause various toxic efects. Nevertheless, less attention has been paid to phthalate induced stress in plants, since plants are equally vulnerable to their exposure as they are immobile and being an important component of the environment cannot be ignored. Moreover, due to their frequent detection in higher amounts in agricultural soils globally, signifcant concern has been raised about phthalate induced stress in plants over the past decade. The main sources of phthalate in agricultural soils are the use of plastic mulching, irrigation with wastewater, pesticide spraying, use of biosolids for improving soil properties, etc. From the soils, phthalates could enter into plants mainly via roots and undergo biomagnifcation at diferent trophic levels in an ecosystem. Phthalates were declared as endocrine disruptors thereby, their accumulation in edible plants raises food security concerns. Moreover, the accumulation of phthalates in plants is observed to afect germination, growth and development as well as reported to interfere with normal plant metabolism which led to modulations in the content of pigments, osmolytes, stress biomarkers and activities of antioxidative enzymes, thus reducing the yield and quality of edible plants.

Keywords Emerging pollutants · Germination · Growth and development · Biochemical responses · Oxidative stress · Accumulation

Introduction

Phthalates are dialkyl or alkyl aryl esters of 1,2-benzenedicarboxylic acid. They are used as plasticizers to enhance their fexibility, durability, and elasticity of plastics or polymers (Mackintosh et al. [2004](#page-18-0)). In polymeric and non-polymeric matrices, phthalates are physically incorporated which leads to their easy escape into the environment because of slight alterations in the environmental factors viz., pH,

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temperature, pressure, and irradiation (Meng et al. [2014](#page-18-1); Benjamin et al. [2015](#page-17-0); Benjamin et al. [2017\)](#page-17-1). The worldwide production of phthalates is increasing globally and from 2007 to 2017, it was predicted to increase from 2.7 to 6.0 million tons per year (Bauer and Herrmann [1997;](#page-17-2) Xie et al. [2007\)](#page-20-0). Among all plasticizers, phthalates contribute approximately 84% of total plasticizers in the global market (ECHA [2013\)](#page-17-3). The most abundant phthalates in the environment are diethyl phthalate, di-*n*-butyl phthalate, benzyl butyl phthalate, di(2-ethylhexyl) phthalate, di-*n*-octyl phthalate (Gavala et al. [2003](#page-17-4)). Phthalates have been extensively studied for their toxicities using animal systems. Humans are also prone to the frequent exposure of phthalates due to the extensive use of plastic products on regular basis. The human exposure to phthalates is confrmed by the detection of their metabolites in the body fuids and tissues (Hines et al. [2009;](#page-17-5) Jensen et al. [2015](#page-18-2); Pan et al. [2015\)](#page-19-0). Furthermore, the detected concentrations of phthalates and their metabolites in humans have been reported to be associated with high blood pressure, pregnancy loss, preterm birth, diabetes,

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enhanced insulin resistance, anti-androgenic efects, cardiovascular disease, hypertension, etc. (Hoppin et al. [2013](#page-18-3); Shiue [2014](#page-19-1); Sun et al. [2014](#page-19-2); Trasande et al. [2014;](#page-19-3) Whyatt et al. [2014](#page-20-1); Bai et al. [2017\)](#page-17-6). As phthalates are reported as potential toxicants to living organisms including humans but little attention has been given to studies on the plant systems. On the other hand, due to immobile nature of plants, they are at high risk to the exposure of phthalates. Thus, a concern regarding the potential toxic efects of phthalates on plants is being investigated by number of researchers. The studies have also demonstrated the negative efects of phthalates on edible plants by adversely afecting the normal metabolic processes. Phthalates are reported to affect seed germination in various edible plants (Ma et al. [2013](#page-18-4), [2014](#page-18-5); Zhang et al. [2016](#page-20-2)). Phthalates also declined the growth and development of diferent plants (Chen et al. [2011;](#page-17-7) Gao and Wen [2016](#page-17-8); Gu et al. [2017\)](#page-17-9). The exposure of phthalates to seedlings as well as plants directly affect the content of pigments, osmolytes, level of oxidative stress biomarkers and also altered the activities of antioxidative enzymes (Huang et al. [2006](#page-18-6); Liao et al. [2006](#page-18-7); Xu et al. [2010;](#page-20-3) Cheng and Cheng [2012;](#page-17-10) Ma et al. [2014;](#page-18-5) Gu et al. [2017;](#page-17-9) Duan et al. [2018;](#page-17-11) Gao et al. [2019;](#page-17-12) Kumari and Kaur [2019;](#page-18-8) Sharma et al. [2019](#page-19-4); Kumari and Kaur [2020;](#page-18-9) Singh et al. [2020](#page-19-5)). The considerable accumulation and translocation of phthalates were observed in vegetables and crop plants (Sun et al. [2015,](#page-19-6) [2018](#page-19-7)). The main contributing factor for phthalates accumulation in plants is their lipophilic nature. After their uptake, they are transported to diferent plant parts and observed to accelerate the generation of reactive oxygen species (ROS) which imparts devastating effects on cellular levels as well as causes membrane disruption *via* lipid peroxidation (Li et al. [2006;](#page-18-10) Xu et al. [2010;](#page-20-3) Cheng [2012](#page-17-10); Zhang et al. [2015a](#page-20-4); Gao et al. [2019](#page-17-12)). Plants regulate these processes by switching the enzymatic and non-enzymatic antioxidative defense system. Thus, the elevation in the amounts of phthalates in diferent environmental media can infuence the normal processes of plants which leads to severe damages at cellular components and ultimately reduce their overall productivity. Therefore, this review highlights the adverse efects of phthalates stress in plants, roles of antioxidative defense system, their accumulation and metabolites formation after being accumulated in plants.

