Environmental Fate of a Herbicide: An Industrialist's Perspective

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ABSTRACT

The approach used by an industry scientist to investigate the environmental fate of a herbicide is presented. Laboratory studies on the hydrolysis, microbial degradation, sorption, and volatility of a herbicide are combined to form predictions for leaching and carryover. The role of field studies in testing these predictions is followed by the use of computer models for extending the laboratory and field results to wider agricultural markets. This article is designed as supplemental reading for survey classes in soil chemistry and microbiology, weed science, and pesticide science.

Long before a herbicide can be sold for use on the farm, its fate in the environment must be determined. This involves a variety of experiments in both water and soil, laboratory and field, to establish the rates and pathways of breakdown of that herbicide. These experiments are performed by industry scientists educated in the environmental and soil sciences. The results of each experiment provide a portion of a complex puzzle; like a detective story, the different pieces of evidence are combined to form an overall picture of that herbicide's environmental fate.

The process is a long one, covering 5 or 6 yr of time and the combined efforts of scientists from many disciplines. It begins in the laboratory, where several experiments under controlled conditions provide a first look at the environmental fate of a compound. Once the laboratory studies are completed, the research moves into the field, where initial conclusions are tested under realistic conditions. Finally, results from laboratory and field are combined with the aid of computer modeling to assess environmental fate in a wide variety of soils and climates.

This article describes the entire process of environmental fate research. The emphasis is on fate in soil, and examples were chosen from studies with one herbicide (fluroxypyr), to provide actual data in a consistent manner. Experiments in the laboratory, including hydrolysis, microbial degradation, volatilization, and sorption are highlighted to show how they can be used to build an understanding of environmental fate of a herbicide in soil. These results are placed within the context of the overall effort of developing an effective, environmentally sound herbicide.

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DEVELOPING THE ENVIRONMENTAL FATE PICTURE

Before environmental testing begins, a great deal of information is already known about the proposed use of the herbicide. In our example, fluroxypyr is intended for control of broadleaf weeds in the North American wheat (*Triticum aestivum* L.) market. It will be a postemergence herbicide, meaning that it will be applied after the farmer has diagnosed a weed problem that is severe enough to demand control.

Fluroxypyr is applied in the form of its methylheptyl ester, abbreviated as fluorxypyr-MHE (Fig. 1). This nonpolar ester enters the plant through the waxy cuticular tissues (Klingman and Ashton, 1982), and then is easily hydrolyzed to fluroxypyr, which is mobile in the plant sap and thus acts as the herbicidal agent (Sanders and Pallet, 1987). Even though much of the treatment is adsorbed by the vegetation, a portion of the spray droplets will fall onto the soil. Also, some of the fluroxypyr-MHE on the plant foliage may wash off during a rainstorm and drip onto the ground. Hence, the ester is the form that first contacts the soil, and is thus the form with which to begin environmental testing.

Hydrolysis

The simplest process of breakdown is hydrolysis, or the splitting of a molecule by water. Hydrolysis is studied in bottles of distilled, sterilized water maintained at realistic pH levels such as 5, 7, and 9. The results are somewhat artificial since sterile water does not actually occur in the environment, but this experiment does provide fundamental stability information for the molecule. Fluroxypyr-MHE hydrolyzed under basic conditions, with a half-life (time for loss of 50% of the original ester) of 3 d at pH 9, 450 d at pH 7, and no hydrolysis at pH 5 (Lehmann and Miller, 1989). Yet when a small quantity of soil was added to the water (pH 7), the hydrolysis reaction was thousands of times faster, with a half-life of only hours. Apparently, some unidentified agent on the soil surface, perhaps an extracellular enzyme or a reactive mineral, catalyzed the reaction. As a result of this hydrolysis, fluroxypyr is released into the soil water and is then available for degradation by the soil microbes.

Microbial Degradation

Complete degradation of a herbicide occurs through the action of soil bacteria and fungi. Since these organisms are typically clumped into colonies on the soil surfaces (Coleman, 1985; Richards, 1987), the process probably involves diffusion of the herbicide through the soil water, followed by uptake into the microbial cells. Inside the cells, the compound is oxidized to CO_2 with the possible formation of intermediate metabolites.

