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Review

Melatonin-Induced Detoxification of Organic Pollutants and Alleviation of Phytotoxicity in Selected Horticultural Crops

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Abstract: Environmental pollution with organic pollutants has increased drastically in recent decades. Despite the importance of minimizing organic pollutant content such as pesticide residue in edible crops, our understanding of induced xenobiotic metabolism in plants is poor. Melatonin is a potent stress-relieving biomolecule, which exerts beneficial effects on xenobiotic metabolism in plants. Exogenous melatonin treatment not only improves photosynthesis, antioxidant defense, and plant growth but also reduces pollutant residue and xenobiotic uptake. The overexpression of melatonin biosynthetic genes enhances organic pollutant metabolism, while the suppression of endogenous melatonin biosynthesis increases organic pollutant residue in horticultural products. Studies have revealed that the glutathione-dependent detoxification pathway plays a critical role in the melatonin-induced enhanced detoxification of xenobiotics. Moreover, a role for *RESPIRATORY BURST HOMOLOG (RBOH)*-derived reactive oxygen species signaling has been revealed which potentially acts upstream of glutathione-dependent xenobiotic metabolism. Based on the literature, here, we reviewed the effects of organic pollutants on plants and how melatonin aids plants in enduring the effects of organic pollutant-induced stress. We also discussed the potential melatonin signaling mechanism in enhanced pesticide metabolism. Our assessment suggests that melatonin has positive impacts on plant tolerance to organic pollution, which can be used to improve the food safety of edible horticultural crops.

Keywords: melatonin; pesticide degradation; food safety; glutathione; xenobiotic; detoxification

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1. Introduction

Thousands of organic synthetic compounds are extensively exploited in a range of industries, including agrochemicals, pharmaceuticals, food processing, toiletries, printing, textiles, petrochemicals, steel manufacturing, and so on [1]. Additionally, new synthetic chemicals are being introduced nearly every day around the world. As a result of extensive production, usage, and frequent release, environmental pollution with organic pollutants has become a serious environmental concern [2]. Organic pollutants can extensively disperse, and many organic pollutants have a long half-life, and thus they continue to pollute the environment [3]. Because of the acute and chronic impacts of toxic organic pollutants on all living organisms, the bioaccumulation of such substances has considerably increased the burden and potential threats to the environment and human health [3,4]. Alarmingly, certain organic pollutants are known to cause cancer, genetic mutations, and birth defects [4,5]. In addition, consuming organic pollutant-contaminated crops for a long time may result in serious illnesses [6]. Nonetheless, individual susceptibility, the duration and mode of exposure, and the kind of organic pollutants play a role in determining the health effects.

Due to the scarcity of freshwater resources, reclaimed water is widely used in agriculture, despite it possibly being a significant contributor of organic contaminants to edible crops [7]. When plants are grown in contaminated soils or irrigated with polluted water, organic pollutants are accumulated in the leaves, fruits, and stems of many crops that are often consumed by humans [6,8]. Nonetheless, the accumulation of organic pollutants in the above-ground sections of plants may vary greatly depending on factors including the hydrophobicity, lipophilicity, and chemical structure of the pollutants as well as the plant species/genotype and absorption mechanism [6,9]. In particular, Cucurbitaceae family members including cucumber, melon, pumpkin, squash, and zucchini have been shown to have elevated levels of organic pollutants in their above-ground sections [6]. Moreover, pesticide residues have been found in a wide variety of ready-to-eat foods and drinks such as vegetables, fruits, and fruit juices, and they are notoriously difficult to remove using normal preparation methods such as washing and peeling [10,11]. If residue levels in crops are too high, farmers have to abandon everything they grow on that polluted land, causing a total financial loss. Therefore, it is imperative to reduce the residue of organic pollutants by establishing growing strategies for safer crop production [12]. Plants can degrade or detoxify organic pollutants [13]. Thus, taking advantage of the in planta detoxification of organic pollutants is critical for ensuring their absence in the human diet [14]. However, the capacity of plants to detoxify organic pollutants is often limited by the high phytotoxicity of the xenobiotic substance at high concentrations [15]. Therefore, cultivating safer horticultural crops requires an in-depth knowledge of how plants efficiently detoxify organic pollutants.

Melatonin, also known as *N*-acetyl-5-methoxytryptamine, is an endogenous signaling molecule found in eukaryotic organisms [16]. It plays a significant role in a variety of biological processes in plants [17]. Since the discovery of phytomelatonin in 1995, numerous studies have investigated its effects on plants over the years. Phytomelatonin is gaining recognition as the plant hormone upon the recently identified first melatonin receptor PMTR1 [18]. Melatonin promotes seed germination, increases the production of lateral roots, delays leaf senescence, and modulates the blooming time in plants grown in unfavorable conditions [16,19–21]. Melatonin is a key antioxidant that removes reactive oxygen species (ROS) and reactive nitrogen species (RNS) [17]. Additionally, it regulates gene expression indirectly by activating or inhibiting stress-responsive transcription factors [22,23]. Exogenous melatonin application improves plant tolerance to a variety of stresses such as drought, salt, heat, cold, waterlogging, heavy metals, and organic pollutants via regulating endogenous melatonin production and the activities of antioxidant enzymes [24–29]. Since climate change and environmental pollution are increasingly threatening agricultural production, crop yields, and food security, melatonin has been the subject of increased study due to its stress ameliorative properties.