Physico‑chemical properties of phthalates

The uptake and accumulation of phthalates directly rely on their physico-chemical characteristics. Moreover, behavior and fate of phthalates in the environment and biological systems are also dependent on these properties. Phthalates vary in their physical properties which are responsible for their diferent chemodynamics in the environment (Staples et al. [1997](#page-19-8)). They are colorless and odorless liquid at ambient temperature. They are the product of esterifcation of phthalic acid and aliphatic alcohol.

The alcohol ranged from methanol (C_4) to texanol (C_{27}) (Sibali et al. [2013\)](#page-19-9). Phthalates which are commonly used as plasticizers fall in the range of methanol (C_4) to tridecanol (C_{13}) . The water solubility (W_S), vapor pressure (Vp), Henry's constant (H), air-water partitioning coefficient (K_{AW}) and octanol-water partitioning (K_{OW}) coefficient are the main indices to address the physico-chemical properties of phthalates (Table [1](#page-2-0)).

Water solubility (W_S)

It controls the distribution of phthalates between water, soil or sediment and atmosphere. In case of phthalates, water solubility is low and observed to be decreased with an increase in carbon chain length. Thus, being hydrophobic compounds, they get adsorbed onto suspended solids and colloids in surface water reservoirs. They also get frmly associated with soluble humic materials which change their solubilities (Ogner and Schnitzer [1970\)](#page-19-10).

Vapour pressure (V_p)

Phthalates are semi-volatile in nature irrespective of their low vapour pressure. They are reported to be present in the vapour phase at environmentally relevant temperatures (Tienpont [2004\)](#page-19-11). The vapour pressure of phthalates decreases with increase in alkyl chain length.

Henry's constant (H)

It indicates the tendency of the pollutants to escape from water into the air and can be calculated from the values of water solubility and vapour pressure. In the case of phthalates, Henry's constant values approximately equal to 1.01×10^{-2} indicate negligible volatility. The higher values of Henry's constant for phthalates with higher alkyl chains (4 to 13) indicates that they can transfer from aqueous phase to gaseous phase (Net et al. [2015\)](#page-19-12).

Air-water partitioning coefficient (K_{AW})

It reflects the affinity of organic compounds for lipid molecules in living beings. It has been commonly employed to know the potential of contaminants to accumulate or concentrate in aquatic organisms (Lyman et al. [1990](#page-18-11)). In phthalates, the value of K_{AW} increases with an

Table 1 Physico-chemical properties of common phthalates with their chemical formula and structure