Microbial breakdown is studied in microcosms containing moist soil, held at a constant temperature and supplied with oxygen (Fig. 2). About 50 of these microcosms, covering four soils with different properties, may be used in a typical experiment. The soil is "spiked" with ^{14}C-labeled herbicide, and periodically a microcosm is "sacrificed" and the soil extracted and analyzed. A solution of NaOH/water is placed in the sidearm of each flask to absorb any $^{14}CO_2$ released during the experiment.

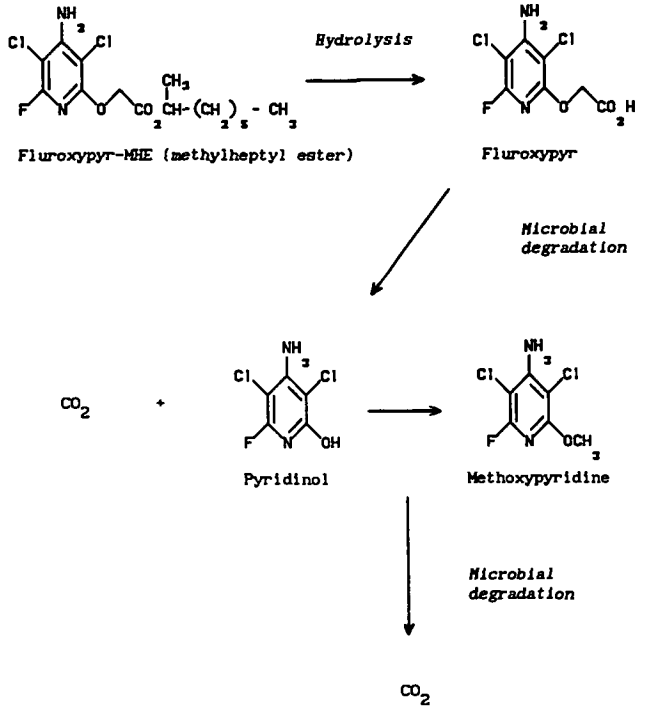

Fig. 1. Structures and degradation pathways of compounds.

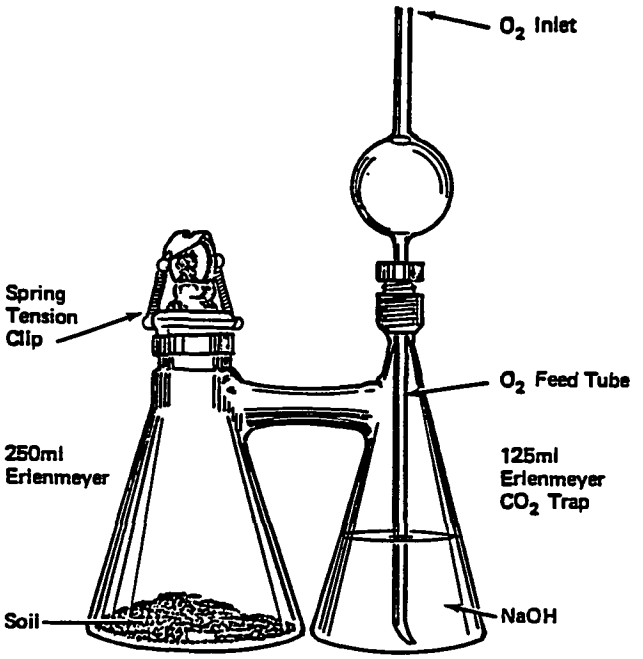

Fig. 2. Microcosm for studying soil degradation.

These and all laboratory experiments are performed with radiolabeled herbicide becaue the ^{14}C is very sensitive to detection and monitoring. Also, the release of $^{14}CO_2$ can be distinguished from naturally occurring CO_2, and any organic metabolites containing that ^{14}C tracer will be easily discovered. Use of ^{14}C also allows a material balance to be calculated, where the ^{14}C in three main categories—$^{14}CO_2$, acetone extracted ^{14}C, and soil residual ^{14}C—is summed to demonstrate that none has been "lost." An overall ^{14}C recovery of 90 to 100% is desirable and lends credibility to all other aspects of the study.

