

Appendix A

Environmental Fate of Imazapyr and Imazapyr Transformation Products

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The non-selective herbicide imazapyr is a water-soluble, weak organic acid that is non-volatile and is both persistent and mobile in soil. Commercial formulations contain either imazapyr acid or the imazapyr isopropylamine salt, both of which are generally dissolved in a water solution. However, imazapyr is mainly in anionic form at typical environmental pHs, and the behavior of the acid and salt forms are expected to be similar.

As indicated in the table of physicochemical properties in the main text of this document, its pK_a is approximately 3.8 (more acidic than acetic acid, less acidic than citric acid). Consequently, at typical environmental pHs imazapyr is mainly in anionic form (61% ionized at pH 4, 94% ionized at pH 5, greater than 99% ionized at pH 6 and higher). Since anions (negatively-charged ions) tend to be weakly sorbed to most soils (in effect, repelled by soil matrix surfaces which are generally negatively charged), imazapyr would be expected to be mobile in most soils. Consistent with this expectation, in several studies involving a total of 11 soils and sediments, adsorption coefficients were low, as demonstrated by batch/bulk equilibrium sorption coefficients that range from 0.04 to 3.4 mL/g, with a median of 0.6 mL/g. There was no apparent correlation with soil organic matter. Since pH dependent complex equilibria generally influence sorption, the variation in sorption coefficients among different soils is understandable. However, the standard battery of environmental fate study data, which we have for imazapyr, are insufficient to demonstrate or correlate systematically the direction and magnitude of any possible pH effects on sorption or other characteristics, such as degradation and metabolism rates.

The fate data requirements for pesticides are primarily designed for neutral organic compounds. To systematically test the effect of pH and other factors on imazapyr fate properties could involve experiments with a minimum of approximately thirty carefully selected soils/sediments. Generally speaking, other factors being the same, sorption would tend to diminish with increasing pH for acidic/anionic compounds.

Aqueous photolysis is the only identified route of degradation for imazapyr in the environment. Imazapyr degraded through photolysis in water with half-lives ranging between 2.5 and 5.3 days. The two major degradates were: 2,3-pyridinecarboxylic acid

(CL 9140, 22.7%) and 7-hydroxy-furo[3,4-b]pyridin-5(7H)-one (CL 119060, 9.7%). Laboratory studies show imazapyr is essentially stable to hydrolysis, aerobic and anaerobic soil degradation as well as aerobic and anaerobic aquatic metabolism. Field study observations are consistent with laboratory studies indicating that imazapyr will persist in soils and move via runoff to surface water and leach to groundwater. Imazapyr does not bioconcentrate.

Within laboratory study conditions and durations, imazapyr was essentially stable (half-lives indeterminately long) to hydrolysis, photolysis in soil, anaerobic soil metabolism, and aerobic and anaerobic aquatic metabolism¹. Minor concentrations of identified and unidentified transformation products were detected in some of the aforementioned processes. Identified minor components are presented below. Slow production and accumulation of relatively low residual concentrations of imazapyr byproducts (identified or unidentified) could be responsible, at least in part, for the long rotational crop intervals and the need for bioassays before planting.

Based on its measured soil-sorption coefficients, its intrinsic acidic/anionic nature, water solubility, and observations from forestry and terrestrial field data, imazapyr is prone to leach and runoff. As discussed later, imazapyr is also persistent. The combination of low sorption and long residence time in soil offers increased opportunities for transport to ground and surface waters. Estimated potential exposure concentrations in water for the purposes of aquatic and drinking water assessments are presented in the main text of this document.

Judging from its calculated Henry's Law constant, anionic nature, and collateral data showing the absence of imazapyr in collection traps for volatile products in various laboratory degradation/ metabolism studies, imazapyr is non-volatile.

Supplemental bare ground and cropped terrestrial field dissipation studies are disparate and inconclusive about routes of dissipation. Because of key deficiencies common to these field studies, only limited, qualitative observations can be made. There was no analysis for metabolites/degradates in these field studies and no water balance to determine potential for leaching or runoff. However, it is not unreasonable to conclude, and in basic agreement with laboratory tests and previous reviews summarizing runoff and leaching data from forestry studies, that imazapyr is prone to leach and is relatively long-lived under field soil conditions.