Phthalates	Chemical formula	MW (g/mol)	W_S (mg/L)	$V_p(Pa)$	$\log\mathrm{K_{OW}}$	$log K_{AW}$	$\, {\rm H}$	Chemical structure
DMP DEP	$C_{10}H_{10}O_4$ $C_{12}H_{14}O_4$	194.2 222.2	5220 591	0.263 6.48×10^{-2} 2.54	$1.61\,$	-5.40 -5.01	9.78×10^{-3} 2.44×10^{-2}	
DAP	$C_{14}H_{14}O_4$	246.2	165	2.71×10^{-2}	3.11	-4.76	4.28×10^{-2}	
DPP	$C_{14}H_{18}O_4$	250.3	$77\,$	1.74×10^{-2}	3.40	-4.64	5.69×10^{-2}	
DBP	$C_{16}H_{22}O_4$	278.4	9.9	4.73×10^{-3} 4.27		8.54	0.133	
DiBP	$C_{16}H_{22}O_4$	278.4	9.9	4.73×10^{-3}	4.27	8.54	0.133	
BBP	$C_{19}H_{20}O_4$	312.4	3.8	2.49×10^{-3} 4.70		$-\,4.08$	0.205	
DOP	$C_{24}H_{38}O_4$	390.6		2.49×10^{-3} 2.54×10^{-5} 7.73		-2.80	3.95	

Table 1 (continued)

Phthalates	Chemical formula	MW (g/mol)	$\rm W_S$ (mg/L)	V_p (Pa)	$\log\mathrm{K_{OW}}$	$\log\,K_{AW}$	$\, {\rm H}$	Chemical structure
$\rm DEHP$	$C_{24}H_{38}O_4$	390.56	2.49×10^{-3}	2.54×10^{-5}	7.73	-2.80	3.95	
DiOP	$C_{24}H_{38}O_4$	309.6		2.49×10^{-3} 2.54×10^{-5}	7.73	-2.80	3.95	
$\ensuremath{\mathsf{DNP}}$	$C_{26}H_{42}O_4$	418.6		3.08×10^{-4} 6.81×10^{-6}	8.60	-2.43	9.26	
$\mathop{\rm DiNP}\nolimits$	$C_{26}H_{42}O_4$	418.6		3.08×10^{-4} 6.81×10^{-6}	$8.60\,$	-2.43	9.26	
DiDP	$C_{28}H_{46}O_4$	446.7		3.81×10^{-4} 1.84×10^{-6}	9.46	-2.06	21.6	

DMP di-methyl phthalate, *DEP* diethyl phthalate, *DAP* diallyl phthalate, *DPP* dipropyl phthalate, *DBP* di-*n*-butyl phthalate, *DiBP* diisobutyl phthalate, *BBP* benzyl butyl phthalate, *DOP* dioctyl phthalate, *DEHP* di(2-ethylhexyl phthalate), *DiOP* diisooctyl phthalate, *DNP* dinonyl phthalate, *DiNP* diisononyl phthalate, *DiDP* diisodecyl phthalate, *MW* molecular weight, *W_S* water solubility, *V_P* vapour pressure, K_{OW} octanol–water partitioning coefficient, K_{AW} air–water partitioning coefficient, *H* Henry's constant

increase in alkyl chain and is directly proportional to bioconcentration/bioaccumulation.

but very slowly from aqueous media (Net et al. [2015\)](#page-19-12).

Octanol-water partitioning coefficient (K_{OW})

It is the measure of the distribution of a substance between air and water. The low molecular weight phthalates are quite volatile and due to their low log K_{OW}

Types of phthalates and their applications

values they can readily volatilize from their pure state

On the basis of carbon chain length, phthalates are categorized into two categories i.e. high molecular weight phthalates (HMWP) and low molecular weight phthalates (LMWP) (Ventrice et al. [2013\)](#page-19-13).

High molecular weight phthalates (HMWP)

These phthalates have 7 to 13 carbon atoms in their carbon chain. The most common high molecular weight phthalates are diisodecyl phthalate (DiDP), diisononyl phthalate (DiNP), di(2-propylheptyl) phthalate (DPHP), diisoundecyl phthalate (DiUP) and ditridecyl phthalate (DTDP). High molecular weight phthalates are primarily used as plasticizers in polyvinyl chloride (PVC). The other plasticized products with high molecular weight phthalates include wires and cables, fooring, truck tarpaulins, wall coverings, selfadhesive flms or labels, synthetic leather, coated fabrics, roofng membranes and automotive applications (Wilkes et al. [2005](#page-20-5); Cao [2010](#page-17-13); ECPI [2014](#page-17-14)).