The degradation pathway of fluroxypyr was determined by Lehmann et al. (1990b) from chromatographic analyses of acetone extracts (Fig. 3). Fluroxypyr decreased over time, while two metabolites formed, reached maximum concentrations, and declined. The fact that the methoxypyridine follows the pyridinol suggests that it is formed from the pyridinol. Hence, the sequence of transformation is believed to be: fluroxypyr → pyridinol → methoxypyridine. This sequence is shown from a structural perspective in Fig. 1.

Throughout the transformation process $^{14}CO_2$ is released. This is critical because it indicates that the herbicide has been completely broken down to natural components. The oxidation of an organic compound to CO_2 is a means of energy capture for the soil microorganisms, and the fact that CO_2 was detected in appreciable quantities from fluroxypyr incubations shows that the herbicide is readily used as an energy supply. It should be recognized that not all of the ^{14}C is released as $^{14}CO_2$; some of it is incorporated into the microflora for the growth and building of new cells. For fluroxypyr, about 20 to 30% of the ^{14}C is incorporated (soil residual), with the remainder being released as $^{14}CO_2$.

The rate of breakdown can be quantified by the half-life, which was about 2 wk in Barnes soil (see Table 1 for nomenclature) (Fig. 3). Half-lives in other soils ranged from 1 to 3 wk (Table 1). These half-lives are relatively short and suggest that fluroxypyr should be gone from the soil before the end of the growing season. This is important to the farmer because it means that fluroxypyr should not "carryover" in a field to harm the next season's crops. The fact that a wide variety of soils rapidly degraded the compound indicates that fluroxypyr can be considered readily biodegradable in the soil.

Table 1. Aerobic soil degradation of fluroxypyr.

Soil	Source	Texture	pH	% Organic C	Half-life (wk)
Barnes†	ND	loam	6.8	3.1	2
Catlin‡	IL	silt loam	5.9	2.2	2
Hanford§	CA	sandy loam	7.5	0.2	3
Mhoon¶	MS	clay	7.0	1.3	1

† Fine-loamy, mixed Udic Haploborolls.
‡ Fine-loamy, mixed, mesic Typic Argiudolls.
§ Coarse-loamy, mixed, nonacid, thermic Typic Xerorthents.
¶ Fine-silty, mixed, nonacid, thermic Typic Fluvaquents.

Degradation in the Greenhouse

The environmental conditions in the incubation flasks are reasonable—but not exact—depictions of nature. The big difference is variability. In the incubation flasks, temperature and moisture are constant, whereas in an open field soil temperature varies over both daily and seasonal cycles, and soil moisture varies from saturated to nearly air dry. Air exchange is more active in the field as soils wet, dry, and rewet. Plant roots, worms, and insects add further complexity to field environments. With this in mind, how realistic are the half-lives derived in laboratory incubation flasks?

One way to answer this question is to perform soil degradation studies in the greenhouse. This will provide conditions that are intermediate in complexity between incubation flasks and a field, while still allowing the scientist a measure of control over those conditions. Lehmann et al. (1990b) compared the breakdown of fluroxypyr-MHE in Barnes soil under three situations: incubation flasks, open cups of soil, and open cups of soil planted with grass. The open cups were exposed to grow lights, daily temperature cycling, and periodic wetting/drying. Yet in spite of this extra variability, the disappearance curves of fluroxypyr and the pyridinol were similar to those in incubation flasks, suggesting that the flasks did provide a believable simulation of nature.

This was not the case for the methoxypyridine. Disappearance of this compound was four to seven times faster in open cups than in incubation flasks (Fig. 4).

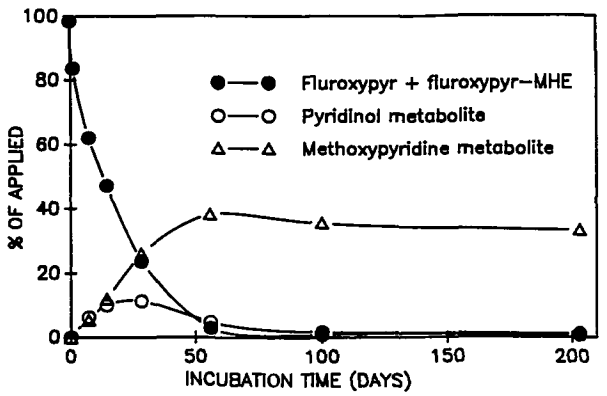

Fig. 3. Degradation of fluroxypyr in Barnes soil.