As stated before, because of slow rates of degradation/metabolism, no major transformation products were identified during the course of laboratory studies, except

¹ Within typical study limitations (study durations), imazapyr was stable under hydrolysis (Acc. No. 251505, MRID 00132359), aerobic aquatic metabolism (MRID 41002301), anaerobic soil metabolism (Acc. No. 251505, MRID 00131619). At the time of its original review, an anaerobic aquatic metabolism study (MRID 40003712) was considered "unacceptable;" however, it was noted then that under experimental conditions imazapyr also appeared to be stable.]

for photolysis in water. Minor soil metabolites were separated in some lab studies, but most were not identified.

Photolysis was the only process that occurred fast enough for imazapyr to produce major degradates (> 10% of parent equivalents) during study periods. Photolysis half-lives of approximately three to five days translate into effective aquatic field half-lives of approximately 300 to 700 days under the more typical aquatic field conditions (water depth, clarity, other factors) used in current EFED modeling scenarios. The major photolysis products were CL 119060 and CL 9140. Their chemical structural dissimilarity from the parent imidazolinone structure is reasonable evidence that these photodegradates are not likely to be toxic to plants. CL 119060 and CL 9140 reached a maximum in the laboratory of approximately 32% and 23%, respectively, of chemical equivalents of parent.

The two major photodegradates were each separately tested for aquatic metabolism under laboratory aerobic aquatic conditions. In a 14-day study for each, their aerobic aquatic metabolism half-lives were in the range of three to eight days in two different sediment/water systems. Nicotinic acid was a metabolite of CL 119060, reaching a maximum equivalent of approximately 10% of parent. CL 9140, based on its structural similarity to CL 119060, would likewise be expected to form nicotinic acid; however, for unclear reasons, it apparently did not. None of these compounds, because of their dissimilarity to parent and/or projected environmental concentrations, have an influence on the risk assessment. Mineralization, as evidenced carbon dioxide production, was significant for each photodegradate in both sediment/water systems, with a range of production amounting to approximately 20 to 50% of photodegradate equivalents.

Laboratory bioconcentration studies with bluegill sunfish, eastern oyster, and grass shrimp indicate that parent imazapyr, even though long-lived in the environment, is not subject to bioconcentration. Bioconcentration in caged fish and crayfish species was also measured as part of an otherwise unacceptable aquatic field dissipation study. The reported limit of quantitation for imazapyr in tissues of the caged animals (three fish and one crayfish species at each of two sites, total of seven different species) was a relatively high 50 parts per billion (ppb). Within the 50 ppb limit, it is not unreasonable to conclude that parent imazapyr did not bioconcentrate during the aquatic field study. There was no attempt to analyze for metabolites or degradates in any of the species tested. Imazapyr's relatively high solubility in water and low n-octanol to water partitioning ratio is also consistent with little likelihood of bioconcentration.

