

Researchers examine ways to break down, track synthetic compound in herbicides

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From left, University of Delaware researchers Hui Li, Deb Jaisi and Sunendra Joshi explore ways to break down, track synthetic compound in herbicides.

Credit: Wenbo Fan/University of Delaware

To examine the fate and persistence of glyphosate, one of the most common commercial herbicides used for agricultural and urban

applications, and aminomethylphosphonic acid (AMPA), a major byproduct of glyphosate, in soils and other environments, researchers at the University of Delaware have used isotopic signatures as a method of source tracking.

The research involves the use of [manganese oxide](#) minerals to break down glyphosate and to identify released phosphate and other byproducts such as AMPA. The researchers used oxygen isotopes of released phosphate from glyphosate and compared that from other phosphorous compounds present in soils and other environments with an aim to discriminate and track the sources.

The research findings were published recently in the *Journal of Agricultural and Food Chemistry* based on work conducted by Hui Li and Sunendra Joshi, both doctoral students working with Deb Jaisi in the Department of Plant and Soil Sciences in UD's College of Agriculture and Natural Resources (CANR).

Glyphosate is integral to agricultural production but because of its widespread application—the United States Geological Survey (USGS) estimated that 283 million pounds were used in 2012—there have been health-related concerns about the presence of the compound and AMPA in soils, streams and other environments.

Jaisi said the research is looking at the different mechanisms and pathways glyphosate can be degraded in the soil that are catalyzed either by the action of bacteria or minerals. The research team focused on the mineral-catalyzed (abiotic) degradation, and compared the degradation kinetics of glyphosate with AMPA.

"Eventually, we would like to see excess of these compounds after herbicidal action that may end up in soil and other [environment](#) degrade down sooner rather than later to minimize any potential environmental

harm," said Jaisi.

They found that manganese oxide, one of the inherent minerals in soil, is an efficient mineral that could break down glyphosate and AMPA. The research group synthesized manganese oxide in the laboratory and found that the half-life—or the amount of time required for the amount of glyphosate and AMPA to fall to half of its initial value—was around 3 and 48 hours for glyphosate and AMPA, respectively.

With regard to AMPA, Li said it is a major intermediate byproduct of glyphosate—formed after a particular bond in the glyphosate is broken down but before it eventually forms final inorganic products—that accumulates in the natural environment at a much higher rate than glyphosate itself because it degrades much more slowly than glyphosate. Some research indicates that it is more toxic than glyphosate.

"We want to figure out whether the mineral we were using can break down AMPA, as well as glyphosate. If it does break down to AMPA, the second question is can we trace the source of AMPA. This is important because AMPA is also a byproduct of other organic phosphorous compounds. Furthermore, glyphosate degrades through another pathway as well and that pathway does not generate AMPA," said Li.

Jaisi said that because the experiment was entirely laboratory-based, it is too early to say how well the results can be extended to a real environment. A lot would depend on how much manganese oxide resides in the environment and how much it would be able to interact with glyphosate. Another challenge is methodological and involves the separation and purification of the two compounds from environmental samples, which they are going to address next in their research.

"There's a lot of things in between to be resolved in a real environment, but at least we have something in the environment that can break it

down, so that's a good thing," said Jaisi.

Source tracking

With regard to tracking the glyphosate, Li said that the most innovative aspect of the paper was "validating a novel method, oxygen isotope signature of the compound, to trace glyphosate sources in the environment and differentiate phosphate released from glyphosate from other sources of phosphates."

Li added, "A natural extension of this research is to apply this tool in real field samples. So we also want to apply a series of advanced methods to address some very basic questions like what minerals in soils induce the degradation of glyphosate, or is there a way to bias reaction towards a relatively harmless product pathway, or catalyze faster degradation to minimize the potential environmental impact."

Jaisi likened the source tracking to an identifying feature in humans, like a fingerprint or DNA. "Your DNA and my DNA is going to be different. Our expertise is on identification of sources of different phosphorus compounds and tracking them in the environment. For this, we need to know first the original isotope signature of the glyphosate that ends up in the environment," said Jaisi. If it does remain in the environment for a good chunk of time, the method has the potential to identify its sources.

"The second question is, if more than one source of glyphosate ends up in soils, can we discriminate them? There is lot more research to be done in that direction but if we are successful in our objectives, it may allow tracking particular sources as they degrade in soils over time. Existing methodology is the lump sum measurement of the compound, but our ability to differentiate each product by isotope signature brings new insights not only to source identification of a particular product but also to identify accurate half-lives of these products," said Jaisi.

For the study, the researchers used five different commercial herbicide brands from different companies to see if the different products had different fingerprints and are still different from other phosphate sources in the environment.

Joshi said the phosphate released from the breakdown of limited [glyphosate](#) products studied "has a unique isotopic signature than other phosphate in the environment we know so far. If we measure the isotopic signatures of all phosphate types in the natural environment and found one having a peculiar isotopic signature, then we would have reasonable certainty to say, 'This phosphorous is coming from that particular source.'"

Provided by University of Delaware

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