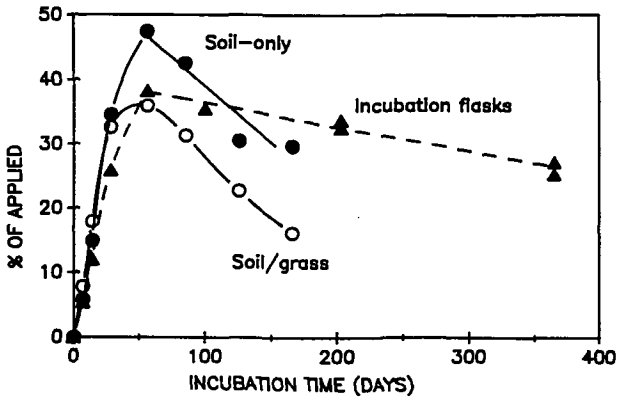

Fig. 4. Dissipation of the methoxypyridine metabolite in laboratory and greenhouse conditions.

Table 2. Mobility of fluroxypyr and metabolites.

Compound	Time of maximum conc.	Averaged desorption K_{oc} (mL/g)	Potential mobility*
Fluroxypyr	1 d	220	Moderate
Pyridinol	14-28 d	580	Moderate/low
Methoxypyridine	56 d	2300	Low

* Determined by matching the desorption K_{oc} with the mobility interpretations of Hamaker (1975).

Table 3. Increase in desorption K_{oc} with incubation time on Catlin silt loam soil.

Compound	Incubation time, mo			
	1	2	3	6
	K_{oc} (L kg^{-1})			
Fluroxypyr	200	370	520	690
Pyridinol	750	980	1300	1800
Methoxypyridine	2100	2600	3200	4300

Possibly the microflora had been stimulated by the variable temperature/moisture conditions, thus leading to faster degradation. Yet a separate experiment showed that the methoxypyridine volatilized off the soil and onto a trapping device, where it could be positively identified. The importance of volatilization is difficult to evaluate, since it is an exceedingly complex and variable process (Spencer, 1987), but it is clear that both microbial degradation and volatilization will operate to remove the methoxypyridine metabolite from soil.

Mobility

Although microbial degradation half-lives predict how long a compound might last in the soil, they don't determine whether the compound will move in the soil profile during that period. Information on mobility is needed for assessing a compound's potential for leaching through the soil and into the water table.

Mobility is described with the K_{oc}, or the tendency of a compound to attach to soil in preference to dissolving in water. A higher K_{oc} indicates a stronger tendency to adsorb to soil. One way of measuring the K_{oc} is by adding water to a sample of soil that has been incubating with a herbicide, and thus contains any metabolites as well. The amount of each compound that leaves (or desorbs from) the soil and dissolves into the water is measured, and the desorption K_{oc} is then calculated according to the formula:

$$K_{oc} = (S/C)/\text{Soil organic C content}$$

where C (mg L^{-1}) is the concentration in the water phase, and S (mg kg^{-1}) is the remaining concentration on the soil.

The K_{oc} values of fluroxypyr and its two metabolites were averaged over four soils (Barnes, Catlin, Hanford, and Mhoon) and four to six incubation times (Table 2; Lehmann et al. 1990a). As discussed earlier, the three compounds reach their maximum concentrations at different incubation times according to the metabolic sequence: fluroxypyr → pyridinol → methoxypyridine. The K_{oc} also increases in this same order, indicating that as residence time in the soil increases, the fluroxypyr aromatic ring is transformed into a less mobile molecule. It is important to realize that descriptions such as "moderately mobile" are value judgments to help interpret the K_{oc} numbers, and not strict statements of mobility.