Table A1. Degradation and Metabolism of Imazapyr

Study MRID	Study Type	System	Imazapyr half-life	Maximum transformation products (% of applied radiation)					CO ²
				CL 288247 ¹	CL 252974	CL 119060	CL 9140	CL 252974 5	
00132359	Hydrolysis (161-1)	pH 5, 7 and 9 at 25°C	Stable	ND ²	ND	ND	ND	ND	ND
00131617	Photolysis in water (161-2)	pH 5 and 9 at 25°C (12 hour exposure cycle)	2.5 - 5.3 days	ND	ND	9.7	22.7	ND	NA ³
40003713	Photolysis in soil (161-3)	Loamy sand soil	Stable (~149 days)	ND	ND	ND	ND	ND	NA
41023201	Aerobic Soil Metabolism (162-1)	Loamy sand soil	Stable	ND	ND	ND	ND	ND	7
45119701	Aerobic Soil Metabolism (162-1) (Supplemental)	Loamy sand soil	(~5.9 years) >296 days	ND	3	ND	ND	ND	6
00131619	Anaerobic Soil Metabolism (162-2)	Loamy sand soil	Stable (>60 days)	ND	ND	ND	ND	ND	ND
40003712	Anaerobic Aquatic Metabolism (162-3)	Total system	>120 days	ND	ND	ND	ND	ND	ND
41002301	Aerobic Aquatic Metabolism (162-4)	Total system	>120 days	ND	ND	ND	ND	ND	1.1
45119702	Aerobic Aquatic Metabolism (162-4) - Degradate metabolism	Total system (CL 119060 metabolism) (CL 9140 metabolism)	4.9 days 3.6 days	NA NA	NA NA	NA NA	20.4 NA	ND ND	44.9 53
42192101	Terrestrial field dissipation (164-1)	Bare ground / Silt loam soil Hillsboro, Oregon	143 days	NA	NA	NA	NA	NA	NA
42192102	Terrestrial field dissipation (164-1)	Bare ground / Sandy loam soil Janesville, North Carolina	64 days	NA	NA	NA	NA	NA	NA
40003714	Forestry Dissipation (164-3)	Aerial application, residues measured	12-40 days (vegetation) 37-44 days (litter)	NA	NA	NA	NA	NA	NA

¹ See chemical structures of degradates in following sections of Appendix A. ²Not detected. ³ Not analyzed.

Table A.2. Sorption Coefficients for Imazapyr in 11 Soils/Sediments			
MRID	Soil/Sediment Texture	Kd (mL/g)	Koc (mL/g oc)
45119705	Sand sediment (Florida)	0.11	31
45119705	Silt loam sediment (Missouri)	0.64	100
43423703	Loamy sand soil	0.04	15
43423703	Silt loam soil	0.86	82
43423703	Sandy loam soil	0.07	8.2
43423703	Loam soil	0.23	17
43423703	Pond sediment	3.4	150
00131620	Sandy loam soil (Princeton)	1.9	110
00131620	Loamy sand soil (Delaware)	0.52	100
00131620	Clay loam soil (North Dakota)	0.84	18
00131620	Silt loam soil (Wisconsin)	2.4	53
Average values (N = 11)		0.998	61.9
Median values		0.64	53
Lowest non-sand value		0.23	17

Summary of Environmental Fate Studies

A.1 Hydrolysis

Imazapyr is stable to hydrolysis at environmentally relevant pH values and temperatures. Imazapyr was stable in aqueous buffer solutions (pH 5 and 7) and distilled water (pH 5.2) for up to 30 days at 25±1°C. Imazapyr degraded slowly in an aqueous pH 9 buffer solution. The only identified degradate was 2-[(1-carbomyl-1,2-dimethylpropyl)carbomyl] nicotinic acid (CL 252974).

A.2 Photolysis

Imazapyr is susceptible to photolysis. Imazapyr degraded with a half-life of 2.5-

5.3 days in distilled water or buffer solution at pH 5 or 9, at 25°C, irradiation with a xenon arc lamp (12 hours/day) for up to 10 days. Two major degradates were formed: 2,3-pyridinecarboxylic acid (CL 9140, 22.7%) and 7-hydroxy-furo[3,4-b]pyridin-5(7H)-one (CL 119060, 9.7%).

Imazapyr degraded slowly on irradiated soil. In laboratory studies, imazapyr degraded with an extrapolated half-life of 149 days on sandy loam soil irradiated a 4-week period. No degradate was >10% of the applied radioactivity

A.3 Aerobic Metabolism

Imazapyr is essentially stable to degradation in soil maintained under aerobic conditions. Imazapyr was studied in Princeton sandy loam soil maintained at 25°C in the dark for up to 365 days. At 365 days, 88% of the applied radioactivity remained as parent imazapyr (calculated half-life of 5.9 years).

