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Environmental Fate and Degradation of Glyphosate in Soil

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Abstract – Commercialisation of glyphosate [N-(phosphonomethyl)glycine] in the early 1970s has left a big leap in the agriculture sector. This is due to its effectiveness in controlling a wide range of weeds. Glyphosate translocates well in plants. In addition, with added surfactant in its formulae, it can also be used in wet conditions. Its ability to kill weeds by targeting the 5-enolpyruvyl-shikimate-3-phosphate synthase (EPSPS) makes no competing herbicide analogs in its class. Considering its cost effectiveness, only small amount is needed to cover a large sector in agricultural land. The most important aspect in the success of glyphosate is the introduction of transgenic, glyphosate-resistant crops in 1996. However, glyphosate is not an environmental friendly herbicide. This systematic herbicide has raised environmental concern due to its excessive use in agriculture. Studies have shown traces of glyphosate found in drinking water. Meanwhile, it's rapid binding on soil particles possesses adverse effect to soil organisms. Glyphosate degradation in soil usually carried out by microbial activity. Microbes' capable utilising glyphosate mainly as phosphate source. However, the activity of C-P lyase in breaking down glyphosate have not clearly understood. This review presents a collective summary on the understanding on how glyphosate works and its environmental fate.

Keywords: Bioremediation, Glyphosate, GP-metabolism, Herbicides.

Introduction

Glyphosate (N-(phosphonomethyl)glycine) is a globally used herbicide due to its ability to control a wide range of weeds. It is known as the only herbicide that targets 5-enolpyruvyl-shikimate-3-phosphate synthase (EPSPS), thus cannot be competed by other herbicide analogs (Duke & Powles, 2008). This organophosphate inhibits the EPSPS, which can only be found in plants and fungi, but not in animals (Funke, Han, Healy-Fried, Fischer, & Schönbrunn, 2006). By inhibiting the EPSPS, the production of aromatic amino acids, hormones, metabolites are interrupted, which eventually kills the plant. Additionally, the excessive use of glyphosate has led to an adverse effect in agricultural. The accumulation of a large amount of glyphosates in the environment possesses a significant environmental concern (Borggaard & Gimsing, 2008).

For instance, in Brazil alone, the increase in glyphosate herbicides was raised up to 95% from 2000 to 2004 in actively increasing agricultural land. Meanwhile in southern Brazil, 4562 tonnes of glyphosate were used to control weeds in soybean and corn culture between 2000 and 2001 (Inoue et al., 2003). The increase in glyphosate displayed a correlation with environmental pollution. A high level of glyphosate concentration was detected in soil sample from agricultural land in southern Brazil (Inoue et al., 2003). Meanwhile, the residue of glyphosate was also detected in small catchment (25 km^2) in Switzerland due to agriculture and urban use of glyphosate (Hanke, Wittmer, Bischofberger, Stamm, &

Singer, 2010). Extensive use of these pesticides has brought a great concern among scientific communities (Jorgenson, 2001). The increasing amount of land cultivated for agriculture demonstrates a parallel increase in the use of glyphosate-based herbicides as a low-cost method to kill weeds. On top of that, the increasing awareness in other countries such as Sri Lanka, Netherlands and Mexico on banning this product have not been seen in another countries although there are countless journals published worldwide linking glyphosate to various health problems such as acute tubular necrosis among humans (Jayasumana, Gunatilake, & Senanayake, 2014; Kristoffersen et al., 2008).

Most of glyphosate formulated herbicides are supplied as the isopropylamine salt in combination with various surfactants including the polyethoxylated amine non-ionic surfactant. This adjuvant allows the herbicides to stay longer on the plant leaves. It is also noted that, the toxicity rising from glyphosate products caused by surfactant is incorporated into the formulation rather than the organophosphate itself (Ratcliff, Busse, & Shestak, 2006). When glyphosate is formulated as in Roundup®, Accord® or Vision®, it becomes slightly more toxic to animal species due to the presence of added surfactants. Besides isopropylamine salt, there are other glyphosate salts commonly found such as mono ammonium, sodium and trimesium salts. Some glyphosates may take up to five months to be naturally degraded, allowing them to contaminate the ground water and directly affects natural soil organisms and aquatic animals (Moneke, Okpala, & Anyanwu, 2010).

Nonetheless, there are several treatment processes available for removing herbicides such as physical, biological and chemical processes. However, these processes are expensive and not feasible at low concentration of toxicants. As an alternative, biological treatment known as bioremediation is proposed as it is cost-effective and safe for the environment (Sviridov et al., 2012; Arif, Ahmad, Syed, & Shukor, 2013).

In this paper, we review the glyphosate composition and its properties; mode of action, factors affecting its translocation in plants; degradation and persistence in soil and microbial degradation. This review was undertaken to produce a comprehensive detail on studies done in biodegradation and the metabolic pathway involved in glyphosate degradation. The studies evaluated in this review included those performed for regulatory purposes as well as previously published research reports.