Recent literature has focused on the remarkable benefits of melatonin in enhancing plant adaptation to unfavorable conditions as well as the unique tolerance mechanisms and the network of regulation in plant defense via melatonin [30–36]. The tremendous potential of melatonin in modulating plant tolerance to organic pollutant-induced stress has been revealed in specific research [7,10,37,38]. Phytomelatonin not only plays a crucial role in alleviating phytotoxicity induced by organic pollutants such as different types of pesticides, polycyclic aromatic hydrocarbons (PAHs), and endocrine disruptor bisphenol-A (BPA) [7,37,39], but it also reduces pollutant concentrations in plant tissue, possibly by decreasing their uptake and/or promoting in vivo degradation [7,10,37,40]. This article reviews the current state of knowledge regarding the role of melatonin in plant tolerance to organic pollutants and associated food safety, with the goal of serving as a reference for future studies of phytomelatonin and pointing researchers in novel directions regarding its applications, particularly with regards to enhancing food safety.

2. Organic Pollutants and Phytotoxicity

Organic pollutants are carbon (C)-based anthropogenic compounds that cause adverse effects on the environment and human health [3]. As a special group of chemical pollutants, organic pollutants are different from inorganic (mostly metals) pollutants. In recent decades, many different types of organic pollutants have been released in large quantities into the environment as a consequence of massive anthropogenic activities [1]. Organic pollutants can be classified in several ways. Based on the degradability of organic pollutants, the pollutants can be divided into two categories: labile organic pollutants and recalcitrant organic pollutants [3]. Again, according to the boiling point, organic pollutants can also be divided into two categories: volatile organic compounds (240 °C~260 °C) and semivolatile organic compounds (250 °C~400 °C) [41]. Despite this classification, the margin between volatile organic compounds and semivolatile organic compounds is to a certain extent unclear, and many pollutants fall into both classes. Many industrial chemicals, pesticides, phenols, ethers, ketones, phthalate esters, pyridines, and anilines belong to semivolatile organic compounds and they are typically more resistant to environmental degradation than volatile organic compounds [3,41]. Organic pollutants such as persistent organic pollutants (POPs), polyaromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) have a long half-life [39,42,43]. In contaminated soils, organic pollutants are absorbed by the roots and then transported to the shoots, where they exert a devastating effect on photosynthesis and other crucial physiological processes [6,15].

Additionally, the shoot can also accumulate lipophilic organic pollutants directly from the atmosphere [43]. Moreover, many pesticides are applied to the foliage, causing their accumulation in the shoot [37,38]. Many hazardous chemicals, including organic pollutants, exert their toxicity primarily via inhibiting photosynthetic processes (Figure 1). Chloroplasts are particularly vulnerable to organic pollutants [44]. Organic pollutants accumulated in chloroplast thylakoids and microsomal compartments interfere with fundamental photosynthetic processes [45]. Both the intact and photo-modified forms of organic pollutants stifle photosynthesis by affecting primary photochemical processes [15]. Organic pollutants block electron transport by obstructing either photosystem II (PSII) or the connection between PSII and PSI at the cytochrome b/f [46]. Moreover, variations in the amounts of photosynthetic pigments (Chl a, Chl b, and carotenoids) due to organic pollutant-induced stress eventually alter the photosynthesis process [47].

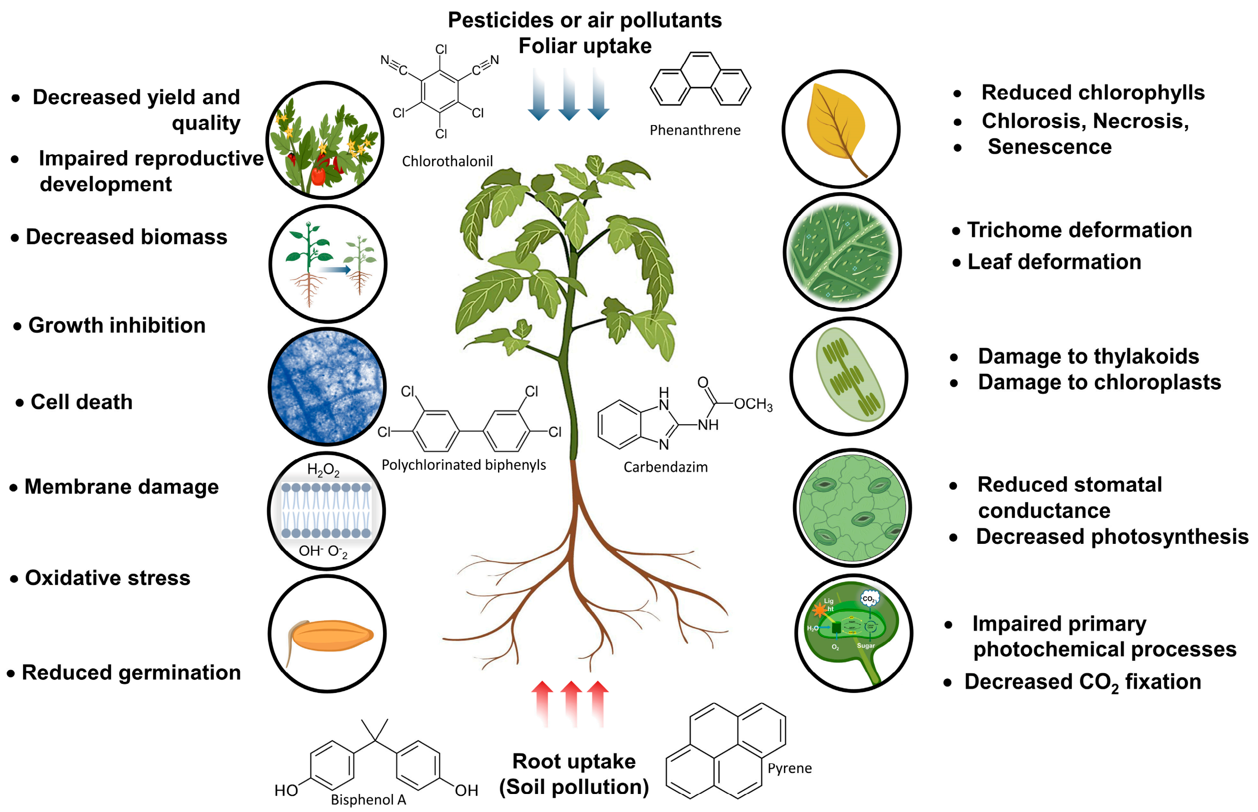

Figure 1. Deleterious effects of organic pollutants on plants and associated phytotoxicity.