Low molecular weight phthalates (LMWP)

These include phthalates with 3 to 6 carbon atoms in their carbon chain backbone. Low molecular weight phthalates are di-*n*-butyl phthalate (DBP), diisobutyl phthalate (DiBP), benzyl butyl phthalate (BBP) and di(2-ethylhexyl phthalate) (DEHP) (Liao et al. [2018](#page-18-12)). They are used in various PVC products as well as in medical devices, adhesives, paints, inks and enteric-coated tablets (Wittassek et al. [2011](#page-20-6); Czernych et al. [2017\)](#page-17-15). The remaining phthalates such as dimethyl phthalate (DMP), diethyl phthalate (DEP) and diallyl phthalate (DAP) have one, two and three carbon-atoms respectively in their hydrocarbon chain. These are not classifed as HMWP or LMWP because they are not used as plasticizers. These are mainly used as solvents and fxatives in fragrances, additives in cosmetics, medical devices, household and personal care products (Schettler [2006;](#page-19-14) Schlumpf et al. [2010;](#page-19-15) Philippat et al. [2012;](#page-19-16) Carlstedt et al. [2013;](#page-17-16) Frederiksen et al. [2013](#page-17-17); ECPI [2014\)](#page-17-14).

Phthalates in soils and sediments

In terrestrial ecosystems, soil acts as a natural sink for diferent pollutants. From soil, phthalates get a route to enter the plants including edible plants (Cai et al. [2008a](#page-17-18)). Phthalates are mainly released to the soils owing to their extensive use as agricultural plastic flms (He et al. [2015\)](#page-17-19). This can lead to potential human health risks *via* food chain. The major factors that contribute to phthalate pollution in agricultural soils are shown in Fig. [1](#page-4-0).

Similarly, in an aquatic ecosystem, sediments act as a sink and source of phthalates deposition especially, which have low water solubility, melting point and volatility (Mit-sunobu and Takahashi [2006\)](#page-18-13). The analysis of five phthalates from the sediments of Gomti river was done using HPLC. The reported mean concentration values of phthalates viz., DEHP, DMP, DBP, DOP, DEP was 31.61, 10.54, 10.41, 5.16, 4.57 µg/kg respectively (Srivastava et al. [2010\)](#page-19-17). A study conducted by Arukwe et al. [\(2012\)](#page-17-20) reported a higher amount of phthalates from the leachates and sediment. The amount of phthalates sediment samples was 1000 times higher than run-off water samples.

Efects of phthalates on plants

In the last decades, the pollution load of phthalates has become a serious environmental issue and cannot be ignored because of their direct or indirect interference with normal physiological processes of living beings. Although, the

Fig. 1 The potential sources of phthalates in agricultural soils

adverse efects of phthalates are extensively documented on animals but in case of plants, the scenario is quite diferent. There are few studies which have examined phthalates induced stress in plants. The stress is a collective term used for both external abiotic or biotic constraints that limit plant growth and development *via* afecting photosynthesis and reducing carbon assimilation ability of plants (Grime [1977](#page-17-21)). Presently, people dealing with the production of food are facing number of challenges as the productivity of crops is not enough to meet the food demands (FAO [2009](#page-17-22)). Abiotic stresses are one of the major factors responsible for low productivity. To deal with such constraints number of strategies are adopted throughout the world. The introduction of mulching into the traditional agricultural practices is one of them. Undoubtedly, it has overcome number of issues but also generated concerns due the presence of high amount of additives. Among additives, main emphasis is laid on phthalates because these are highly preferred plasticizers. Phthalates are also reported to cause phytotoxic consequences among plants. However, under the exposure of pollutants they respond diferentially and some of the plant species can withstand the adversities, while some of them are sensitive to the pollutants. Plants provide countless services to mankind as well as also play various important ecological functions (Beare et al. [1995;](#page-17-23) Kuzyakov and Blagodatskaya [2015\)](#page-18-14). The survey of literature revealed that plants under phthalates stress showed adverse efects on germination, growth & development, biochemical and physiological processes.