History

Glyphosate is a phosphonomethyl derivative for the amino acid glycine (Nandula, 2010). It is a white and odourless crystalline solid comprising one basic amino group and three ionisable acidic sites. The glyphosate was first discovered in 1950 by a Swiss chemist named Henri Martin at the pharmaceutical company called Cilag (Franz, Mao, & Sikorski, 1997). At the early stage, this chemical has no pharmaceutical application until in the seventies when glyphosate was discovered to have an herbicidal activity.

The discovery of Glyphosate begins when a company known as Cilag was bought by Johnson & Johnson in 1959, which later sold Cilag's research samples including the organophosphate to Aldrich Chemical (Nandula, 2010). Aldrich then sold a small amount of the research samples to several companies in the 1960s for unrevealed purposes; however, no claims of biological finding were reported. In its Inorganic Division, Monsanto has developed the compounds as possible water-softening agents with over 100 related aminomethylphosphonic acid (AMPA) analogs were synthesised using glyphosate (Nandula, 2010).

These compounds were tested as herbicides by Dr. Phil Hamm with two of them demonstrating some herbicidal activity on weeds (Halter, 2007). In May 1970, Monsanto began to sysnthesise glyphosate and ran several test in the greenhouse later that year. The compound advanced through the greenhouse screens and field testing system swiftly and was first introduced as Roundup® herbicides by Monsanto Company in 1971.

Currently, over 130 countries are labelled for glyphosate use with a global volume projected to be approximately 600 kilotons annually (Nandula, 2010). The Monsanto Agriculture Herbicides has listed

over 100 annual broad-leaves and grass species controlled. In addition, over 60 perennial weed species are also incorporated. Based on the approved pesticide listing, there are more than 200 herbicide products formulated using glyphosate. These products can be classified into two main categories, which are organochlorine or organophosphate (Leong, Tan, & Mustafa, 2007).

Properties of Glyphosate

In its pure physical form, glyphosate is a white crystalline powder. Table 1 shows the properties of glyphosate. Even though glyphosate is highly soluble in water, it is almost insoluble in organic solvents (Roberts et al., 1998). Glyphosate is also known as organophosphate herbicide due to the carbon-phosphorus bonds (Franz et al., 1997). Considering its low vapour pressure, this compound is stable at room temperature, thus all its derivative salts are non-volatile. Therefore, it cannot be photochemically degraded in air. Glyphosate is stable to hydrolysis at pH 3, 6 and 9 with the temperatures ranging from 5°C to 35°C.

Table 1: Glyphosate Properties (IPCS 2010).

Property	Value
Chemical Formula	$C_3H_8NO_5P$
IUPAC name	2-(phosphonomethylamino)acetic acid
Molar mass	169.07 g/mol
Melting Point	184.5°C
Boiling Point	187°C
Solubility	1.2 g/100 mL @ 25°C
Vapour Pressure	9.8X10-8 mm Hg /1.31X10-2 mPa/ at 25°C

The structure of glyphosate (Figure 1) is made from three functional groups known as carboxyl, amino and phosphonate where the molecules are held together by a network of hydrogen bonds (Nandula, 2010).

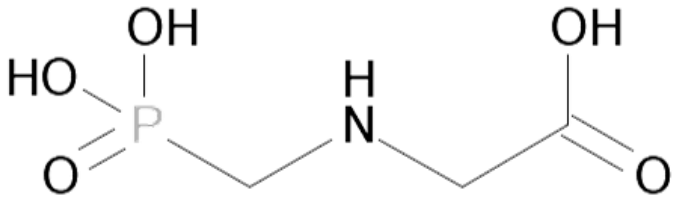

Figure 1: Structure of Glyphosate Molecule (Nandula, 2010).

Mode of Action

The uniqueness of glyphosate made it the only herbicide that targets 5-enolpyruvyl-shikimate-3-phosphate synthase (EPSPS). Hence, there are no rival herbicide analogues or classes for this herbicide (Duke & Powles, 2008).

The transfer of enolpyruvyl moiety of phosphoenolpyruvate (PEP) to 5-hydroxyl of shikimate-3-phosphate (S3P) is catalysed by this EPSPS synthase through shikimate pathway located in the chloroplast region (Figure 2) (Della-Cioppa et al., 1986). This metabolic sequence converts the primary metabolites PEP and erythrose-4-P to chorismate. Chorismate is known as the precursor of aromatic amino acids such as tyrosine, phenylalanine and tryptophan, which function as the building blocks of protein (Gibson, 1964). Besides, it also serves as a crucial precursor in producing auxins and salicylate (Tzin & Galili, 2010). According to Herrmann (1995), in higher plants (tracheophyte), aromatic amino acids also governs the secondary metabolites such as flavonoids, phytoalexins, indole acetate, and lignin, which are essential for the plant growth. By inhibiting ESPSP, the plants can no longer synthesise all these essential amino acids and secondary metabolites, which led to death.

