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Environmental Fate & Effects Division
Office of Pesticide Programs
U.S. Environmental Protection Agency
Washington, DC 20460

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MEMORANDUM

SUBJECT: Leaching Potential of Azoxystrobin and its Degradates

TO: James Hetrick

FROM: Michael Barrett MB

THRU: Elizabeth Behl EBehl

I have attached a couple of comments on your draft environmental fate review. Please revise the recommendations as outlined below (I have added specific language recommendations for the ground-water label advisory). Azoxystrobin parent has at best a very modest leaching potential, but that some of the degradates of azoxystrobin are sufficiently mobile and potentially sufficiently persistent to present a high risk for leaching to ground water. The ground-water section recommends the following:

> A ground-water label advisory that reads:
> "The active ingredient, azoxystrobin, in this product can be persistent for several months or longer in soil. Azoxystrobin has degradation products wich have properties smilar to chemicals which are known to leach through soil to ground water under certain conditions as a result of agricultural use. Use of this chemical in areas where soils are permeable, particularly where the water table is shallow, may result in ground-water contamination."
>
> Deferral to Toxicology Branch II, Health Effects Division regarding a decision whether to include degradates, especially, the acrylic acid degradate of azoxystrobin in the residues of concern (If it is, small-scale prospective ground-water monitoring studies will likely be required).
>
> Reevaluation of the leaching potential of azoxystrobin and its degradates once the environmental fate data package is complete and levels of concern are determined for ecological effects.

Appendix

Although the data are somewhat equivocal (azoxystrobin is persistence in soil metabolism studies, but apparently is not particularly persistent under actual field conditions), azoxystrobin parent does not appear to be likely to leach under typical use scenarios.

Justification for concerns about degradates, particularly the acrylic acid degradate (compound 2):

The degradation of azoxystrobin was not necessarily as rapid and as extensive as implied by the registrant in their written report. The registrant stated that "Laboratory photolysis and microbial metabolism studies using radiolabeled material show that the main single degradation product, from all three rings of the molecule, is CO_2." However, in two of seven aerobic soil treatments (one treatment each of azoxystrobin radiolabeled on one of the three rings for the Hyde farm sandy loam and the 18 Acres sandy clay loam and a ^{14}C-pyrimidinyl labeled treatment only for Visalia sandy loam, the only soil tested which was from the United States) less than one or two percent of the applied fungicide was evolved as CO_2. The two treatments with very low CO_2 evolution were ^{14}C-pyrimidinyl azoxystrobin on Visali sandy loam and ^{14}C-phenylacrylate on 18 Acres sandy clay loam. The registrant claimed that the acrylic acid degradate ("compound 2") was not persistent in aerobic soil: "Compound 2 ... has a relatively short half-life, estimated at around 2 weeks." However, in the only United States soil tested, Visalia sandy loam, the amount of compound 2 was steadily increasing up to 12.1 % at 120 days after treatment, the last sampling interval for which residue data have been reported. At 120 days, it was estimated that 54.9 % of the applied azoxystrobin remained in the form of the parent compound. The pattern of degradation has not been sufficiently established as of yet, but it is clear that a considerable amount of the acrylic acid could form (perhaps 20 or 30 % of the applied) and there is also a possibility that the acrylic acid could persist for several months rather than weeks as the registrant estimated. The residue analysis (by thin-layer chromatography) appears to show that the acrylic acid was the major degradate in Visalia sandy loam, although the amount of radioactivity unaccounted for was about 21 % by 120 days after treatment. In the Eighteen acres soil, the acrylic acide was again the major degradate, but residues appear to be less persistent [this study, however, also has not been carried out long enough since 31 % (phenyl acrylate label), 34 % (cyanaophenyl label), or 41 % (pyrimidinyl label) of the applied pesticide remained at 120 days after treatment]. Similar results were obtained with the Hyde farm soil. It appears the registrant's estimate of a two-week half-life for the acrylic acid degradate is low for many soils. Considerable amounts of the radioactivity were unaccounted for in the thin-layer chromatographic analysis (nearly 50 % at 120 days in some analyses - TLC analysis was performed separately with three different solvent systems for the Eighteen acres and Hyde farm soils). Some of the remaining radioactivity was accounted for as trapped ^{14}CO2 (15 to 27 % for five of the seven treatments in three soils, but only 1 or 2 % in the other two treatments in two soils).

The available data appear to indicate that the acrylic acid degradate is only very weakly adsorbed and therefore highly prone to leaching, especially in alkaline soils (Tables 1 and 2). Based on the six soils for which data are available (three acidic and three alkaline), it appears that adsorption coefficients for the acrylic acid are strongly correlated with soil organic matter and pH.

