Review

Glyphosate: Its Environmental Persistence and Impact on Crop Health and Nutrition

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Abstract: Glyphosate-based herbicide products are the most widely used broad-spectrum herbicides in the world for post-emergent weed control. There are ever-increasing concerns that glyphosate, if not used judiciously, may cause adverse non-target impacts in agroecosystems. The purpose of this brief review is to present and discuss the state of knowledge with respect to its persistence in the environment, possible effects on crop health, and impacts on crop nutrition.

Keywords: glyphosate; herbicide degradation; crop health; nutrient availability

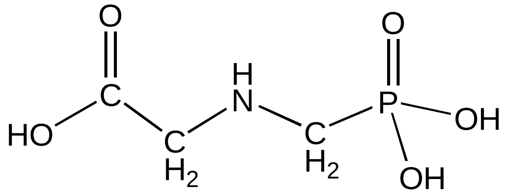
Introduction

Glyphosate, after its introduction in the 1970s, became a popular herbicide among farmers because of its broad-spectrum weed control. The use of glyphosate as a ‘burn down’ application alone, or in combination with other PRE or POST emergent herbicides, became standard practice in cropping systems throughout the world. Glyphosate is a non-selective, post-emergent herbicide known to control more than 150 weed species, which include mono- and dicotyledonous plants of annual or perennial nature [1]. Glyphosate (N-(phosphonomethyl) glycine) is the active ingredient in many herbicide products (example trade name: Roundup) and is commercially available in its various salt forms such as isopropylamine, ammonium, potassium, and trimesium salt. It is used to manage annual broadleaf weeds, grasses, and sedges in various field and row crops around the globe. Furthermore, its usage has expanded to urban and natural areas, pastures, forestry, and aquatics.

Generally applied to foliar parts of weeds, glyphosate can enter plants through four potential routes: through the leaves or other green tissues, the roots, the trunk, or shoots emerging from root or the trunk [2]. After entering the plants, it is rapidly translocated to regions of active growth within the plant. The mechanism of action of glyphosate is to block the activity of the enzyme called 5-enol-pyruvyl-shikimate-3-phosphate synthase [EPSPS], which catalyzes the sixth step in the shikimic acid pathway [3,4]. By blocking the enzyme, it prevents the biosynthesis of aromatic amino acids viz. phenylalanine, tyrosine, and tryptophan produced through the shikimate pathway [5]. Plants treated with glyphosate normally die within a period of 1-3 weeks, and because of its even distribution in the plant, no plant parts can survive [6].

Chemically, glyphosate is a phosphonomethyl derivative of the amino acid glycine [7]. It is a white and odorless crystalline solid having one basic amino group and three ionizable acidic sites (**Table 1**) [8]. Glyphosate is a non-volatile chemical, does not undergo photochemical degradation and is stable in air. Glyphosate has been considered a relatively safe compound in the environment because of its rapid inactivation in soil by adsorption and degradation [9]. However, owing to its extensive use, concerns and studies on the behavior of glyphosate in plant and the environment are growing.

Table 1. Selected physical and chemical properties of glyphosate.

Chemical structure	
CAS number	1071-83-6
Chemical name	N-(phosphonomethyl) glycine
Empirical formula	$C_3H_8NO_5P$
Molecular weight (g mol^{-1})	169.08
Water solubility (mg L^{-1} at 25^{o}C)	10,000 to 15,700 [10]
Octanol-water coeff. (*Kow*)	-4.6 to -1.6 [10]
Vapor pressure (mm Hg at 25^{o}C)	4.3 x 10-10 [10]
Freundlich adsorption coeff.(*Kads*) (L Kg-1)	0.6 to 303 [11]
Degradation half-life in soil (T1/2) (days)	7-60 [12]
Photolysis half-life (days)	Not substantial
EPA maximum contamination level (µg L-1)	700 [10]