Plants exposed to organic pollutants, such as pesticides and PAHs showed visible symptoms including white spots on leaves, trichome and leaf deformations, chlorosis, and necrosis as well as a decrease in biomass accumulation [15,48]. Moreover, oxidative stress, ultrastructural abnormalities, cell death, modifications to antioxidant systems, and reduced plant growth are critical signs of organic pollutant-induced negative consequences [44,49]. Bisphenol A is a xenoestrogen that can cause serious health problems in humans. BPA has been shown to be hazardous to plants as well [50]. Reduced seed germination, decreased photosynthesis, stunted growth, and delayed reproductive development are common effects of BPA on plants [51,52]. BPA treatment also reduced the quantum yield of photosystem II (Fv/Fm) and increased ROS accumulation, lipid peroxidation, and BPA accumulation [7]. Likewise, synthetic pesticides are also phytotoxic [8,15]. Most pesticides suppress PSII activity, cause photoinhibition, inhibit the electron transport chain in the thylakoid, degrade chlorophylls, inhibit photosynthesis, and reduce plant growth [15,38,40].

Organic pollutants cause phytotoxicity by triggering excessive ROS production, which eventually induces oxidative stress [49]. In particular, the oxidation of certain organic pollutants such as phenanthrene leads to ROS production within cellular compartments [53]. Despite being one of the most critical signaling molecules in plant biology, excessive ROS produced under stress as byproducts of aerobic metabolism can be seriously harmful [54,55]. The peroxidation of cell membranes caused by ROS is a critical sign of oxidative stress, and highly bioactive ROS can damage lipids, nucleic acids, and proteins [56]. Plants have evolved a robust antioxidative defense mechanism, comprising both enzymatic and non-enzymatic antioxidants, to remove ROS from different cellular compartments [57]. However, antioxidant-based ROS scavenging is largely rate-limiting. Chlorophyll degradation, decreased photosynthesis, and reduced protein and RNA levels are commonly the results of excessive ROS accumulation in plant cells [35,58,59].

3. Mechanisms of Pollutant Detoxification

To counteract the harmful effects of organic pollutants, plants use several detoxification methods [8]. In the classical detoxification mechanism (Figure 2), the three main steps in xenobiotic metabolism in higher plants are: phase I: conversion or transformation; phase II: conjugation; and phase III: compartmentalization (transport and sequestration) [13]. Typically, organic pollutants are initially hydroxylated by cytochrome P450 family enzymes, and then the modified organic pollutants are conjugated with glutathione (GSH), followed by transportation and sequestration in the vacuole [14]. Glutathione, which is synthesized from cysteine, is an important thiol in plant xenobiotic detoxification. The processes of GSH production in cells are enzyme-catalyzed and ATP-dependent [60,61]. The initial synthesis of γ-glutamylcysteine from γ-glutamate and $\grave{\alpha}$-cysteine occurs through the rate-limiting enzymatic action of the γ-glutamylcysteine synthetase enzyme (γ-ECS) encoded by *GSH1* [7]. Afterward, the *GSH2*-encoded glutathione synthetase enzyme (GS) adds glycine to the dipeptide (γ-glutamyl-$\grave{\alpha}$-cysteine). In plants, glutathione is found in both its reduced and oxidized forms. The enzyme glutathione reductase (GR), which is encoded by the *GR1* gene, catalyzes the conversion of oxidized glutathione disulfide (GSSG) back into reduced glutathione (GSH) [61,62]. Notably, the detoxification of xenobiotics in plants often involves glutathione *S*-transferases (GSTs), a well-known detoxifying enzyme, catalyzing the conjugation process between organic pollutants and GSH [7,50]. To neutralize the electronegative sites of xenobiotics, GSTs promote the nucleophilic conjugation of GSH (at the thiol group). Finally, transformed organic pollutants are contained inside vacuoles or the cellular walls [13] When key detoxification genes such as *GSH1*, *GR1*, and *GST1* are silenced in tomato plants, silenced plants show impaired detoxification potential characterized by increased ROS accumulation, lipid peroxidation, and organic pollutant accumulation as well as decreased GST activity [7]. Even while plants have their inherent detoxifying systems, they are not particularly efficient at breaking down stubborn xenobiotics [6,8]. As various plant growth regulators can promote xenobiotic metabolism in plants, the use of growth regulators is considered a useful strategy for increasing plant tolerance to organic pollutants and xenobiotic degradation in vivo [14,40,63].