The aerobic soil metabolism of imazapyr was also studied for 121 days in Sassafras sandy loam soil maintained at 25°C in the dark. Because the 121-day study period was short compared to the persistence of imazapyr, there was insufficient time for the full pattern of formation and decline of products to develop. The extrapolated first-order kinetics regression half-life for parent imazapyr for the 121-day period is 296 days ($r^2 = 0.89$, 95% confidence interval of 247 to 370 days).

Imazapyr did not degrade in water or sediment under aquatic conditions. Over the course of the study, >96% of the applied radioactivity remained in the aqueous phase while <2% was bound to soil. Analysis by thin-layer chromatography determined that parent imazapyr accounted for >97% of the applied radioactivity after 4 weeks.

A.2.1 Aerobic Metabolism of Imazapyr Photolysis Transformation Product

The aerobic degradation of the imazapyr degradation products, furo[3,4-b]pyridine-5-(7H)-one-7-hydroxy (CL 119060) and pyridine 2,3-dicarboxylic acid (CL 9140), was studied in each of two pond water:sediment systems. A pond water:sediment system from Florida, and a pond water:sediment system from Missouri were studied for 14 days in darkness at 25±1°C. For both test compounds and systems, aerobic conditions were maintained in the water layers of the sediment:water systems, but the sediment layers remained anaerobic throughout the study.

In the water layer, the major nonvolatile transformation product of furo[3,4-b]pyridin-5(7H)-one,7-hydroxy- was pyridine 2,3-dicarboxylic acid. This compound was detected at maximums of 20% of applied at 1 day and 28% at 3 days in the sand and silt loam sediment systems. Nicotinic acid was identified as a nonvolatile transformation product, and detected at maximums of 6% at 2 days and 10% at 1 day in the sand and silt

loam sediment systems, respectively. The first-order kinetics regression half-life for furo[3,4-*b*]pyridin-5(7*H*)-one,7-hydroxy- in the Florida pond system (water + sediment) was 3.9 days ($r^2 = 0.95$, 95% confidence interval of 3.4 to 4.5 days). The Missouri pond system first-order regression half-life (water + sediment) for furo[3,4-*b*]pyridin-5(7*H*)-one,7-hydroxy- was 5.8 days ($r^2 = 0.80$, 95% confidence interval of 4.5 to 8.2 days). The average half-life for the Florida and Missouri systems for furo[3,4-*b*]pyridin-5(7*H*)-one,7-hydroxy- was 5 ± 1 days with an upper 90% confidence bound on the mean of 8 days.

No major nonvolatile transformation products of [pyridine-6-¹⁴C]pyridine 2,3-dicarboxylic acid were detected in the water layers. The first-order kinetics regression half-life for of pyridine 2,3-dicarboxylic acid for the Florida pond system (water + sediment) was 3 days ($r^2 = 0.56$, 95% confidence interval of 1.9 to 5.9 days). The Missouri pond system first-order regression half-life (water + sediment) for pyridine 2,3-dicarboxylic acid was 4 days ($r^2 = 0.88$, 95% confidence interval of 3.5 to 5.5 days). The average half-life for the Florida and Missouri systems for pyridine 2,3-dicarboxylic acid is 4 ± 1.0 days with an upper 90% confidence bound on the mean of 5.7 days.

A second study addressed the aerobic aquatic metabolism of 2,3-pyridinedicarboxylic acid (CL 9140) and 7-hydroxy-furo[3,4-*b*]pyridin-5(7*H*)-one (CL 119060) over a 4-week period. The degradates were added to pond water and sediment from a wetland in New Jersey. The study presented evidence that furo[3,4-*b*]pyridin-5(7*H*)-one,7-hydroxy- is rapidly converted to pyridine 2,3-dicarboxylic acid which, in turn, is metabolized to CO₂.

A.4 Mobility

The batch-equilibrium adsorption/desorption characteristics of imazapyr and the metabolites (photoproducts) pyridine 2,3-dicarboxylic acid and furo[3,4-*b*]pyridin-5(7*H*)-one,7-hydroxy- were each studied separately in a sand sediment from Florida and a silt loam sediment from Missouri. The equilibrating solution used was 0.01 M CaCl₂, at a soil/solution ratios of 1:2 (w:v). The desorption phase of the study was carried out at $20 \pm 1^\circ\text{C}$ for 27.5 hours for imazapyr, 24 hours for pyridine 2,3-dicarboxylic acid, and 44 hours for uro[3,4-*b*]pyridin-5(7*H*)-one,7-hydroxy-. The desorption phase was conducted once.