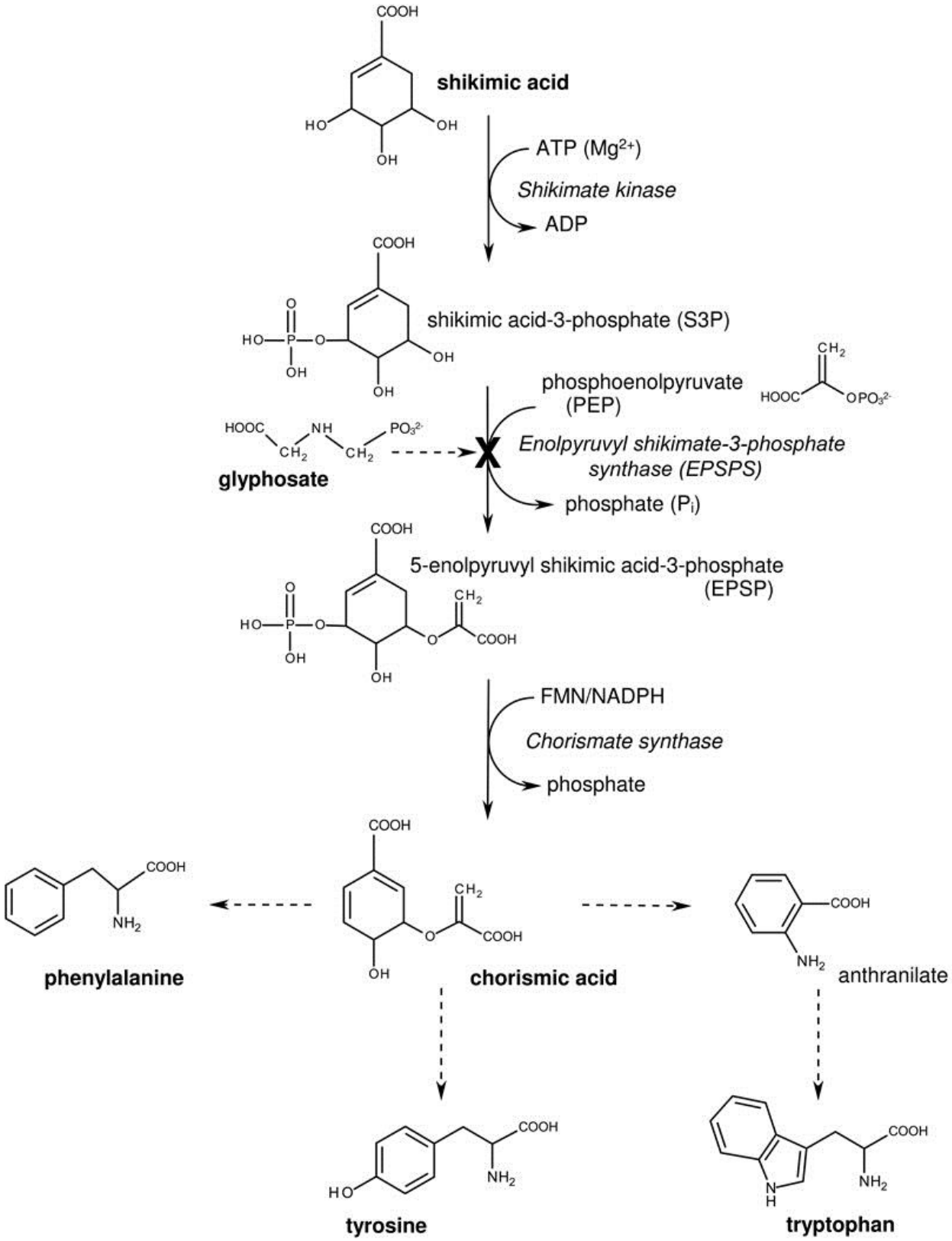

Figure 2: The shikimate pathway that leads to the formation of aromatic amino acids and the inhibition of EPSPS by glyphosate (Pollegioni et al., 2011).

Uptake and translocation

According to Franz et al. (1997), Glyphosate is a systemic, non-selective herbicide used to control annual and perennial weeds. The success of glyphosate effectiveness relies on its ability to penetrate the plant. Moreover, the herbicide is able to be translocated throughout the plant within four-hour application via phloem (Sprankle et al., 1975). Thus, it is worth stating that glyphosate can be rapidly absorbed through the plant surface. However, the uptake rate varies considerably between species depending on morphological differences such as the size of leaf, age of plant, waviness of leaf surface, location of growth and root depth. Furthermore, environmental factors such as sunlight intensity, temperature, wind speed, and humidity are also said to significantly affect chemical intake and translocation (Coupland & Caseley, 1979).

It was reported that increased temperature and solar intensity facilitates glyphosate uptake in plants, while a windy environment decreases glyphosate uptake by causing drift (Coupland & Caseley, 1979; Sharma & Singh, 2001). Using the vascular system of the plant, glyphosate is able to reach the meristems, roots and leaves. Once the glyphosate enters the soils, it tightly binds to the soil particles, preventing them from being absorbed into the plant root. Therefore, it is safe to say that glyphosate is not an effective pre-emergence herbicide (Sprankle et al., 1975). However, rapid translocation from the foliage to the roots, apical meristems and rhizomes still make glyphosate a better weed killer compared to paraquat herbicide (Sprankle et al., 1975).