Especially due to improper application practices and excessive spray, the widespread presence of glyphosate has been observed in the aquatic and terrestrial environments [13]. In many studies, glyphosate has been detected in the soil, in the crop products, in the animals that feed the crop products, in humans, in freshwater and the organisms that live there [14]. Despite favorable evaluations of weed control efficacy and environmental risks of glyphosate, an increasing number of more recent observations suggest a relationship between extensive glyphosate application and adverse non-target effects in agroecosystems [15]. The more significant among these concerns are *1) Persistence in the environment, 2) effects on crop health, and 3) interaction with crop nutrition* **(Figure 1).**

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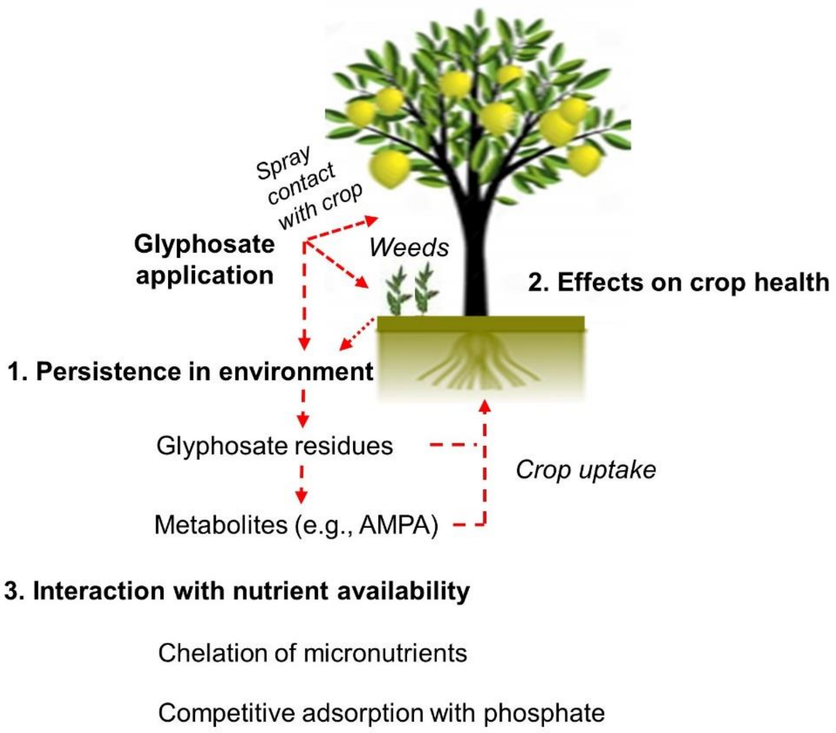

Figure 1. Schematic representation of the potential effects of glyphosate in crop production.

1. Glyphosate persistence in the environment

Applied as foliar spray to control weeds, glyphosate may end up in different soil pools and non-target sites **(Figure 2).** Wash-off from the foliage or undirected spray drift [16], death and decay of glyphosate-treated plant residues, and exudation from the roots [17] may transport glyphosate to the soil. Glyphosate in soil may reach groundwater, surface water, and several other non-target sites through processes such as leaching, surface runoff, and mass transport. Owing to extensive usage, this chemical may pose chronic and remote hazards to the ecological environment [18]. The major route of degradation of glyphosate from soil is microbial mediated degradation or biodegradation [19].