Germination, growth and development

Germination is a process that starts with the uptake of water in order to set the metabolic events required to accomplish seed germination (Nonogaki [2008\)](#page-19-18). It is considered as a crucial stage of higher plants as subsequent vegetative and reproductive growth of plant also depends upon it (Ma et al. [2013](#page-18-4)). The exposure of pollutants is more detrimental during early growth stages like germination and seedling growth in a plant life cycle (Macoustra et al. [2015](#page-18-15)). The process of germination was adversely afected by the exposure of phthalates in *Vigna radiata* (mung bean), *Cucumis sativus* (cucumber), *Brassica chinensis* (rape) (Ma et al. [2013](#page-18-4), [2014](#page-18-5); Zhang et al. [2016](#page-20-2)). The authors revealed little effects on germination of rape and mung bean and it may be related to developmental behavior of seeds. Rape and mung bean are dicotyledonous seeds and during seed germination they mainly rely on their own nutritive material *via* hypertrophic cotyledons rather than uptake of nutrients from soil (Shu et al. [1999\)](#page-19-19). Whereas, cucumber seeds showed inhibition in germination under DMP stress. Thus, the efect on seed germination may be plant-specifc or depends upon type of phthalate exposure. Phthalates may have disturbed the physiological and metabolic processes especially mobilization of food reserves of barley seeds during germination as shown in Supplementary Fig. 2. Moreover, phthalates may have imbalanced the level of plant growth regulators and enzymes which might have led to the reduction in seed germination and also afected the other associated parameters.

Phthalates are also reported to reduce the growth of plants at higher concentrations but at lower concentrations, they show plant hormone like properties (Ma et al. [2013,](#page-18-4) [2014](#page-18-5)). The exposure of phthalates was observed to decline the growth of algae, duckweeds, various monocotyledonous and dicotyledonous plants (Melin and Egneus [1983;](#page-18-16) Dueck et al. [2003;](#page-17-24) Liao et al. [2009;](#page-18-17) Gao and Wen [2016](#page-17-8); Duan et al. [2018\)](#page-17-11). The stress-induced by phthalates also declined the length of shoots and roots as well as biomass of the plants. The biomass of diferent plants like *Phaseolus vulgaris, Brassica campestris* var. *chinensis, Picea abies, Trifolium repens, Plantago major* and *Holcus lanatus* was declined under the expsoure of DBP (Dueck et al. [2003\)](#page-17-24). The fresh weight was declined in *Raphanus sativus* treated with DEP and DEHP and in DBP treated *Brassica rapa* subsp. *chinensis* (Saarma et al. [2003](#page-19-20); Liao et al. [2006](#page-18-7)). Thus, due to adverse efects of phthalates on germination, the growth and development of barley seedlings and plants was also afected. Because seed germination determines the subsequent growth quality of the plant.

Phthalates stress induced consequences on germination and growth according to previous studies are listed in Table [2](#page-6-0).

Physiological responses

The primary source of phthalates in the agricultural soils is the application of plastic agricultural flms (He et al. [2015](#page-17-19)). From soil, phthalates are reported to accumulate in plants which disturb the normal functioning of plants. The plants under phthalate stress show morphological and physiological responses. They also employ various strategies to maintain homeostasis under stressful environments. These strategies include alterations in morphological and developmental patterns (i.e. growth plasticity) as well as biochemical and physiological processes (Tuteja [2007;](#page-19-21) Saud et al. [2014](#page-19-22)). Phthalates are reported to affect the biochemical and physiological processes by afecting the contents of pigments, osmoloytes and stress metabolites.

Pigments

The alteration in the levels of chlorophyll pigment is a well avowed index in plants under stressed environment. The pigments posses an important role among the plants as they regulate photosynthesis rate (Zai et al. [2012](#page-20-7)).

Table 2 Effects of phthalates on seed germination and growth of different plants **Table 2** Efects of phthalates on seed germination and growth of diferent plants

Table 2 (continued)

Table 2 (continued)

Abiotic stresses are reported to affect the photosynthesis. For crops, reduction in photosynthetic capacity is directly related to their yield. For carbon assimilation, plants have to perform a series of complex reactions to form carbohydrates which are direct or indirect sources of energy for heterotrophs including human beings. The photosynthetic apparatus consists of pigments (Chl a, Chl b, pheophytins, and carotenoids), photosystems (PS), light reactions (for the generation of NADPH and ATP) and dark reactions (for CO_2 assimilation) (Singh and Thakur [2018\)](#page-19-23).