There is a reasonable possibility that azoxystrobin degradates could have a significant impact on ground water as a result of its agricultural use. Based on data supplied so far, leaching of parent alone might not be extensive at most sites because of: (1.) its fairly strong adsorption in most soils, and (2.) the fact that it is foliarly applied and substantially degrades under most use conditions before residues are incorporated in the soil. The leaching potential of the parent becomes very low if it turns out the field dissipation half-lives of 1 to 3 weeks in several soils represent predominantly degradation rather than transport. Undoubtedly, some of the degradates will be extremely mobile and persistent in some soils. While there are a number of degradation products, the bulk of the parent molecule is not readily degraded in most soils.

There are important outstanding issues such as:

- How do the asorptivities of azoxystrobin and its degradates change over time?
- Is photodegradation the only important route of degradation in the field?
- Will photodegradation still be predominant if a heavy rain occurs soon after application, presumably washing much of the applied material into the soil?
- How toxic is this compound to nontarget organisms and how does this relate to amounts which might reach surface water or ground water used for irrigation or drinking?

<u>Screening Model Assessment</u>.

From a basic screening model assessment that we have conducted, it appears that, in spite of its high persistence in soil, azoxystrobin parent has little potential to leach to ground water under <u>most</u> actual field conditions. Azoxystrobin is a fungicide for which most of the applied material initially contacts foliage and is subject to photodegradation before it has a chance to leach. Even if azoxystrobin parent becomes quickly incorporated into soil in the field where it is not subject to photodegradation, it appears to primarily remain in the adsorbed phase. When compared to benchmark pesticides (all herbicides, because these are the chemicals with the most abundant ground-water monitoring data) azoxystrobin has much less leaching potential than two chemicals which have been found most frequently in ground-water in proportional to their use (DCPA acid, atrazine) and only appears to have some leaching potential when worst-case assumptions about persistence (which may not be applicable to real use situations given that azoxystrobin is foliarly applied and photodegrades) are made (Table 3). On the other hand, azoxystrobin acrylic acid is much less strongly adsorbed in soils than parent azoxystrobin and may have significant potential to leach to ground water.

Table 1. Analysis of variance and regression analysis (log Koc versus pH) for the effect of soil pH on the organic carbon partition coefficient for azoxystrobin acrylic acid.[1]

Regression Statistics	
Multiple R	0.977771641
R Square	0.956037381
Adjusted R Square	0.945046727
Standard Error	0.148897357
Observations	6

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1.928525066	1.928525066	86.98639102	0.000735658
Residual	4	0.088681691	0.022170423		
Total	5	2.017206758			

Table 2. Calculation of azoxystrobin acrylic acid Koc values for various soil pH values using results of linear regression of log Koc with soil pH.

Koc	1609	561	196	68	24
pH	4	5	6	7	8

[1] The soils for which sorption coefficients were measured:

Soil Series	pH	Koc	Log Koc	Kd
Kenny Hill sandy loam	7.9	28	1.447	0.35
East Anglia	7.8	21	1.322	0.82
Hyde Farm sandy clay loam	7.5	49	1.690	0.85
Pickett Piece clay loam	5.5	360	2.556	10.00
Lilly Field sand	5.5	490	2.690	6.80
Nebo silty clay	4.9	420	2.623	1.40

Table 3. Ranking of azoxystrobin leaching potential compared to pesticides with an extensive ground-water monitoring data base (Gustafson, 1989[2])

Compound	t1/2	log t1/2	Koc	log Koc	GUS	Assumptions:	Type**	Impact Summary	Leacher?
Benchmark pesticides:*									
DCPA acid	1000	3.00	47	1.67	6.98	median	H	Very high where used	always
atrazine	75	1.88	89	1.95	3.85	median	H	Relatively high, high use	often
2,4-D	10	1.00	20	1.30	2.70	median	H	Moderate, but high use	sometimes
alachlor	17	1.23	180	2.26	2.15	median	H	Moderate, but very high use.	sometimes
glyphosate	25	1.40	5000	3.70	0.42	median	H	Very low, high use.	rarely
trifluralin	87	1.94	8000	3.90	0.19	median	H	Very low, high use.	rarely
Azoxystrobin residues:									
azoxystrobin	16	1.20	1590	3.20	0.96	median	F	turf & grapes	rarely
azoxystrobin	162	2.21	715	2.85	2.53	worst	F	turf & grapes	sometimes
acrylic acid	100	2.00	24	1.38	5.24	worst (pH 8 soil)	F	turf & grapes	usually
acrylic acid	25	1.40	68	1.83	3.03	median	F	turf & grapes	often

* These all happen to be herbicides because more data are available for herbicides, and herbicides are more often directly applied to soil in the spring, increasing the chance for leaching to occur. Because azoxystrobin is a fungicide which will generally contact foliage first, and is relatively immobile in soil, the median half-life value was taken from field dissipation studies (this value corresponded with soil photodegradation half lives).
**H= herbicide, F= fungicide.

[2] Gustafson, D.I. 1989. Groundwater ubiquity score: A simple method for assessing pesticide leachability. Environmental Toxicology and Chemistry 4:339-357.