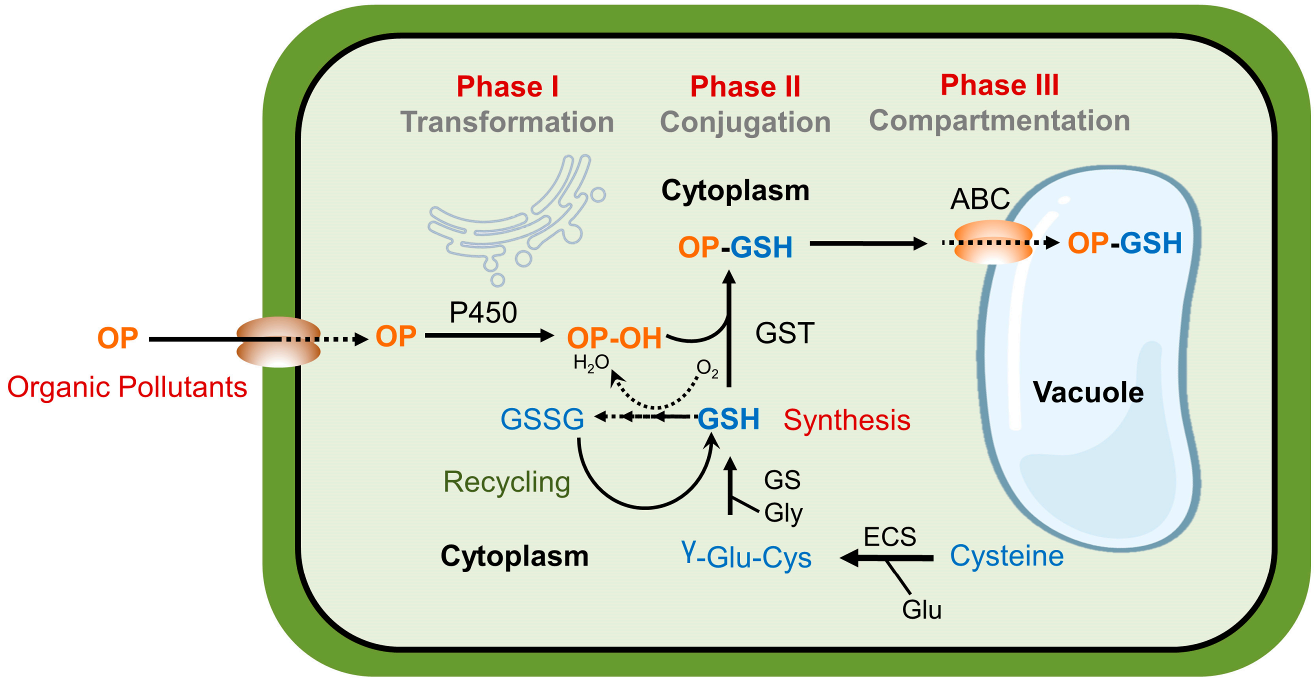

Figure 2. Mechanisms of organic pollutant detoxification in plants.

4. Melatonin: A Master Growth Regulator of Plant Stress Tolerance

4.1. Melatonin Synthesis and Sources

Researchers have uncovered the essential steps of melatonin synthesis in plants [64]. Although melatonin is synthesized in both chloroplasts and mitochondria, the chloroplastic pathway is thought to be the major route of melatonin synthesis [23]. Typically, melatonin is synthesized from tryptophan through the enzymes tryptophan decarboxylase (TDC), tryptamine 5-hydroxylase (T5H), serotonin *N*-acetyltransferase (SNAT), and *N*-acetylserotonin *O*-methyltransferase (ASMT) [59]. To be more specific, TDC converts tryptophan into tryptamine, and T5H hydroxylates tryptamine to generate 5-hydroxytryptamine (serotonin) (Figure 3). Afterward, serotonin is transformed to *N*-acetyl serotonin by SNAT, and melatonin is produced from *N*-acetyl serotonin by ASMT [65]. However, plants also use a catalytic enzyme called caffeic acid *O*-methyltransferase (COMT, involved in phenylpropane metabolism) to convert serotonin to melatonin [66,67]. COMT can substitute for ASMT to catalyze the production of melatonin from *N*-acetyl serotonin, and it can catalyze the transformation of serotonin to 5-methoxytryptamine as well [16]. The recruitment of COMT makes plant melatonin synthesis more versatile than animal synthesis [65]. Although tryptophan is required for the production of melatonin in all organisms, animals can not synthesize tryptophan and thus have to obtain it from plant-derived food [64].

There are essentially two sources of natural melatonin: 'melatonin' from animal origin and melatonin from plant origin, with the latter also being known as 'phytomelatonin' [68]. As for animal sources, melatonin was previously isolated from the pineal glands of cows; however, the risks of viral infection have led to synthetic melatonin production being the preferred option [68,69]. Despite the high yield of synthetic melatonin, the occurrence of unwanted compounds with chemically synthesized melatonin results potential health risks [68]. Notably, significant progress has been achieved in synthetic melatonin production through the use of greener protocols, resulting in the production of new melatonin derivatives with lower cytotoxicity and higher water solubility, such as sodium 4-(3-(2-acetamidoethyl)-5-methoxy-1H-indol-1-yl) butane-1-sulfonate [69,70]. As opposed to chemically synthesized melatonin, phytomelatonin derived from different plant parts such as fruit usually does not contain contaminants that are commonly found in chemical synthesis [71]. Rather, compounds associated with phytomelatonin extracts such as flavonoids, vitamins, phenols, tocopherols, and carotenoids have beneficial health effects on humans [68]. Phytomelatonin is abundant in several families of plants such as Rosaceae, Poaceae, Vitaceae, Apiaceae, and Brassicaceae [72]. In particular, fruits including cherries, grapes, apples, tomatoes, bananas, and pineapples have been reported as important sources of phytomelatonin [33]. Concentrations of phytomelatonin in different plant parts in a range of plant species were listed in our recent review [16]. However, the efficient isolation of phytomelatonin and the development of phytomelatonin-rich extracts still remain challenging tasks, which warrant further intensive studies [68,71].