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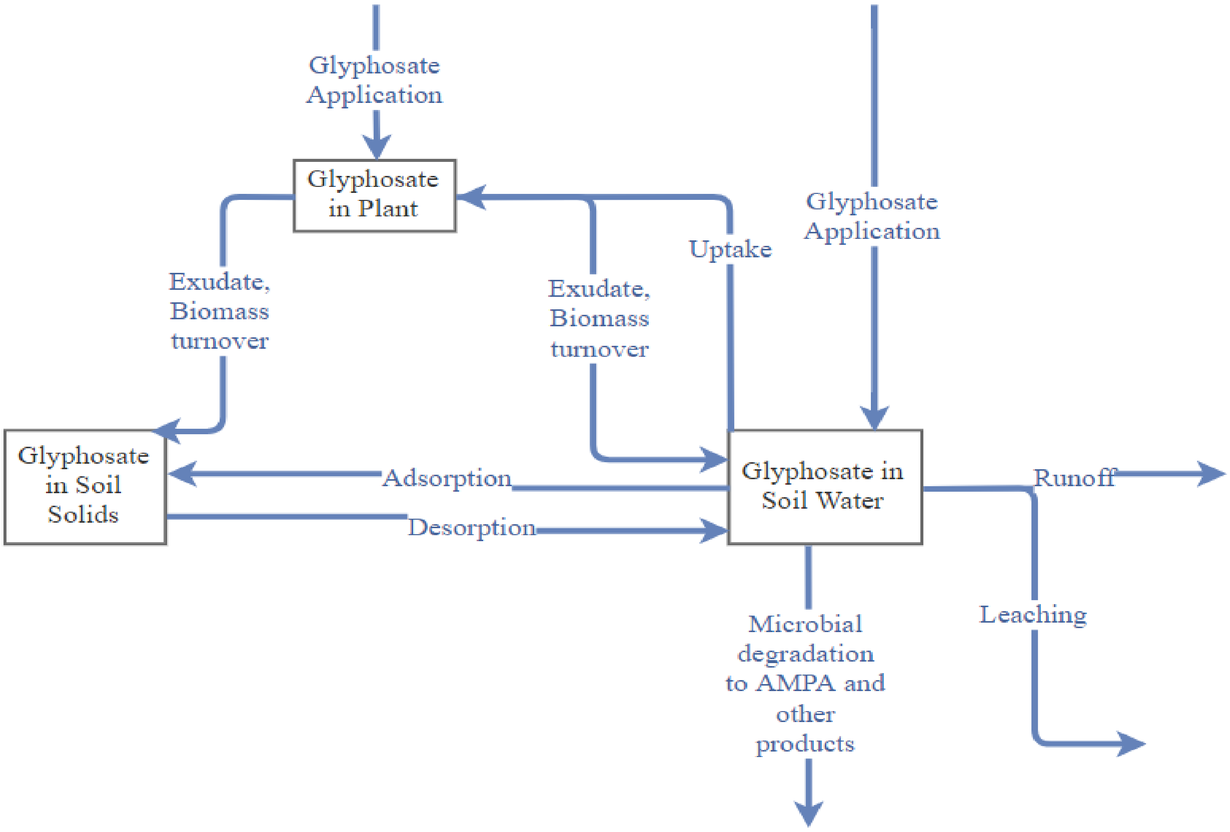

Figure 2. Fate and movement of glyphosate in different pools.

Glyphosate degradation is mainly microbial mediated process [20,21], and the pathway has been widely studied in laboratories [22]. It degrades at a relatively rapid rate in most soils, with half-life estimated between 7 to 60 days [12]. Many studies indicate that the presence of glyphosate in the soil can enhance microbial activity [23,24], while some studies have also shown the toxic effects of glyphosate on soil microorganisms [25].

The extent and rate of glyphosate biodegradation are influenced by processes such as adsorption and desorption in soil, along with other chemical, physical, and biological factors. Both aerobic and anaerobic conditions favor the degradation of glyphosate, even though anaerobic degradation is generally slower than aerobic [26]. Similarly, soil temperature can also play an important role in determining glyphosate degradation [27]. The rate of mineralization of glyphosate was found to be correlated with the abundance of *Pseudomonas spp.* in soil by Gimsing et al. [21]. They also found that the addition of phosphate in the soil stimulates glyphosate mineralization. Lancaster et al. [28] compared the amount of $^{14}CO_2$ production from mineralization of ^{14}C-glyphosate in single herbicide application versus repeated applications. They found reduced production of $^{14}CO_2$ from multiple applications, suggesting that long term herbicide treatment was not favoring acclimation of glyphosate mineralizing microorganisms .