Osmolytes

The carbohydrates are the fnal products of photosynthesis. In carbohydrates, disaccharides viz. sucrose, trehalose, raffinose, and fructans are the main forms of sugar that are observed to be involved in adaptation strategies during stress (Keunen et al. [2013;](#page-18-21) Song et al. [2019](#page-19-24)). They are soluble sugars and participate in osmotic adjustment (Kumari et al. [2018\)](#page-18-22). Thus, they provide osmoprotection to stabilize the membrane structures as well as maintain turgidity of the cells (Gil et al. [2011](#page-17-26)). Proteins are also observed to be accumulated during stress in plants especially heat shock proteins (HSPs). They are commonly referred as 'molecular chaperones' and play roles in protein folding and assembly. They are categorized based on molecular weight e.g. Hsp70 family, chaperonins (GroEL and Hsp60), Hsp90 family, Hsp100 family and small Hsp family (Wang et al. [2004](#page-20-8)). A study showed the induction of the various genes and HSPs which acted together in diferent cascades to combat the heat stress consequences in rice (Chandel et al. [2013](#page-17-27)). There are other proteins which participate during stress regulation such as late embryogenesis abundant (LEA) proteins. These proteins are observed to accumulate in plants in response to water stress and are reported to act synergistically with trehalose to prevent protein aggregation during stress especially under water stress (Goyal et al. [2005](#page-17-28)). The exposure of DEP also observed to enhance the expression of HSP in *Spirodela polyrhiza* and *Raphanus sativus*. The accumulation of proline is commonly observed in plants under stressed conditions. It is also reported to act as a signaling molecule to modulate mitochondrial function (Szabados and Savouré [2010](#page-19-25)). It participates in number of functions like act as an osmolyte, ROS scavenger, and redox bufer. It also acts as a molecular chaperone and stabilizes the proteins and membranes (Krasensky and Jonak [2012](#page-18-23); Hos-sain and Dietz [2016](#page-18-24)).

Oxidative stress markers

The environmental and biotic stresses trigger a common stress response *i.e*. oxidative stress in which the generation of reactive oxygen species (ROS) gets enhanced that causes damages to cell components (Demidchik [2015\)](#page-17-29). ROS are the inevitable entities of plant's life and are produced in cells *via* diferent pathways and homeostasis is maintained by the antioxidant defense system. The high level of ROS leads to reversible or irreversible variations in biomolecules like proteins, carbohydrates, polynucleic acids and lipids (Møller et al. [2007;](#page-19-27) Farmer and Mueller [2013](#page-17-30)). Among these, oxidation of lipids is considered more damaging because it generates free radicals *via* chain reactions. Lipid peroxidation is referred as a 'hallmark' of oxidative stress in plants (Farmer and Mueller [2013](#page-17-30)). Malondialdehyde (MDA) and hydrogen peroxide (H_2O_2) are considered as indicators of oxidative stress among the plants. MDA is considered as a marker of lipid peroxidation of membrane (Hu et al. [2020](#page-18-25)). Stress mediates the generation of ROS which leads to decrease in membrane integrity due to lipid peroxidation. Moreover, under stress, H_2O_2 is generated along other with ROS. The generation of H_2O_2 gets accelerated *via* glycollate oxidase reaction that occurs in peroxisomes (Anjum et al. [2012](#page-16-0)). Phthalates are observed to enhance the level of ROS.

Antioxidative defense system

The generation of reactive oxygen species (ROS) is an inevitable response of plants under stressed environments. They are produced in plants *via* partial reduction of oxygen and referred as a collective term for oxygen species and nonradical oxygen species (Ahmad [2018](#page-16-1)). The presence of unpaired electrons is responsible for their high reactivity which can even mediate the oxidation of cell structures, biomolecules as well as disturb the cell integrity (Kanojia and Dijkwel [2018](#page-18-26)). The ROS formation also takes place under normal conditions because of various metabolic processes but their level observed to be accelerated during abiotic or biotic stresses. The cellular organelles like chloroplast, mitochondria, and peroxisome, with high metabolic activity act as main sites for ROS formation. Thus, to combat with the enhanced levels of ROS, plants have a defense grid that relies on endogenous enzymatic and non-enzymatic antioxidants (Yu et al. [2019\)](#page-20-9). The enzymatic antioxidative defense system is intricate, efficient and includes enzymes like superoxide dismutase (SOD), guaiacol peroxidase (POD), catalase (CAT), ascorbate peroxidase (APX), glutathione reductase (GR), etc. (Supplementary Fig. 3).