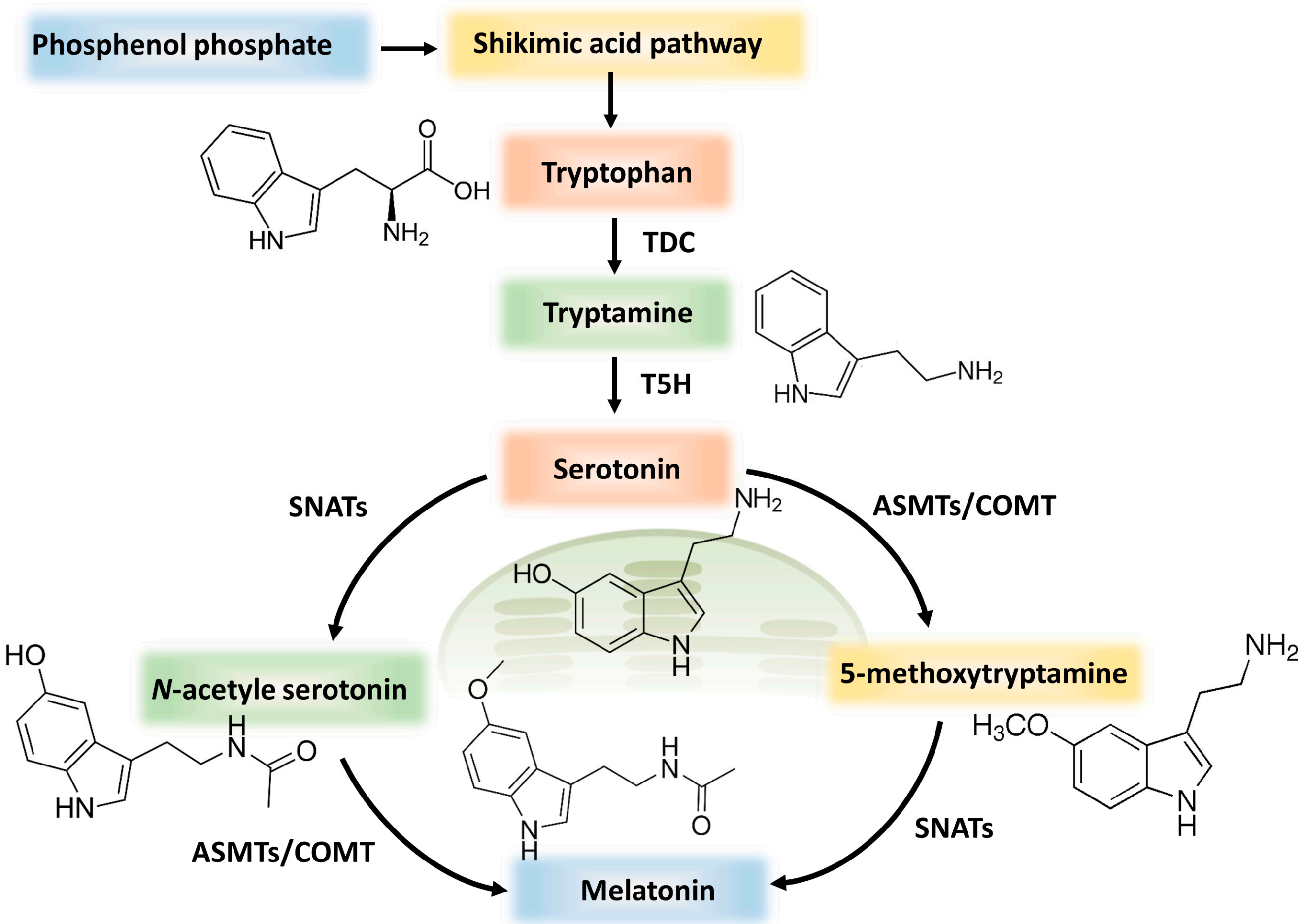

Figure 3. Melatonin biosynthetic pathway in plants.

4.2. Melatonin in Plant Physiology, Metabolism, and Abiotic Stress Tolerance

Due to the widespread effect of melatonin on gene transcription in plants, melatonin likely has a pleiotropic function in a wide variety of cellular processes [16,18,73]. Exogenous melatonin application or endogenous melatonin over-production has been shown to promote plant growth, development, and a variety of metabolic and physiological processes, including photosynthesis, carbohydrate metabolism, and nitrogen assimilation, hormone homeostasis, and so on [19,25,35,36,74]. Melatonin presumably delays postharvest fruit senescence [75–77]. The principal function of melatonin against stresses is attributed to efficient ROS scavenging [28,35]. Melatonin not only plays a role in direct ROS scavenging but also significantly improves the antioxidant defense, which includes both enzymatic and nonenzymatic antioxidants [56]. Melatonin protects plant cells and tissues from oxidative stress by increasing antioxidant gene expression and encoded enzyme activity, thus allowing plants to efficiently scavenge a wide range of ROS and RNS [17]. Recent research has shown that melatonin not only promotes primary metabolism but also stimulates secondary metabolism in plants, leading to the increased synthesis of a wide range of secondary metabolites such as polyphenols, glucosinolate, terpenoids, and alkaloid contents [23,24]. Notably, polyphenols such as flavonoids play an important role in ROS scavenging [78]. Melatonin improves the cellular redox state by maintaining the stability of GSH levels [10,40,79].