Glyphosate appears to be biodegraded co-metabolically [29] since microorganisms are not able to utilize it as a source of carbon [30]. Co-metabolic involvement of microbes in the degradation of this chemical is also denoted by the fact that glyphosate degradation and general microbial activity in the soil are correlated. Another evidence presented for co-metabolic degradation of glyphosate is the absence of lag phase in soil [19], which implies that the degrading enzymes must already be present in the soil before glyphosate application. On the contrary, a few studies have shown that microbes can utilize glyphosate as a substrate for carbon [24, 31], phosphate [30], or nitrogen [23].

Degradation or mineralization of glyphosate has been found to have a negative correlation with the soil adsorption capacity for glyphosate [32], possibly because of low bioavailability. Despite being highly water-soluble, glyphosate has limited movement within the soil profile because of strong adsorption to soil particles [33]. Adsorption of glyphosate to soil is determined by the amount of clay, organic matter, and iron and aluminum oxides present in soil [34,35]. Soil processes such as adsorption/desorption may control the glyphosate degradation rate, as strong adsorption by soil solids such as iron and aluminum oxides may prevent microbial access to the compound [36,37]. There have been several studies on the adsorption characteristics of glyphosate, but only a few have studied the effect of adsorption on glyphosate bioavailability in soil. Sorensen et al. [32] found limited bioavailability of glyphosate in higher depths of sandy soil profile, where high adsorption and low desorption of glyphosate corresponded with negligible mineralization. On the other hand, in a study by Schnurer et al. [38], adsorbed glyphosate was found to be microbially degradable even though the microbial activity was reduced in the presence of the herbicide.

Glyphosate degradation by microbial activity has been broadly studied, and bacterial species involved in the degradation have been isolated and characterized [39]. Bacteria are considered to be the main drivers behind its degradation in soil, even though the fungi have also been found to play an important role [40]. Degradation studies of glyphosate as a source of Phosphorus (P) in the pure culture and soil media seem to show differences in the degradation kinetics. Furthermore, the rate of glyphosate degradation also varies when different microorganisms are used [41]. A slow lag phase followed by accelerating phase is observed in the degradation of glyphosate by a pure culture, while no lag phase is seen in the soil [41]. Results from such studies imply that pure culture studies may yield important information on degrading potential of microbes, but the application of such information to *in situ* conditions requires further investigations.

Primarily, there are two pathways of microbial degradation of glyphosate [30]. In one pathway, the intermediate compound formed is aminomethylphosphonic acid (AMPA) and in the other, sarcosine and glycine are formed. However, AMPA is considered to be the most common metabolite of glyphosate degradation since it accounts for more than 90% of the reported metabolites. The enzyme glyphosate oxidoreductase breaks the C-N bond in glyphosate to produce AMPA and glyoxylate [42]. The bacterial enzyme glyphosate oxidoreductase employs flavine adenine dinucleotide (FAD) as a co-factor, which is crucial in the degradation pathways of glyphosate. The FAD is believed to be reduced at the active site by glyphosate. Glyphosate oxidoreductase enzyme is inserted into the plant genomes for making glyphosate-tolerant Roundup Ready® crops [43].

2. Glyphosate's effects on crop health

Among several concerns pertaining to unintended effects of glyphosate, its negative effects on non-target plants are of serious concern among the producers. Glyphosate applied to manage weeds can reach the crops through means such as drift, runoff, leaching, and biomass turnover. The subsequent uptake of glyphosate in plants occurs through above- and below-ground plant parts. Accumulation of sub-lethal doses of glyphosate in the crops could negatively impact their development and vigor.

Glyphosate blocks the synthesis of essential amino acids, through binding and subsequent inactivation of an enzyme (EPSPS) that is critical in the shikimate pathway [19]. An array of phenolic compounds that play a significant role in plant immunity are derived from the same metabolic pathway. Glyphosate by disrupting the synthesis of such defense compounds in plants predisposes the crops to attack by soil-borne pathogens [44]. Hence, it could be argued that continuous crop exposure to glyphosate may increase plant susceptibility to diseases [15,45]. Excessive glyphosate application has been linked to disease development in many crops. For instance, glyphosate applications were found as the main factor in the development of diseases such as Fusarium head blight in agronomic crops [46]. There are documented reports of increased colonization of pathogen in wheat and barley roots correlated with burndown applications of glyphosate before planting [47]. Moreover, the effects of sub-lethal doses of glyphosate on perennial plants sometimes take a year after exposure to appear and continue for two or more years [48]. Glyphosate can also predispose plants to diseases indirectly by reducing the overall growth and vigor of the plants, modifying soil microflora that affects the availability of nutrients required for disease resistance and altering the physiological efficiency of plants.