The waxier the leaf surface, the more difficult for glyphosate to penetrate. However, with the help from surfactant, the effectiveness of glyphosate penetration into the plant can be further increased. Glyphosate herbicides often contain other chemical substances; for instance, surfactants, which significantly improves the solubility and effectiveness of glyphosate. This surfactant acts as an herbicides sticker that allows the herbicides to stay in the waxy surface of the plants. In addition, it assists the herbicides stay longer on plants with wet condition including as rain (Molin & Hirase, 2005).

Degradation and Persistence in Soil

Although glyphosate is water soluble, it can readily bind to soil particles (Rueppel, Brightwell, Schaefer, & Marvel, 1977; Sprankle et al., 1975). It is noted that the adsorption of glyphosate to the soil particles can be increased with cation exchange capacity, composition of clay and decrease in pH content of the soil (Nomura & Hilton, 1977; Rueppel et al., 1977; Sprankle et al., 1975). Moreover, it binds to soil particles via phosphoric acid moiety, hence competing with other inorganic phosphates for sorption site. Therefore, sorption with soil particle is reliant upon the availability of unoccupied binding sites (Hance, 1976). Glyphosate sorption in organic matter containing cations is defined by $Na^{+}=Mg^{2+}<Zn^{2+}<Ca^{2+}=Mn^{2+}=Fe^{3+}=Al^{3+}$, whereas the cation sorption in clay is represented as $Ca^{2}<Mn^{2+}<Zn^{2+}< Mg^{2+}<Fe^{3+}<Al^{3+}$ (Hui, Sheng, Johnston, & Boyd, 2003; Sharma & Singh, 2001). The high affinity of glyphosat e binding with aluminium oxides and iron oxides has been reported by Sprankle et al. (1975). It is observed that soil containing low inorganic phosphate, high iron or aluminium concentration and a decrease in pH level promotes a strong binding of glyphosate (Sprankle at al., 1975).

The primary route for glyphosate degradation in soil is usually achieved by microorganisms (Sprankle et al., 1975; Rueppel et al., 1977; Franz et al., 1997). Photodegradation, oxidation (with chlorine, permanganate, air or ozone), and chemical degradation have been tested; however, they did not appear to be the major pathways for degradating glyphosate (Rueppel et al., 1977). **The** degradation of glyphosate using chemical is exceptionally slow due to the presence of a strong carbon-phosphate bond that is highly resistant to chemical breakdown (Gimsing, Borggaard, & Sestoft, 2004).

Toxicity of polyethoxylated tallow amine

The major formulation in Roundup comes with an isopropylamine (IPA) salts and a surfactant known as polyethoxylated tallow amine (POEA) to enhance the efficacy of the herbicides. POEA is generally used as a wetting agent and emulsifier for agrochemical formulation. Mesnage et al. (2013) found that POE-15 possessed the greatest effect in a human cell (embryonic, placental and hepatic) toxicity resulted from ethoxylated surfactants of glyphosate-based products. Furthermore, all formulations derived from surfactant were found more toxic than the glyphosate itself. These findings were supported

by results as it was found that Roundup is 125 times more toxic to human cells than glyphosate itself (Mesnage et al., 2014.) Meanwhile, POEA alters three different cell types of human cell permeability (embryonic, umbilical, and placental) and further amplifies glyphosate toxicity through apoptosis and necrosis (Benachour & Séralini, 2009). The adverse effect of surfactants depends on the final concentration reached in the aquatic water.

Effects on non-target aquatic plants and algae

Herbicides are mainly used to kill and destroy unwanted terrestrial weeds. However, the tendency of roundup formulation to be washed away during raining seasons has ended up in an aquatic medium. Aquatic plants and algae are consequently the most sensitive group of aquatic non-target organisms. Aquatic plants and algae play an important role in aquatic ecosystems. These plants aid in stabilising the sediments in lakes and running waters from breaking down. Furthermore, the presence of aquatic plants and algae affects the sedimentation flow rates, nutrient uptake and recirculation. In addition, insects, crustaceans and fish take refuges provided by the plants. Meanwhile, algae provide foods and play important role in food-webs in the aquatic environment and therefore fundamental to the functioning of aquatic ecosystems (Wetzel, 2001).

Table 2 shows the effects of glyphosate, different commercial formulations of glyphosate and POEA on algae and aquatic plants. Microalgae have been found to present EC_{50} values for glyphosate treatment ranging from 0.68 mg/L in the *Skeletonema costatum* (Ware, 2000) to around 600 mg/L in the green algae *Chlorella pyrenoidosa* (Maule & Wright, 1984). Meanwhile, additional work done by other researcher showed that 10% of reduction (EC_{10}) could be achieved from between 3 to 16 folds lower concentrations compared to EC_{50}. This can be seen in 10% growth inhibitions in green algae *Scenedesmus subpicatus* observed when 1.6 mg/L of glyphosate was introduced (Vendrell, Ferraz, Sabater, & Carrasco, 2009). Furthermore, 10% growth inhibition was observed in *Chlorella sorokiniana* at the concentration of 2 mg/L glyphosate. In general, commercial glyphosate formulation is toxic than the glyphosate itself.