The averaged K_{oc} is somewhat misleading, because it blends together the individual K_{oc} values from which it was calculated. For example, the individual K_{oc} values of fluroxypyr and metabolites differed to some extent among soil types, and were even found to increase two- to threefold with incubation time (Table 3; Lehmann et al. 1990a). Although K_{oc} is often interpreted as the simple partition of a molecule between soil surfaces and the surrounding water, the situation is undoubtedly more complex: The molecule could be contained inside microbial cells (which should not be surprising since metabolites are actually formed inside microbial cells), or it could be trapped beneath layers of natural organic materials that were deposited on top of the pesticide (Calderbank, 1989). The relative importance of surface adsorption, containment within cells, and entrapment inside or beneath humic materials should change with incubation time and may be responsible for the observed change in K_{oc}. However, the averaged K_{oc} will still be used by scientists and regulators as a rough estimate of mobility, and the reader should be aware of the origin and limitations of these numbers.

Predictions

The degradation and mobility information must now be combined to create a prediction of a compound's fate in the environment. To understand the reasoning, consider the striking contrast between fluroxypyr and its methoxypyridine metabolite. Fluroxypyr has a moderate mobility in soil, which could suggest leaching; however, its short half-life means that it probably will not last long enough to leach. The methoxypyridine is quite the opposite, in that its longer half-life is balanced by a low mobility in soil; hence, it should remain in place as it degrades. The pyridinol lies in between these two extremes, but its low concentration in laboratory studies, rapid transformation to the methoxypyridine, and moderate/low mobility suggest little leaching potential. Fluroxypyr-MHE, the originally applied ester form, is so rapidly hydrolyzed to fluroxypyr that it can be considered to have no leaching potential.

The potential for this herbicide and its metabolites to leach into aquifers is thus limited. If there is a problem, it could occur in very sandy soils with low organic matter content (low adsorptive capacity), in regions with high rainfall; however, this would not be unique to fluroxypyr, since these conditions are favorable for the leaching of any herbicide. With regard to carryover, fluroxypyr's degradation is so fast that only in cold climates with short, dry summers should the problem be addressed.

EXPANDING THE ENVIRONMENTAL FATE PICTURE

At this stage the environmental chemist has invested 2 yr of effort into piecing together a herbicide's fate in the soil. A solid understanding of processes and chemistry has been developed, and predictions have been made. Fluroxypyr is currently at this stage in the cycle; the next step is to test the environmental predictions in the field, to see whether the knowledge gained in the laboratory actually applies to a real-life situation.

Field Studies

Environmental predictions are tested under actual use conditions. Typically the herbicide is applied to the land in the same manner that a farmer would apply it, and soil samples are taken over one or more growing seasons to examine the degradation patterns of herbicide and metabolites. Leaching predictions are checked by sampling to depths of 90 cm and analyzing each 15-cm increment for evidence of downward movement over time. These studies are performed at several locations across the country, reflecting different climates, soils, and cropping patterns. For fluroxypyr, possible locations in the wheat market could include Kansas, Saskatchewan, and eastern Washington. The studies may be performed by a field specialist, but often the laboratory scientist, who knows more about the compound than anyone else at this time, will serve as the field scientist.

The lab results are needed because they help the field scientist design the study (Cheng and Lehmann, 1985). Without prior information on degradation rates, the field scientist wouldn't know how often to collect soil samples; and without knowing the identities of metabolites, the analytical chemist wouldn't know which compounds to expect. Field studies are expensive and can involve the rent of land, hiring of pesticide applicators and soil samplers, travel to and from different sites by the scientist and assistants, and analysis of a thousand or more soil samples by analytical chemists. The laboratory studies provide the basic knowledge to ensure that field studies are properly designed.

The field studies will show how the herbicide actually performed in the environment. If the results are encouraging, which for fluroxypyr will mean that dissipation was as rapid and leaching was as negligible as predicted, this will be communicated as evidence that the compound has a favorable environmental behavior. But the work is not yet completed. Simply having results from several field studies does not answer the question of how the herbicide will perform throughout its agricultural market. This is because each field study is highly localized to a specific soil and a specific, 1-yr weather pattern. What, for example, will happen in a different part of the country? Or what will happen in the exact same field, but in a different year? Computer modeling can assist in answering these and other questions.