The non-enzymatic antioxidants include glutathione, ascorbate, carotenoids, tocopherols, and polyphenolic compounds, etc. The efects of phthalates on pigments, osmolytes and oxidative stress markers and activities of antioxidative enzymes in different plants are given in Table [3](#page-10-0).

Accumulation of phthalates

The advent of industrialization and other anthropogenic activities are responsible for the release of pollutants into the environment on a regular basis. The irregular or unorganized disposal of wastes on soils leads to potential risks to the biotic components particularly microorganisms, nematodes and plants (Bender and Heijden [2015\)](#page-17-31). Moreover, the use of the untreated or partially reclaimed water for irrigation in some arid or semi-arid areas of the world contributed to soil pollution (Li et al. [2018\)](#page-18-27). Sometimes, biosolids are also employed to improve the properties of the soil. The wastewater and biosolids contain variety of harmful inorganic and organic contaminants. The soil acts as a primary sink for diferent types of wastes such as chemical, domestic, industrial and agricultural wastes (Teng et al. [2014;](#page-19-28) Qing et al. [2015](#page-19-29)). These can also cause alterations in the physical and chemical characteristics of the soils. Plants being primary producers of terrestrial food chains are more prone to the exposure of these contaminants. Plants also have potential to uptake and accumulate such pollutants from soil and participate in their mitigation and transformation (Scheringer et al. [2004\)](#page-19-30). Phthalates are one of such contaminants which are listed as priority pollutants by USEPA and due to their ubiquity throughout the world, they are also referred as world's second PCBs (polychlorinated biphenyls) (Zhou [1989\)](#page-20-10). In plants, phthalates are reported to induce diferent morphological and physiological consequences. Furthermore, plants are reported to uptake phthalates mainly *via* roots from soil or aqueous media (Liao et al. [2006](#page-18-7), [2009;](#page-18-17) Cai et al. [2008a,](#page-17-18) [2008b](#page-17-25)). In soil, phthalates are reported to decline the diversity of microbial communities and also afect the quality of crop plants (Kapanen et al. [2007\)](#page-18-28).

Mechanism of uptake and metabolism

Several studies have been carried to explore the mechanisms of organic pollutant's uptake and translocation. There is number of reports which have revealed that the uptake of these pollutants takes place by the roots. During the process of uptake, frstly the organic pollutant gets enriched at root surface and then enters into the plant *via* roots along with water (Zhang et al. [2017](#page-20-11)). The contaminants including phthalates are reported to enter through the cuticle free

unsuberized cell wall (Müller and Kördel [1993](#page-19-31); Kvesitadze et al. [2006](#page-18-32)). Furthermore, the cell wall between the cells of root cortex is porous, thereby contaminants can move freely before they reach the endodermis (Trapp and McFarlane [1994\)](#page-17-33). Organic pollutants are reported to be translocated to diferent plant parts after their uptake (Lin et al. [2007](#page-18-33)). The two types of organic pollutant transport pathways are reported in higher plants i.e. intracellular and intercellular transport and frst method is meant for short-distance transport, whereas the second relies on conducting tissue and meant for long-distance transport (Taiz and Zeiger [2002](#page-19-32)). The long-distance movement can occur either via apoplastic or symplastic way (Miller et al. [2016\)](#page-18-34). It is general mechanism of contaminant uptake but there are also other factors that regulate the phenomenon of uptake like solubility, molecular mass of contaminant, pH, temperature and phase of plant growth, etc. (Korte et al. [2000;](#page-18-35) Kvesitadze et al. [2006](#page-18-32)). In case, if the solubility of contaminants is low, even then they can also be absorbed by the roots *via* passive or active uptake (Inui et al. [2008\)](#page-18-36). Most studies reported that the uptake of organic contaminants by roots is passive as well as difusive in nature except in some case like phenoxy acid herbicides, where active uptake is reported rather than passive (Ryan et al. [1988](#page-19-33); Bromilow and Chamberlain [1995](#page-17-33); Collins et al. [2006](#page-17-34)). During active uptake, lipid content and plant metabolism play important roles (Paterson et al. [1990](#page-19-34); Collins [2008\)](#page-17-35).

After uptake, in plants, phthalates may undergo enzymatic transformation to enhance the hydrophilicity to lower their toxicity. This process of contaminant's transformation in plants is referred as Sandermann's Green Liver Concept (Sandermann [1994\)](#page-19-35) (Fig. [2](#page-15-0)).