In recent years, numerous studies have revealed that melatonin can increase plant tolerance to a wide variety of biotic and abiotic stresses, including drought, salinity, heat, cold, water logging, heavy metal toxicity, and organic pollutant stress [7,80–82]. It is now well-established that melatonin has a critical role in regulating responses to abiotic stress (Figure 4). Melatonin interacts/crosstalk with hormones and signaling molecules to systematically regulate plant resistance [17,31,83,84]. Notably, increased resistance to photo-oxidative stress is mediated by melatonin-induced GSH homeostasis in cucumber [85]. Moreover, melatonin participates in xenobiotic detoxification by modulating the ascorbate (ASA)-GSH cycle and GST activity [10,38,40]. There are several lines of evidence to infer that the use of melatonin to reduce organic pollutant phytotoxicity and pollutant residue could be feasible for edible horticultural crop production.

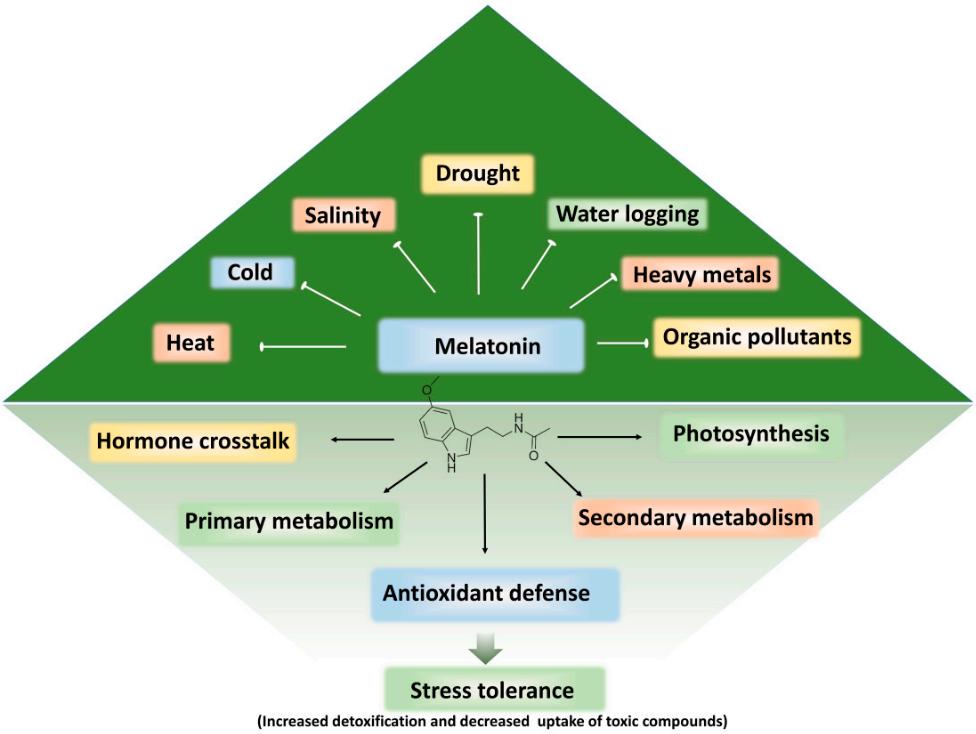

Figure 4. Melatonin effects on plant physiology, metabolism, and abiotic stress tolerance.

5. Melatonin-Induced Detoxification and Alleviation of Phytotoxicity

5.1. Exogenous Melatonin Alleviates Organic Pollutant-Induced Stress

Melatonin regulates a variety of physiological and biochemical processes in plants under stress [25,35]. It has been proposed as a possible natural safener that can protect plants from organic pollutants such as pesticide- and herbicide-induced phytotoxicity [86]. Previous studies have shown that residues of pesticides such as carbendazim, chlorothalonil, and imidacloprid in tomato and cucumber plants can be significantly decreased with the administration of exogenous melatonin [37,38,40]. However, not much is known about the detoxification mechanism triggered by melatonin in response to organic pollutants. Current knowledge of melatonin-induced detoxification is largely based on the exogenous application of melatonin and/or endogenous suppression of melatonin accumulation by using melatonin biosynthetic inhibitor p-chlorophenylalanine (CPA) [10,37]. The effects of exogenous melatonin on the detoxification of xenobiotics and alleviation of phytotoxicity are listed in Table 1. Additionally, there are a small number of pieces of genetic evidence that further strengthen the proposition that melatonin is involved in plant responses to organic pollutant-induced stress [7,38].

Table 1. Effects of exogenous melatonin on xenobiotic detoxification and alleviation of phytotoxicity.