In green algae, *Selenastrum capricornutum,* the lethal dose was found seven times higher in Roundup formula than the glyphosate's IPA salt (Tsui & Chu, 2003). Cedergreen & Streibig (2005) reported four folds higher toxicity of Roundup formulation then glyphosate in *Selenastrum capricornutum.* Most of the toxicities were contributed by POEA itself with values ranging from 45% for *Skeletonema costatum* to 85% for *Selenastrum capricornutum* (Tsui & Chu, 2003). Phosphorus is an essential element for the growth of phytoplankton and plays a critical role in controlling its biomass and composition in freshwater systems (Dyhrman, Ammerman, & van, 2007; Paerl, 2008). Three algae species, which are *Microcystis aeruginosa*, *Chlorella pyrenoidosa* and *Pseudokirchneriella subcapitata* were identified able to utilise dissolved organic P (DOP) in glyphosate to sustain their growth (Ren et al., 2017).

Schaffer & Sebetich, (2004) reported 161% increment in net primary production for phytoplankton community treated with 0.13 mg/L Rodeo formulation (without POEA). However, Goldsborough & Brown, (1988) reported a 50% reduction in periphyton primary production when supplemented with 35.4 to 69.7 mg a.i./L of Roundup® (with POEA). Both studies showed that the presence of POEA has significantly reduced the ability of phytoplankton to utilise glyphosate. The propagation of harmful algal blooms caused by algae and cyanobacteria is further assists by the contamination of glyphosate in an aquatic medium. Dyhrman et al. (2007) reported that *Trichodesmium erythraeum* IMS101, a marine harmful cyanobacteria, has a gene responsible for phosphonate utilisation, which proliferates well in glyphosate-contaminated water.

Table 2: Effects of glyphosate, different commercial formulations of glyphosate and POEA on algae and aquatic plants

Aquatic algae and plants	Assessed chemical	Effects concentration	References
Phytoplankton and periphyton			
Chlorococcumhypnosporum	Glyphosate	96h EC_{50} = 68.0	Maule & Wright., (1984)
Chlorella pyrenoidosa	Glyphosate	96h EC_{50} = 590.0	Maule & Wright., (1984)
Skeletonema costatum	Glyphosate	EC_{50} = 0.64 NOEC = 0.28	Ware., (2000)
Periphyton community	Roundup	4h EC_{50} = (between 35.4 to 69.7)	Goldsborough & Brown., (1988)
Scenedesmus acutus	Glyphosate	96h EC_{50} =10.2; NOEC = 2.0	Gardner et al., (1997)
	Ron-do	96h EC_{50} = 9; NOEC = 3.2	
Ankistrodesmus sp.	Rodeo	96h EC_{50} = 74.0	Gardner et al., (1997)
Phytoplankton community	Rodeo	0.13 mg/L elicited NPP increment	Schaffer & Sebetich., (2004)
Selenastrum capricornutum	Glyphosate	96h EC_{50} =41.0	Tsui & Chu., (2003)
	Roundup	96h EC_{50} =5.81	
	POEA	96h EC_{50} =3.91	
Skeletonema costatum	Glyphosate	96h EC_{50} =5.89	Tsui & Chu., (2003)
	Roundup	96h EC_{50} =1.85	
	POEA	96h EC_{50} =3.35	
Selenastrum capricornutum	Glyphosate	48h EC_{10} = 95.5; 48h EC_{50} = 270.0	Cedergreen & Streibig., (2005)
	Roundup	48h EC_{10} = 13.6; 48h EC_{50} = 64.7	
Scenedesmus subspicatus	Glyphosate	72h EC_{10} = 3.0; 72h EC_{50} = 46.6 72h EC_{10} = 1.6; 72h EC_{50} = 26.0	Vendrell et al., (2009)
(Periphyton community)	Roundup	8 mg/L elicited changes in community structure	Vera et al., (2010)
Macrophytes			
Myriophyllum sibiricum	Glyphosate	14d IC_{10} = 0.59; 14d IC_{50} = 0.84	Roshon et al., (1999)
	Roundup	14d IC_{50} = 1.22	
Lemma minor	Glyphosate	7d EC_{10} =3.8; 7d EC_{50} = 46.9	Cedergreen & Streibig, (2005)
	Roundup	7d EC_{10} =3.5; 7d EC_{50} = 11.2	
Myriophyllum spicatum	Roundup	21d IC_{50} = 1.0 (for weight) 21d IC_{50} = 2.8 (for length)	Sánchez et al., (2007)
Lemma gibba	Glyphosate	10d IC_{10} =4.6; 10d IC_{50} = 20.5	Sobrero et al., (2007)
	Roundup	10d IC_{10} =2.5; 10d IC_{50} = 11.6	

Effects on non-target aquatic vertebrates

Aquatic fish and amphibians appeared to have low sensibility towards glyphosate itself. The lethal dose LC_{50} was observed in channel catfish *Ictalurus punctatus* (Folmar, Sanders, & Julin, 1979) ranging from 130 mg/L to 620 mg/L for carp *Cyprinus carpio* (Nešković, Poleksić, Elezović, Karan, & Budimir, 1996) in glyphosate treated water. Exposure to glyphosate on amphibians has resulted in develop abnormalities. A high percentage of morphology alterations was observed in sharp-snouted tree frog (*Ssinax nassicus*) when incubated with 3 to 7 mg/L of glyphosate, which was the exact amount used in the sub-agricultural field. The effect of dose and time dependent external morphological malformations absorbed in tadpoles includes eye and cranial abnormalities and mouth deformities (Sviridov et al., 2014). Meanwhile, when glyphosate is treated as IPA salt, LC_{50} had increased to 340 mg/L in Australian frogs.