Imazapyr: Freundlich adsorption parameters and average simple adsorption/desorption coefficients are given in Table A-1 below. Average simple adsorption coefficients (K_{ads}) for the experimental concentration range were 0.144 and 0.639 mL/g for the sand and silt loam sediments, respectively. Corresponding simple adsorption coefficients adjusted for organic carbon (K_{oc}) were 30.6 and 99.8 mL/g organic carbon.

Pyridine 2,3-dicarboxylic acid: Freundlich adsorption parameters and average simple adsorption/desorption coefficients are given in the results synopsis and in Table

A-2 below. Average simple adsorption coefficients (K_{ads}) were 1.02 and 38.74 mL/g for the sand and silt loam sediments, respectively. Corresponding K_{oc} values were 217 and 6053 mL/g organic carbon.

Furo[3,4-b]pyridin-5(7H)-one,7-hydroxy-: Freundlich adsorption parameters and average simple adsorption/desorption coefficients are given in the results synopsis and in Table A-3 below. Average simple adsorption coefficients (K_{ads}) for the experimental concentration range were 0.628 and 6.532 mL/g for the sand and silt loam sediments, respectively. Corresponding K_{oc} values were 134 and 1020 mL/g organic carbon.

A.5 Field Dissipation

The isopropylamine salt of imazapyr dissipated from one test site with a calculated half-life of 143 days. Sprinkler irrigation was applied at 0.5 to 3.0 inches, 1-3 times/month. The temperature ranged from 6 to 100°F, total precipitation was 67 inches, and irrigation total was 29 inches. Imazapyr residues were found primarily in the 0-6-inch soil layer. In the 6-12-inch layer, residues were ≤ 6 ppb at 1-30 days, 14-17 ppb at 240 days, and 6-13 ppb at 452 days. In the deeper soil layers residues were < 8 ppb immediately posttreatment, and not detected at later sampling times. A half-life of 143 days was calculated. Residues in a control plot were ≤ 4 ppb. Routes of dissipation were not provided.

The isopropylamine salt of imazapyr dissipated from one test site with a calculated half-life of 64 days. The test material was applied by backpack sprayer to a bareground plot of sandy loam located in Janesville, North Carolina. Sprinkler irrigation was applied at 0.58 to 2.0 inches, 3-5 times/month. The temperature ranged from 18 to 98°F, total precipitation was 67 inches and irrigation totaled 22 inches. Imazapyr residues were found primarily in the 0-6-inch soil layer. Routes of dissipation were not provided.

In another study, cropped corn fields in Iowa and Nebraska were used as study sites. Apparent, simple first-order regression half-lives at all sampled depths (0-36 inches) were 94 days in Iowa (95% confidence limits 84-107 days, $r^2 = 0.88$) and 126 days in Nebraska (95% confidence limits 113-143 days, $rP^2 = 0.88$). The degree to which the apparent loss/dispersal of imazapyr was due to transformation, plant uptake, volatilization, leaching, runoff, etc. was not determined. There was no analysis for transformation products (degradates or metabolites), no measurement of plant uptake, and there was no water or simple attempt to correlate daily rainfall/irrigation with pesticide disappearance or potential for movement in soil during the course of study. Therefore, disappearance half-lives represent only lower limits for what may be very much longer effective half-lives, and cannot be assumed to be attributable to degradation or detoxification of parent (or any possible by-products).