Environmental Fate Modeling

An environmental fate computer model is an attempt to simulate reality with a complex set of mathematical equations, which are based on our understanding of soil chemistry, biology, and physics. The model itself is general in nature, but it can be made specific to fluroxypyr by inputting properties such as K_{oc} and the degradation half-life of fluroxypyr. The model can be made specific to a location by inputting soil properties (pH, organic C, and texture), and climatic variables (daily temperatures and rainfall). The model can be run for fluroxypyr at any specified location, and the results will be in the form of predictions: how long fluroxypyr *should* take to degrade, and how far it *should* leach through the soil.

The computer model must first be validated before its results can be believed. This is done by checking it against results from field studies: Soil and weather details from each field study are entered into the model and the model is run for each of these specific situations. The model predictions for fluroxypyr's half-life and extent of leaching should closely match what actually happened in the field studies. If this happens, the model can be trusted to predict the environmental fate of fluroxypyr under numerous other circumstances. This has the effect of extending the laboratory and field work far beyond what could be accomplished by strictly experimental means.

By combining laboratory-based properties such as half-life and K_{oc}, with actual degradation and leaching results from the field, and then extending those results with computer modeling predictions, the environmental fate of a herbicide can be assessed for the entire agricultural market in which the compound will be used (Laskowski et al., 1990). This allows a company to make decisions about where to sell—and where not to sell—that herbicide to avoid future environmental problems, such as contamination of aquifers or carryover of harmful concentrations of herbicide into the next growing season.

Registration

In addition to determining fate in soil, the environmental chemist will be building an analogous data package showing fate of the herbicide in water. This could consist of photolysis studies, degradation in anaerobic sediments, and field studies in lakes and ponds. Other scientists will be contributing separate data packages to answer questions about the herbicide's uptake and metabolism in plants and its toxicity to nontarget plants, mammals, and aquatic organisms. Coordination of these activities is done by a product registration specialist, who is versed in the scientific issues as well as in matters of business and government policy.

Eventually, the registration specialist submits the environmental fate picture, as part of the overall data package, to a governmental regulatory agency such as the USEPA, for official registration of the herbicide.

Table 4. Overall plan of environmental fate research.

Type of study (and examples)	Purpose of studies
1. Laboratory studies (hydrolysis, soil degradation, sorption, photolysis, anaerobic transformations)	Construct the environmental fate picture; make predictions
2. Field studies (dissipation in wheat fields, forest ecosystems, ponds)	Test the environmental fate predictions under actual use conditions
3. Computer modeling	Assess environmental fate throughout the entire market

"Registration" means that the herbicide is legally approved for use within that country, and it usually applies to specific crops or agricultural regions. But the value of a solid environmental package goes far beyond a particular government agency. If the work is published in the scientific literature, it can be referenced by university and government scientists for developing local pest control strategies. Herbicide dealers and distributors appreciate a well-written summary because they must have the knowledge to answer questions from customers about the environmental properties of their products. In fact, a good environmental package can be considered part of the herbicide's overall product offering: That is, when farmers buy that herbicide they are also receiving the benefit of years of research that will help them use the herbicide in an effective and environmentally sound manner.

APPLICATION TO STUDENT RESEARCH PROGRAMS

In industry, environmental research includes three main stages: laboratory (and greenhouse) studies, field studies, and computer modeling (Table 4). The environmental fate picture is developed in the laboratory, tested in the field, and extended by computer modeling to encompass the entire market.

Environmental fate research in undergraduate and graduate programs usually concentrates on a small portion of the above sequence. The challenge is to place a specific project within the context of the overall environmental picture. For example, a research project on soil degradation of a compound should be planned with questions about mobility and carryover in mind. A field project should be preceded by an extensive literature search, and perhaps some key laboratory experiments, to define the environmental picture as completely as possible before field work is attempted. A modeling project must be validated with field data.

Student research programs can add to the environmental field in several important ways. The research can focus on a specific process, such as microbial degradation, to further the understanding of that process. Industry and other scientists can use that basic knowledge to refine their own experimental approaches. Student programs can also build on the general knowledge of a herbicide's environmental fate by testing it in specific soils or climates not tested before. When planning a thesis project on a specific herbicide, a student should search the literature for the articles of that company's scientists, and phone a scientist for suggestions on relevant research directions. The goal is to design a research program that is enjoyable and valuable. If planned well, a thesis project will contribute significantly to the environmental field, and it will earn the respect of colleagues and potential employers.

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