However, when glyphosate is treated as acid, lower values ranging from 82 to 121 mg/L were obtained (Mann & Bidwell, 1999). Wide differences were observed in the toxicity of glyphosate itself and commercial formulation in fish. In nile tilapias juvenile (*Oreoachromis niloticus*), the LC_{50} was observed to be 1.05 mg/L for 96 h when glyphosate is introduced (Ayoola, 2008). Acute deformity was observed in filament cell proliferation, lamellar fusion and epithelial lifting in livers. Several physiological abnormal behaviours such as relentless jumping and gulping of air, surface to bottom movement, passively resting at the bottom were found similar to the observation. The liver of fish exposed to glyphosate showed an infiltration of leukocytes, increasing hepatocyte size with pykrotic nuclei and presence of vacuoles.

Similar pattern was reported in rainbow trout *Oncorhynchus mykiss* when treated with Vision formula (Morgan & Kiceniuk, 1992). However, a lower concentration of Roundup formula has shown changes in biometry, metabolism and adverse effect on the enzyme activities of the fish. Crestani et al. (2007) reported that a significant decrease in ACh enzyme activity and TBARS levels (a measure of oxidative stress) in the brain of *Rhamdia quelen* when exposed to very low concentration of 0.2 mg/L glyphosate. Furthermore, a significant reduction in the biometry (weight and length) of Piava *Leporinus obtusidens* was observed when treated with 1 mg/L of glyphosate. Meanwhile, a reduction in 15% of length and weight was observed on both fish.

Photodegradation

Initially, it has been reported that degradation of glyphosate was unaffected by sunlight (Rueppel et al., 1977). However, later study found that the organophosphate is susceptible to photodegradation (Carlisle & Trevors, 1988; Kare & Hakon, 1986). It was noticed that long wavelength light does not have any photodegradation effect on glyphosate; meanwhile, UV-light has a strong influence in this respect (Kare & Hakon, 1986). Therefore, glyphosate was stated to be degraded faster in clean water than in polluted water. Glyphosate in deionised water under UV light poseses a half-life of four days (Chen et al., 2007).

Glyphosate Metabolism

The mechanism of glyphosate interaction with the environment has been widely studied. Environmental removal of this organophosphate is usually slow due to the rapid binding with the soil particle (Malik, Barry, & Kishore, 1989). Usually, the removal of glyphosate in the environment is done by microbial degradation since the chemical process involved in degradation is less effective due to highly stable carbon-phosphorus bond (Franz et al., 1997). The utilisation of glyphosate by soil microbes can occur in both aerobic and anaerobic conditions; however, aerobic condition generally favour higher degradation rates (Kah et al., 2007). Microorganism are able to utilise glyphosate as carbon or phosphorus source (Sprankle, Meggitt, & Penner, 1975). It is notable that glyphosate undergoes rapid detoxication in soil due to the rapid binding with soil particles and microbial degradation (Malik et al., 1989). The enzyme involved in initial step of degradation is oxidoreductase, a flavoprotein capable of metabolising under both aerobic and anaerobic conditions (Kishore & Jacob, 1987).

Utilisation of glyphosate leads to the production of aminomethylphosphonic acid (AMPA), and glycine when utilised as the phosphorus source (Rueppel et al., 1977; Sprankle et al., 1975). The most common pathway used in microbial degradation involves AMPA as the primary degradation product (Rueppel

et al., 1977). Meanwhile, the secondary pathway involves sarcosine and glycine (Kishore & Jacob, 1987). The AMPA pathway starts with cleaving off carbon-nitrogen bonds to produce AMPA and glyoxylate. From there, then carbon-phosphate bond is broken down by C-P lyases, producing inorganic phosphate and methylamine. Meanwhile, in sarcosine pathway, the C-P bond is cleaved by CP-lyases, which produces phosphate and sarcosine (Kishore & Jacob, 1987). Both pathways end with the production of CO_2 and NH_4^+ (Dick & Quinn, 1995). Some studies have shown that glyphosate is initially degraded to AMPA and glyoxylate, which is then processed via the glyoxylate cycle in TCA pathway (McAuliffe, Hallas, & Kulpa, 1990). Since glyphosate degradation is co-metabolic in favourable condition, glyphosate is utilised as a source of phosphorus rather than carbon (Dick & Quinn, 1995; Franz et al., 1997).