For the present study, casual inspection of the soil concentration data shows quick infiltration of imazapyr into moist surface soil, and close correlation between

rainfall/irrigation events with eventual leaching of imazapyr into the lower soil depths (down to 30 or 36 inches). Rainfall/irrigation was said to be typical or average for the experimental sites in Iowa and Nebraska. These penetrations into soil are evidence of high mobility. Furthermore, the leaching occurred in soils with characteristics that are not usually associated with high potential for leaching. The soils had relatively high cation exchange capacities, organic matter, and moisture retention capacity. Subsoil clay content was approximately 25-30%.

Imazapyr rapidly dissipated from shallow ponds in Florida and Louisiana during summer months. Imazapyr dissipated with half-lives of 3 and 4 days in pond water and sediment, respectively. In a similar study carried out in Louisiana, imazapyr dissipated with half-lives of 2 and 4 days in pond water and sediment, respectively

Imazapyr applied by aerial spray to a forest dissipated primarily by runoff, and to a lesser degree, by foliar absorption. Imazapyr was applied by helicopter at 2.24 kg/ha (2 lb ae/acre) with Igepal DM-710 as a surfactant, over two forested watersheds in Fayette and Randolph counties, Alabama, in May and June, 1985. Each site was divided into two water sheds, one treated and one control.

Description, Fayette county site. This was a 121-ha site of mixed hardwoods. Pines in the plot had been harvested earlier. The application took place over 4 days due to weather conditions of intermittent fog and drizzle. The plot was drained by a single stream. The soil was sand loam (1.92% organic matter, CEC 3.7 meq/100 g).

Results, Fayette county. Imazapyr dissipated from vegetation with a half-life of 12 days (highest mean residue, about 100 ppb at 3 days posttreatment), from litter with a half-life of 44 days, from 0-4-inch depth of bareground soil with a half-life of 24 days, and from 0-4-inch depth litter-covered soil with a calculated half-life of 19 days. Residues were found primarily in the 0-12-inch soil depth. Residues in stream grab samples were highest during application (up to 680 ppb) and following storm events. Stream residues declined to trace amounts at later sampling intervals. Only one stream sediment sample contained a detectable residue, 52 ppb.

Description, Randolph county site. This was a 40-ha area of loblolly pine seedlings and mixed hardwoods. The plot was drained by a single stream. The underlying soil was loam (4.4% organic matter, CEC 4.17 meq.100 g). Precipitation was measured at each site, and stream water levels were monitored. Samples were taken of water, suspended sediment, vegetation (composited), litter, and soil (up to 20 inches depth), the latter by area of ridge, midslope and lower slope.

Results, Randolph county. Imazapyr dissipated from vegetation with a half-life of 40 days (highest mean residue, 122 ppb immediately posttreatment), from litter with a half-life of 37 days, from 0-4-inch depth of bareground soil with a half-life of 26 days, and from 0-4-inch depth litter-covered soil with a calculated half-life of 34 days. Residues were found primarily in the 0-12-inch soil depth. Visual observation indicated

at least 99% kill of all targeted vegetation.

A.6 Bioaccumulation

Imazapyr did not bioconcentrate appreciably in the fish and crayfish species tested (three fish and one crayfish species at each site, total of seven different species). There were no tests for degradates or their concentration in any of the test species. It should be noted that the reported limit of quantitation for parent in tissue was a relatively high 50 ppb. In several instances, for unknown or unverified reasons, there was some limited mortality of some test species and/or their partial disappearance, such that for some sampling intervals there were insufficient amounts of tissue for analysis. However, this does not significantly alter the general conclusion of no appreciable bioconcentration of parent above a concentration of 50 ppb.

There was no bioconcentration of imazapyr [bioconcentration factor (BCF) <1] under test conditions of 28-day exposure periods at mean measured concentrations of 250 ppb for oysters and 260 ppb for shrimp followed by 14-day depuration periods. Overall results for the two test species, oyster and shrimp, are essentially the same. The study was deficient for both oyster and shrimp because of relatively high levels of quantitation (LOQ; 72 ppb for oyster, 128 ppb for shrimp) compared to exposure concentrations. Consequently, because of the relatively low and variable concentrations of residues compared to the LOQ, uptake and depuration rates of imazapyr could not be calculated meaningfully, and no metabolite identification work was conducted.