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Another potential side effect of glyphosate that needs to be discussed is its effect on the root formation. Bott and coworkers [49] demonstrated glyphosate's ability to inhibit root elongation, lateral root formation, and root biomass production in soybeans. It was even demonstrated that glyphosate released from the dead weeds could be absorbed through the roots of the growing citrus plants [17]. After entering the plant system, glyphosate is rapidly translocated to young growing tissues of roots where it can accumulate and inhibit the growth [50]. By blocking the production of tryptophan, glyphosate prevents the synthesis of a major growth promoter called indolyl acetic acid (IAA), which can explain the reduction in root growth of plants [15].

There are also some concerns on deleterious effects of glyphosate on fruit retention in tree crops such as citrus. Fruit drop in citrus is a natural phenomenon, but an increase in fruit drop has been reported after glyphosate application, especially in late summer and fall with early-season oranges and grapefruits [51,52] with an impact on fruit yield. The reason for this glyphosate-linked drop is far from understood, as it is not even consistent across different seasons. However, it is known that glyphosate enhances ethylene production in plant tissues, and ethylene exposure of mature citrus fruit may result in early abscission and fruit drop. More research is needed to understand the causes of this fruit drop and the exact role of glyphosate in this process.

3. Glyphosate's interaction with crop nutrition

Glyphosate's interaction with soil occurs when a foliar spray hits the soil surface or when glyphosate is released from decomposing weed tissue [17]. Glyphosate in the soil will be immobilized by adsorption or binding to the soil colloids and hence persists in the soil. Adsorption characteristics of glyphosate are different from most of other herbicides. Adsorption of glyphosate on the soil is more influenced by the soil minerals rather than organic matter [53]. Glyphosate is a divalent metal cation chelator and has been purported to reduce the uptake and translocation of nutrients in crops. The recent evaluations on the chelating ability of glyphosate highlighted it as a key factor in nutrient deficiencies in crops. These reduced availabilities of nutrients as a result of external (in the soil) or internal (in the plants) interaction of glyphosate with cationic nutrients are observed in production systems that heavily rely on glyphosate for weed management. For instance, Bai et al. [54] and Eker et al. [55] found that glyphosate reduced the uptake and translocation of micronutrients such as Mn and Fe in row crops and orchards. These chelated complex formation of glyphosate with micronutrients hindered their root uptake by the crops. There are many similar studies that link the ability of glyphosate to inhibit the acquisition of micronutrients such as Mn, Fe, Zn and B in plants [56,57,58]. Such interactions of glyphosate with plant nutrition may potentially pose consequences on crop health. For instance, in tree crops like citrus, it is well known that these micronutrients are involved in disease, particularly Huanglongbing (HLB), resistance mechanisms [59,60].

The mechanism of binding of glyphosate and phosphate (P) compounds to the soil solids, and adsorption sites have been found to be similar [61]. Thus, the mobility of P in the soil is affected by the presence of glyphosate. The interaction between glyphosate and P in soil was reported shortly after the herbicide was launched into the market [20]. Many of the studies conducted later have verified that P and glyphosate compete for adsorption in the soil and the competition substantially differs in various kinds of soils [54,62,63]. Therefore, the competition between glyphosate and P for adsorption sites in soil seems to be vital and makes a significant impact on mobility and crop availability aspects of P as a crop nutrient.

4. Conclusion

Glyphosate has often been termed as a "once in a century herbicide" because of its tremendous impact on weed management and crop production industry. However, the extensive use of glyphosate and the environmental risks associated with it warrant awareness among its users about its judicious utilization and also necessitate further intense investigations to mitigate, avoid or remove the problems resulting from its use.

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