The *phn* gene involved in phosphonates degradation is controlled by Pho regulon in which its expression is regulated by exogenous phosphate and its activity is best studied in *Escherichia coli*. Therefore, when the C-P lyases enzymatic activity has induced phosphate starvation, microbes may use phosphonates as an alternative source of phosphorus (Kishore & Jacob, 1987). This is in accordance with a study done by Dick & Quinn (1995), where glyphosate is utilised as a phosphorus source rather than carbon or nitrogen source (Fitzgibbon & Braymer, 1988; Wackett, L. P., Shames, Venditti, & Walsh, 1987). This allows the phosphate to negatively affect glyphosate degradation. Nevertheless, microorganisms capable of utilising glyphosate as carbon or nitrogen source have been isolated even in the presence of phosphate source (Schnurer et al., 2006). The cleaving of the C-P bond by C-P lyases can occur even when phosphate is presence (Krzyśko-Łupicka & Orlik, 1997).

The C-P lyases enzyme is responsible for C-P bond cleavage and phosphonate uptake by the cells. Prior studies have implied that C-P lyases are nonspecific and could breakdown a whole range of alkyl and aminoalkyl phosphonates, including organophosphate and are responsible for the production of carbon residue (White & Metcalf, 2004). However, it was noticed that C-P lyases involved in the cleavage of (amino) alkylphosphates from *E. coli* differ from C-P lyases that cleaves C-P bond of glyphosate in glyphosate degrading bacteria, suggesting that the function of both systems is independent. This hypothesis is later proven in *Arthrobacter* sp. GLP (Kertesz, Elgorriaga, & Amrhein, 1991) and *Achromobacter* sp. MPS 12A (Sviridov et al., 2012) where both strains have specific C-P lyases involved in the cleaving of glyphosate's C-P bond, which differs with C-P lyases found in *E. coli*. Apparently, glyphosate degrading bacteria consists of more than two species of C-P lyases.

The mechanism of microbial glyphosate degradation is yet to be understood. Moreover, the origin of enzyme complex responsible for the cleavage of C-P bond in glyphosate remains unclear. The ability to utilise glyphosate was detected in bacteria that are never been previously exposed to organophosphate. On the other hand, *Pseudomonas stutzeri* contains two different C-P lyases operons with different substrate specificities, but neither have the ability to breakdown glyphosate (White & Metcalf, 2004). This suggests that there are possible natural glyphosate analogs that could serve as a substrate for specific C-P lyases (Sviridov et al., 2015). Figure 3 shows the metabolic and degradation pathway of glyphosate by a soil microorganism.

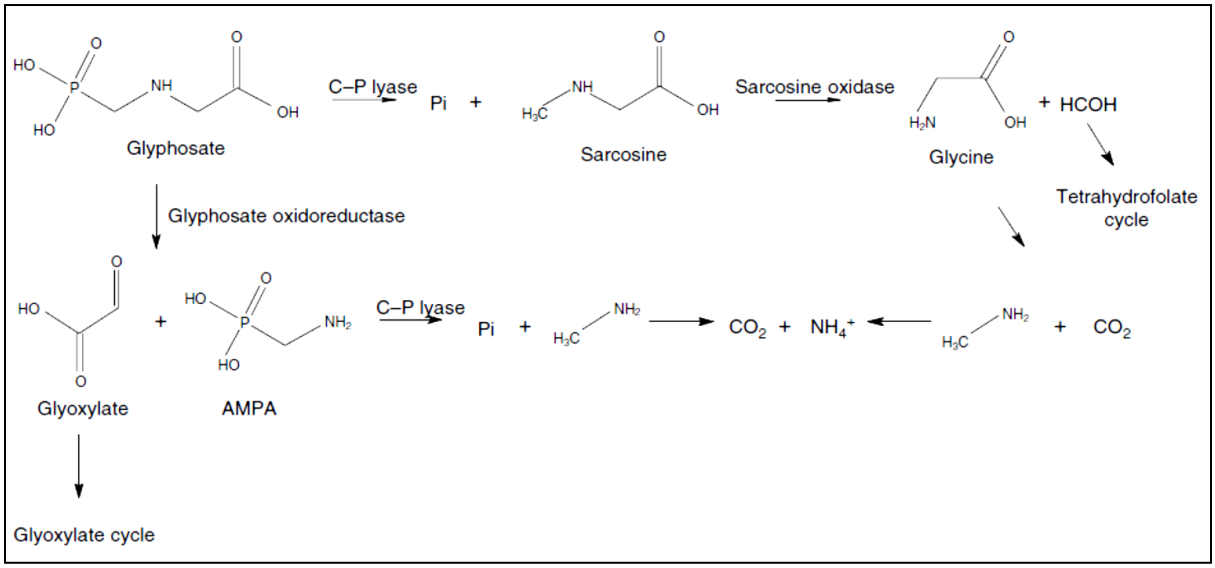

Figure 3: Glyphosate Metabolic Pathways (Borggaard and Gimsing 2008).

