APPENDIX B
PHYSICAL AND CHEMICAL PROPERTIES

1) Molecular characteristics of glyphosate and its relevance to its mode of herbicide action and its sorption behavior on soils and sediments

The chemical structure of glyphosate is presented in Figure 1.

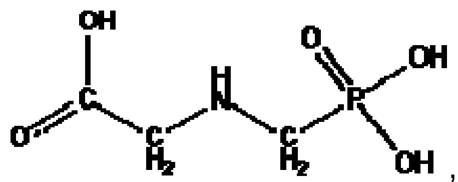

Figure 1. Chemical Structure of Glyphosate

The molecule of glyphosate can be envisioned as a polydentate and/or monodentate ligand that binds to "substrates" via the oxygen atoms. These molecular characteristics of glyphosate have major implications in its mode of herbicide action[1] and in the sorption behavior of glyphosate on soils/sediments.

Glyphosate is a zwitterion, illustrated in Figure 2. Glyphosate has four dissociation constants (pK_a), Table 1.

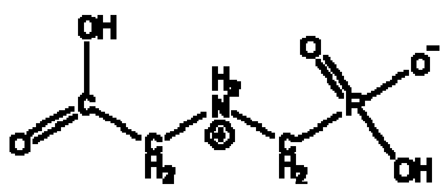

Figure 2 Glyphosate zwitterion from dissociation of the first phosphonic proton

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[1] Mode of Action of Glyphosate

Glyphosate is a non-selective, systemic herbicide. It is a potent and specific inhibitor of the enzyme 5-enolpyruvyl 3-phospate synthase. This enzyme is the six enzyme on the shikimate pathway, which is essential for the biosynthesis of aromatic amino acids and other aromatic compounds in algae, higher plants, bacteria, fungi, and apicomplexian parasites, but the shikimate pathway is absent in mammals. Although the structural and chemical changes of the interaction of glyphosate and ESPS synthase are complex, glyphosate appears to occupy the binding site of the phosphenol pyruvate substrate of the ESPS synthase without perturbing the structure of the active site cavity and may be explained by the structural characteristics and dissociation (pK_a) of glyphosate and its behavior as a monodentate and/or polydentate ligand. References 5-7

Table A-1 Acid Dissociation Constants of Glyphosate

Acid Dissociation Constants of Glyphosate	Value of Dissociation Constant of Glyphosate	Dissociated Proton in Glyphosate
pK_{a1}	0.8	First phosphonic
pK_{a2}	2.3	Carboxylate
pK_{a3}	6.0	Second phosphonic
pK_{a4}	11.0	Amine

In the environmentally significant pH range of 5 to 9, the first phosphonic and carboxylate protons are fully dissociated. The dissociation of the second phosphonic proton increases above pH 6, but the amine proton is unlikely to dissociate in the environment.

Conclusions

The pH-dependent dissociation of glyphosate determines the speciation of glyphosate in aquatic systems. However, the estimation of environmental exposure concentration in water does not take into account the dissociation of glyphosate in water. The effect toxicity of each dissociated form of glyphosate is not known.

2) Colloidal transport

The environmental fate studies conducted on soil and water-sediment systems do not take into account the adsorption of glyphosate onto colloidal-range particulates[2]. The importance of particulate matter in the transport of pollutants and subsequent deposition is recognized[3]. Since glyphosate adsorbs strongly to soil particulates, the higher surface area of colloidal matter may result in higher concentrations of glyphosate when compared to higher particulate sizes. That is, colloidal particulates could behave as "scavengers" of glyphosate. Transport of glyphosate by colloids have the potential for off-site deposition

Conclusions:

Presence of colloidal matter in natural waters can vary with season. Furthermore, the concentration distribution of the chemical through a water body is not likely to be homogenous. Therefore, the estimated environmental concentrations in water could be overestimated or underestimated at specific sites.

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[2] Particulate size in disperse phase range from 5 to 200 nanometers

[3] DeLonge, L.W., Kjaergaard, and Moldrup, P. 2004. Colloids and Colloid-Facilitated Trnsport of Contaminats in Soils: An Introduction. Vadose Zone Jounar, Vol, pp 321-325.

3) Surfactants

The role of a surfactant[4] in a herbicide product is to improve wettablility of the hydrophobic surface of plants for maximum coverage and aid penetration through the plant surface.

A surfactant can be a pesticide inactive ingredient ("inert") in a formulated end-use product, which is classified as Confidential Business Information (CBI). A surfactant is usually added as an adjuvant to a tank mix. This further improves wettability and penetration, thus enhancing the effectiveness of the pesticide.

In glyphosate, both in the formulation (CBI) and the adjuvant are nonionic surfactants. Surfactants are not usually a single chemical of defined composition, but structurally related compounds of varying number of carbons in the hydrophobic tail.
A very important property of surfactants is the formation of micelles , which are ordered assemblages (structured) of disorder surfactant molecules. The concentration at which micelles start forming is known as the Critical Micelle Concentration (CMC). The CMC also depends of the characteristics of the medium, such as pH, temperature, and ionic strength. Each type of surfactants has a different CMC, which also depends on the length and structure of the hydrophobic tail.

Alkyl poly(ethylene) oxide (PEO) is the generic name for some nonionic surfactants, which vary among them in the number of carbons in the alkyl chain and the number of ethylene oxide groups. Although the name and composition of the surfactant in the formulated end-use product is CBI, the labels of glyphosate recommend the use of nonspecific nonionic surfactants in the tank mix.

The surfactant POEA has been associated with glyphosate formulations and/or adjuvant. The name POEA is used for "Polyethoxylated tallow amine". Unlike the nonionic PEO, POEA is a cationic surfactant derived from quaternary amine cations.

The uncertainty in the chemical nature of surfactant in the formulated end-use product makes difficult to ascertain which is more toxic, the surfactant or the glyphosate-surfactant. Furthermore, the role of CMC in the overall behavior of a formulated end-use product in a tank mix with an adjuvant is not known and makes difficult to interpret the effects of different formulations/adjuvant combinations.

Conclusions:
A major uncertainty remains on the nature of the surfactant used in the formulated end-use product and the plausible enhanced effect with the adjuvant.

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[4] "**Surf**ace **act**ing **a**ge**nt".** Surfactants are amphiphilic meaning that they contain both hydrophobic groups (their "tails") and hydrophilic groups (their "heads"). Therefore, they are soluble in both organic solvents and water. Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Surfactants can be cationic, anionic, or nonionic.