The oxidation, reduction, hydrolysis, etc. are the main enzymatic reactions which mediate the conversion of hydrophobic contaminants into hydrophilic ones. This step leads to increases in the affinity of formed intermediate towards the enzymes and further transformations occur (Kvesitadze et al. [2009](#page-18-37)). After functionalization, the phthalates undergo conjugation. The process of conjugation enables them to react with intracellular endogenous components. There is another process that also operates besides conjugation i.e. deep oxidation but the amount of contaminant degraded through this process is very less (0.1 to 5%) and also depends upon the contaminant's structure (Kvesitadze et al. [2009\)](#page-18-37). The conjugation proceeds towards the compartmentalization. It is the fnal step and in this, the soluble conjugate of phthalates may be accumulated in cellular compartments especially in vacuole. In plant cell, the soluble conjugates of various contaminants are reported to couple with peptides, amino acids, sugars, etc. On the other hand, the insoluble ones in plant cells get coupled with starch, lignin, xylan, pectin, etc. are carried out of the cell and accumulate mainly in the cell wall (Sandermann [1994\)](#page-19-35). Thus, these insights into phthalates uptake and bioaccumulation can act as a signifcant cue for their transformation and mitigation in the environment. But the less attention was paid on the possible mechanism of phthalates metabolites in plants. In last few years, researchers explained possible mechanisms of frequently detected phthalates in the environment mainly in monocots. The existing literature have shown that a large proportion of hydrophobic xenobiotics taken up by plants can be transformed and formed transformation intermediates exert diferent biological activities than their parent form (Sun et al. [2015\)](#page-19-6). Carboxylesterases (CXEs, EC 3.1.1.1) are specifc esterases are reported to be involved in the metabolism of phthalates in plants that display hydrolyzing activity against carboxylic esters (i.e. de-esterifcation)

Fig. 2 Proposed mechanism of phthalates transformation in plants. Source: modifed from Kvesitadze et al. [\(2009](#page-18-37))

Fig. 3 Proposed mechanism of phthalates metabolites formation in plants (Sun et al. [2015;](#page-19-6) Lin et al. [2017](#page-18-38)). *DMP* dimethyl phthalate, *MMP* mono-methyl phthalate, *DBP* di-n-butyl phthalate, *MBP* mono-

n-butyl phthalate, *DEHP* di(2-ethylhexyl) phthalate, *MEHP* monoethylhexyl phthalate, *p.a.* phthalic acid, *R-Alc* respective alcohol

as well as that are also documented to be involved in many functional roles in plants, including xenobiotics detoxifcation (Haslam et al. [2001;](#page-17-36) Gershater and Edwards [2007](#page-17-37); Sun et al. [2015](#page-19-6)). Moreover, phthalates are derived from the esterifcation of phthalic acid and two alcohol molecules, belong to the carboxylic esters. Thus, the chemical structure of phthalates and literature reveals that CXEs play a signifcant role in the metabolism of phthalates in plants, especially in phase I hydrolysis (Lin et al. [2017](#page-18-38)). After hydrolysis, these metabolites conjugates rapidly in diferent components of plants and can be accurately determined via radioactive labeling. However, information about the importance of plant CXEs to phthalates metabolism is still limited. Furthermore, there is less knowledge regarding the activity of CXE in the subcellular fractions of phthalates exposed plants, which might refect the localization and mechanisms of the enzymes involved in phthalates detoxifcation. The proposed mechanism for phthalates metabolism in plants is given in Fig. [3.](#page-16-2)

Conclusions

The present review is the outcome of extensive literature survey which highlighted the consequences of phthalates in plants in detail. This also provided insights into phthalates uptake, accumulation, and mechanism of metabolites formation. Plants have evolved tiered mechanisms for the metabolization and detoxifcation of pollutants. However, in case of phthalates, the exact mechanism of these processes is still unclear and there are number of lacunae. Therefore, further research is required especially to determine the occurrence of phthalate monoesters with parent contaminant during normal agronomic practices in vegetables and other edible crops under feld conditions to know potential health risks. Thus, for better understanding of mechanism of phthalates action in plants, many detailed studies are required and the outcomes of this work will helpful for the generation phthalate tolerant varieties as well as to sustain the agricultural yield.

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