Microbial Degradation

Several studies were initiated to obtain bacterial strains with degrading ability to be used in biological treatment (Bazot & Lebeau, 2008). The initial discovery of isolates utilising glyphosate as a source of phosphate is *Pseudomonas* sp. PG2982 where it metabolises glyphosate into sarcosine by clevaging the C-P bond instead of metabolising i into AMPA. Significant discovery has been also made in *Arthrobacter* sp. GLP-1 (Pipke & Amrhein, 1988), *Alcaligenes* sp. GL (Lerbs, Stock, & Parthier, 1990), *Pseudomonas* sp. 4ASW (Dick & Quinn, 1995), *Agrobacterium radiobacter* (McAuliffe et al., 1990), and *Achromobacter* sp. MPS 12A (Sviridov et al., 2012) which utilising the same mechanism as *Pseudomonas* sp. OH 2982. Meanwhile, *Flavobacterium* sp. GD1 (Balthazor & Hallas 1986), *Pseudomonas* sp. LBr (Jacob et al, 1988), *Achromobacter* sp. LW9 (McAuliffe et al., 1990), *Ochrobactrum anthropi* LBAA (Kishore & Barry 1992), *Ochrobactrum anthropi* GPK3 (Sviridov et al., 2012), and *Ochrobactrum* sp. GDOS (Hadi, Mousavi, Noghabi, Tabar, & Salmanian, 2013) were found to degrade glyphosate via AMPA and utilise it as the phosphate source.

However, the ability of microbes to utilise glyphosate beyond inorganic phosphate are extremely rare. Nevertheless, *Arthrobacter* sp. GLP/Nit mutant strain was observed to utilise glyphosate as its nitrogen source (Pipke & Amrhein, 1988). On the other hand, *Achromobacter* sp. LW9 (McAuliffe et al., 1990) was known to utilise glyphosate as a source of carbon and nitrogen. In general, the most widespread pathway of glyphosate metabolism is its conversion to AMPA as this is a common trait among laboratory and wild-type isolated strains (Dick & Quinn, 1995; Rueppel et al., 1977). Besides, strains that are able to convert AMPA into inorganic phosphate are more abundant than those capable utilising it as a carbon or nitrogen source (Dick & Quinn, 1995).

According to Dick & Quinn (1995), bacteria isolated from previously glyphosate-exposed soil showed greater resistance compared to isolates from non-treated sites. Laboratory isolated strains demonstrated higher tolerance to glyphosate compared to wild types. Tolerance towards glyphosate varies from strains to strains. For example, *Alcaligenes* sp. GL was discovered to be able to utilise glyphosate up to 100 mM without any noticeable alteration to the growth rate (Lerbs et al., 1990). Furthermore, *Pseudomonas* sp. GLC 11 (Selvapandiyan & Bhatnagar, 1994) and *Ochrobactrum* sp. GDOS (Hadi et al., 2013) have displayed the ability to tolerate of 120 mM of glyphosate. These bacteria use glyphosate as a source of inorganic phosphate. Table 3 shows list of bacteria capable utilising glyphosate via AMPA or sarcosine pathway.

Table 3: List of known glyphosate degrading bacteria.

Bacteria	Source	Metabolic pathway	Gram status	Reference
Achromobacter sp. MPS 12A	Soil culture	Sarcosine	-	Sviridov et al., (2012)
Achromobacter sp. LW9	Activated sludge of glyphosate process waste stream	AMPA	-	McAuliffe et al., (1990)
Agrobacterium radiobacter	Activated mixed sludge	Sarcosine	-	McAuliffe et al., (1990)
A*rthrobacter atrocyaneus* ATCC 13752a	German collection of microorganisms and cell cultures	AMPA	+	Pipke & Amrhein, (1988)
Flavobacterium sp. GD1	Activated sludge of GP process waste stream	AMPA	-	Balthazor & Hallas, (1986)
Pseudomonas sp. 4ASW	Glyphosate contaminated soil	Sarcosine	-	Dick & Quinn, (1995)
Pseudomonas sp. LBr	Activated sludge of GP process waste stream	AMPA (95%), Sarcosine (5%)	-	Jacob et al., (1988)
Rhizobium meliloti 1021	Spontaneous streptomycin-resistant mutant of wild type	Sarcosine		Liu et al., (1991)
Stenotrophomonas maltophilia	Oil palm plantation soil	AMPA	-	Nourouzi et al., (2011)
Ochrobactrum anthropi GDOS	Glyphosate contaminated soil	AMPA		Hadi et al.,(2013)

Conclusion

As a conclusion, problems on glyphosate are very complex and versatile. It was named as "once-in-a-century herbicide" for its effectiveness in weed control and its impact on the rise of transgenic crops. However, it was found that the excessive use of glyphosate has become as environmental hazard by the scientific communities. Increased awareness on the profound effects of environmental problems such as traces of glyphosate in drinking waters and accepts of herbicide usage has encouraged necessary investigations to avoid, reduce or eliminate these problems. To solve this problem, microbial degradation was proposed as a better alternative than chemical degradation due to the presence of strong C-P bond. Degradation of organophosphate in soils is mainly done by microorganism. Microbial degradation mostly involves AMPA pathway rather than sarcosine pathway. However, the rate of utilisation can be affected by factors such as the availability of phosphate source, composition of clay and the physical environmental factor.

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