Plant Species	Melatonin Concentrations *	Treatment Methods	Organic Pollutants	Melatonin Effects	References
Tomato (*Solanum lycopersicum* L.)	20 µM	Foliar application	Bisphenol A (BPA, 10 mg L^{-1})-root treatment	• Increased transcripts of *TDC*, *T5H*, *SNAT*, *GSH1*, *GST1* and *GR1* • Decreased ROS accumulation and lipid peroxidation • Increased *Fv/Fm*, GSH biosynthesis and regeneration • Increased BPA glutathionylation by GSH • Decreased BPA uptake	[7]
Tomato (*S. lycopersicum* L.)	100 µM	Foliar application	Chlorothalonil, 11.2 mM-foliar treatment	• Increased photosynthesis and Fv/Fm • Increased detoxification enzyme activity and gene expression • Decreased pesticide residue via H_2O_2 signaling	[37]
Tomato (*S. lycopersicum* L.)	0.5 µM	Foliar application	Carbendazim (MBC, 1 mM)-foliar treatment	• Increased chlorophyll content, Fv/Fm, photosynthesis • Decreased MDA content, decreased MBC residues in leaves (48–73%)	[38]
Lettuce (*Lactuca sativa* L.)	0.5 µM	Foliar application	Carbendazim (MBC, 1 mM)-foliar treatment	• Significantly decreased MBC residues in leaves	[38]
Chinese cabbage (*Brassica campestris* L.)	0.5 µM	Foliar application	Carbendazim (MBC, 1 mM)-foliar treatment	• Significantly decreased MBC residues in leaves	[38]
Spinach (*Spinacia oleracea* L.),	0.5 µM	Foliar application	Carbendazim (MBC, 1 mM)-foliar treatment	• Significantly decreased MBC residues in leaves	[38]
Celery (*Apium graveolens* L.)	0.5 µM	Foliar application	Carbendazim (MBC, 1 mM)-foliar treatment	• Significantly decreased MBC residues in leaves	[38]
Cucumber (*Cucumis sativus* L.)	0.5 µM	Foliar application	Carbendazim (MBC, 1 mM)-foliar treatment	• Significantly decreased MBC residues in leaves	[38]
Cucumber (*C. sativus* L.)	50 µM	Root pretreatment	Imidacloprid (IMD, 2.75 mM)-foliar treatment	• Increased Fv/Fm, chlorophyll contents, photosynthesis, improved redox state, increased antioxidant enzyme activity, GST activity, and its transcripts • Decreased H_2O_2, $O_2{\cdot}-$, and MDA content, decreased IMD residues in leaves	[40]
Jujube (*Ziziphus jujuba* Mill. cv. Dongzao)	0.1 mM	Mature jujube fruits (post-harvest spraying)	Fruits treated (immersed) with chlorothalonil (CHT, 10 mM), glyphosate (Gly, 2 mM), and malathion (Mal, 3 mM) solution for 2 h	• Improved firmness, reduced fruit weight loss, and decay index • Increased GSH content • Enhanced activity of GR and GST, increased antioxidants and phenolics, promoted pesticide degradation	[10]

* Only the most effective concentrations of exogenous melatonin which alleviated organic pollutant-induced phytotoxicity and/or improved the degradation of organic pollutants are presented.

5.2. Potential Mechanisms of Melatonin-Induced Xenobiotic Detoxification

Various modes of application with respect to melatonin can stimulate plant detoxification potential. The foliar spraying of melatonin is a common and practically feasible mode of application that was found to be effective for the detoxification of both shoot-sourced pesticides and root-absorbed organic pollutants such as BPA. The negative effects of BPA as manifested by decreased photochemical efficiency and increased lipid peroxidation, ROS generation, and BPA uptake were mitigated by the addition of exogenous melatonin [7]. Melatonin is a redox network modulator that promotes the detoxification of xenobiotics via the modulation of the AsA-GSH cycle, GST activity, and vacuolar sequestration [10,40]. The expression levels of melatonin biosynthesis genes such as *COMT*, *T5H*, and *SNAT* were upregulated in response to the imposition of BPA stress [7]. These transcriptional changes were accompanied by the elevated expression of *GSH1*, *GR1*, and *GST1* and the activity of GST and GR upon melatonin treatment in BPA-treated plants. Functional genetics research highlights the cooperation between melatonin and GSH in xenobiotic detoxification in plants [38]. The manipulation of GSH metabolism and the expression of associated genes, such as *GSH1*, *GR1*, and *GST1*, by virus-induced gene silencing impairs the melatonin-controlled uptake, transport, and degradation of BPA in tomato plants, indicating the mechanistic involvement of melatonin in BPA detoxification [7].

Moreover, the overexpression of *COMT1* in tomato plants promotes pesticide metabolism, which was associated with increased endogenous melatonin levels in tomato plants [38]. *COMT1* overexpression enhances antioxidant capacity and the detoxification process, leading to the alleviation of oxidative stress and a reduction in carbendazim residue in tomato leaves. Similarly, melatonin can significantly decrease chlorothalonil residue in tomato leaves along with increasing photosynthetic efficiency and antioxidant capacity [37]. Notably, the *RESPIRATORY BURST HOMOLOG (RBOH)*-dependent H_2O_2 signaling-mediated differential expression of detoxification-related genes, GSH production and/or regeneration, and GST activity, appear to play a significant role in the reduction of pesticide residue in tomato plants [87]. Similarly, endogenous H_2O_2 signaling is crucial for facilitating the melatonin-mediated detoxifying response to pesticides (Figure 5). When endogenous H_2O_2 signaling was suppressed, either by limiting NADPH oxidase-dependent H_2O_2 generation or H_2O_2 elimination by ROS scavengers, the potential of exogenous melatonin to confer a detoxifying response to pesticides was reduced, further confirming the involvement of H_2O_2 signaling in melatonin-induced xenobiotic metabolism in plants [37].

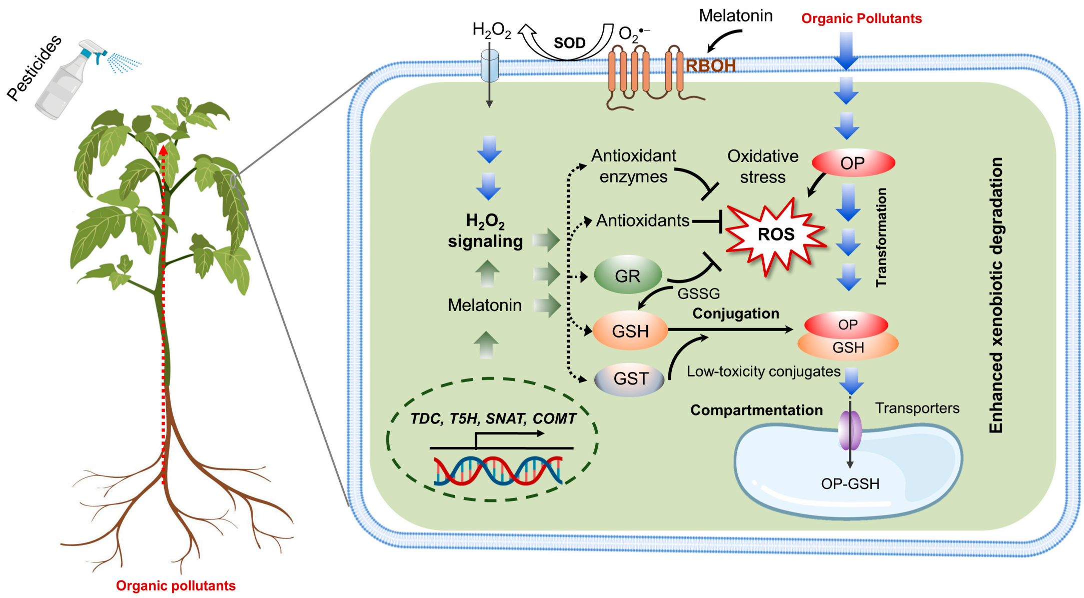

Figure 5. Mechanisms of melatonin−induced organic pollutant detoxification.

5.3. Melatonin-Induced Reduction in Pesticide Residue in Postharvest Horticultural Management

The malpractice of treating harvested fruit with pesticides to prevent fungal diseases is common in postharvest horticultural management. Although this practice can increase the shelf life of fruit, pesticide residue can harm human health [10]. Interestingly, pesticides in postharvest fruit can be degraded by melatonin treatment [75]. For instance, exogenous melatonin application can accelerate the degradation of chlorothalonil, malathion, and glyphosate in postharvest jujube fruit; however, the efficacy of melatonin-promoted pesticide degradation was significantly blunted by the administration of CPA and GSH biosynthesis inhibitor L-buthionine-sulfoximine [10]. This implies that melatonin enhances GSH-dependent detoxification, hence promoting xenobiotic metabolism in plant organs [37]. Melatonin also prolonged pesticide-delayed fruit senescence, as evidenced by increased fruit firmness and decreased weight loss and decay incidence [10].

Similar to foliar treatment, root-sourced melatonin promotes pesticide detoxification in leaves [38]. Melatonin administration increased the activity of the enzyme GST and transcripts of *GST1*, *GST2*, and *GST3*, leading to the accelerated degradation of imidacloprid [40]. Moreover, melatonin treatment improved the AsA/DHA and GSH/GSSG ratios, as well as the activity of AsA-GSH cycle enzymes, showing that melatonin might reduce imidacloprid-induced oxidative stress in cucumber via modulating the AsA-GSH cycle. In addition to in vivo detoxification, melatonin promotes soil bacterial population and the activity of dehydrogenase and peroxidase in soil polluted with PAHs, which potentially resulted in the maximum PAH removal rate, suggesting that melatonin played a beneficial role in increasing plant biomass and elevating the soil bacterial population that favored the degradation of the selected PAHs (phenanthrene and pyrene) [39].

6. Conclusions and Future Perspectives

Despite the innate ability of plants to take in and detoxify organic pollutants from environments, the accumulation of organic pollutants in plant tissue has been shown to affect plant growth and development. Most mechanistic investigations supporting organic pollutant degradation have been conducted in vitro in a chemical rather than physiological context, thus limiting our ability to comprehend the mechanisms by which plants actually degrade organic pollutants in vivo. Previous research revealed that melatonin acts as a superb biostimulator, helping in the degradation of different types of organic pollutants such as pesticides, herbicides, and BPA. Moreover, there is a close relationship between endogenous melatonin levels and organic pollutant metabolism in plants. Melatonin triggers apoplastic ROS signaling, which eventually activates antioxidant and detoxification systems to mitigate oxidative stress and pollutant metabolism in plants (Figure 5). Among different kinds of stress, organic pollutant categories are the least investigated with regard to the melatonin effect, and thus additional research into melatonin function in the stimulant category is warranted for future consideration. As melatonin has great potential for the detoxification of a broad variety of organic pollutants, future remediation technology is expected to benefit from the ongoing effort to maximize the effectiveness of melatonin in xenobiotic metabolism.

Most studies concerning organic pollutant stress have primarily investigated organic pollutant accumulation in plant tissue and subsequent phytotoxicity, wherein less attention has been paid to the molecular mechanism underlying plant tolerance to organic pollutant stress. To comprehend plant uptake, storage, and transport of organic pollutants, however, relevant knowledge is necessary. Moreover, studies revealing the melatonin effects on plant tolerance to organic pollutants have been based on exogenous application or the chemical genetic approach. To elucidate the metabolism of organic pollutants in plants and ensure food safety, functional genomic approaches have to be used. The safe cultivation of horticultural plants in areas polluted by organic pollutants is an issue that calls for researchers from the disciplines of plant physiology, molecular biology, and environmental science to work together.

The degradation of organic pollutants is closely associated with the environmental factors and activity of living organisms including plants and microbes. Moreover, endogenous melatonin biosynthesis and exogenous melatonin actions are affected by abiotic factors such as temperature and light conditions. Thus, environmental factors should be taken into consideration when exploring the role of melatonin in organic pollutant detoxification. The putative ability of melatonin to increase plant resistance to organic pollutants and decrease organic pollutant residue might provide a novel strategy to secure horticultural production. However, further research employing cutting-edge molecular techniques and mutant plants is necessary to fully comprehend the mechanisms of melatonin-induced resistance to organic pollutants.

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