Summary of Aminopyralid Toxicity and Fate for Application to Sensitive Areas of Rights-of-Way

The following summary addresses use of the herbicide aminopyralid in Sensitive Areas of Rights-of-Way in Massachusetts. The review was jointly conducted by the Massachusetts Department of Environmental Protection (MassDEP) Office of Research and Standards (ORS) and the Massachusetts Department of Agricultural Resources (DAR) in accordance with the cooperative agreement issued between the two agencies in 1987 and updated in 2011 pursuant to the provisions of Section 4(1)(E) of 333 CMR 11.00 Rights-of-Way Management Regulations.

The conclusions summarized in this memo are based upon several sources of information, including a comprehensive review of this herbicide by the USDA Forest Service (Durkin 2007), scientific documents contained in the US Environmental Protection Agency (EPA) docket of information for aminopyralid to support pesticide registration decisions and the results of literature searches for recent pertinent studies on this chemical. As aminopyralid is a relatively new product, very little primary information was found in the literature that was pertinent to the scope of this review and therefore the review was primarily based on information provided by the secondary summary documents described above. The purpose of this review is to ascertain the suitability of this product for use within sensitive areas of rights-of-way, based upon consideration of available information on the potential toxicity of the active ingredient aminopyralid as well as its fate and transport in the environment.

Aminopyralid (2-pyridine carboxylic acid, 4-amino-3,6-dichloro-2-pyridine carboxylic acid) is a pyridine carboxylic acid herbicide manufactured by Dow AgroSciences LLC (DAS) for use in controlling annual and perennial broadleaf weeds. At the time of this active ingredient review, two end-use products containing aminopyralid were requested: Milestone (EPA Reg. No. 62719-519) and OpenSight (EPA Reg. No. 62719-597). Additional details on the evaluation of the products can be found in separate review documents.[1]

Aminopyralid is structurally similar to other pyridine carboxylic acid herbicides that preceded it in development, including clopyralid, picloram and triclopyr. Technical grade picloram and clopyralid contain the carcinogen hexachlorobenzene as well as other carcinogenic chlorinated benzenes as impurities that are byproducts of their synthesis process. According to DAS, the manufacturing process for aminopyralid does not produce these byproducts (John Jachetta, DAS product manager for aminopyralid as cited in Durkin, 2007). EPA has labeled aminopyralid a "reduced risk pesticide" that has a favorable human health toxicity profile when compared to the registered alternatives, because it has a lower application rate, which should alleviate the need for repeat applications and thus result in a lower overall amount used.

Similar to other pyridine carboxylic acids, aminopyralid is a synthetic analogue of an auxin, a plant hormone that regulates development, growth and other plant functions. Though the specific mode of action of these compounds is not fully known, they produce effects on the plant including alterations in

[1] Product review of Milestone Herbicide; Product Review of Opensight Herbicide

cell wall elasticity and gene expression, and non-productive tissue growth that results in leaf curl and disruption of the plant phloem, interfering with transport of nutrients and causing death in days to weeks.

Summary of fate and transport:

Aminopyralid is generally very persistent in the environment. Under favorable light conditions, it can rapidly photodegrade in shallow, clear water (though not in murky deeper water), with a half-life of 0.6 days. It photodegrades slowly in soil, with a half-life of about 72.2 days. It is stable to microbial degradation in sediment and water systems. In aerobic soils, it is metabolized at a moderate rate depending on the type of soil, with a half-life range of about 31.5 days to 193 days in eight soils[2]. It is expected to be stable in anaerobic soils (USEPA, 2014).

Under environmental conditions and pH, 99.9% of aminopyralid will dissociate to its anionic form, which contributes to its high solubility, lack of volatility and very low adsorption to soils. As a result, aminopyralid partitions to water and is expected to have high mobility in most soils. The major route of dissipation of aminopyralid from soil is through runoff and leaching.

Once aminopyralid enters surface water, any residue that is not subject to photolysis will persist and be mobile in aquatic environments. Aquatic field dissipation studies in treated ponds showed half-lives in the range of 10.8 to 14.6 days. Any part of aminopyralid applied to terrestrial vegetation that reaches the soil has a high potential to run off into surface water or leach into the soil profile and groundwater. Once aminopyralid reaches anaerobic depths in soil, degradation will dramatically slow and only its high mobility will determine the rate at which it will contaminate groundwater. Field dissipation in bare ground studies showed dissipation half-lives in the range of 9 to 54 days and leaching depths in the range of 6 to 36 inches. The potential for groundwater contamination with aminopyralid is expected to be higher in areas with shallow groundwater (because there is less depth to travel before reaching groundwater) or when rain occurs soon after application. Additional information on the expected concentrations in surface water and groundwater following the terrestrial applications in rights-of-way is available in the companion document to this review.

[2] Recent assessments by USEPA (2014) and the European Union (EFSA, 2013) provide updated information for aerobic soil metabolism and soil binding parameter values of aminopyralid. USEPA (2014) considered the data from eight soils. The soil half-life values ranged from 31 to 193 days, with an average of 103.7 days. The soil-water partitioning constant (K_D) values ranged from 0.03 to 0.29 mL/g for soils with pH values of 6.1 to 7.8; K_D values of acid soils were in the range of 0.15 to 0.72 mL/g. The K_{OC} values for soils with near-neutral pH values were in the range of 1.05 to 7.54 mL/g and for acidic soils the values were in the range of 19.95 to 24.3 mL/g. In general, K_{OC}-values increase with decreasing pH. USEPA (2014) indicated that these data on soil half-life and soil binding (soil-water distribution coefficient data) are acceptable for use in exposure modeling and risk assessment.
In addition to the USEPA assessment, aquatic exposure modeling conducted as part of a European risk assessment (EFSA, 2013) was reviewed to provide additional data and information. The model input value for soil half-life geometric mean of 54.8 days was lower than the values used in the SERA risk assessment (Durkin, 2007) and the values used by USEPA. The model input value for soil binding parameter (mean $K_{F,OC}$ of 6.64 mL/g) was within the range of values used in the other modeling efforts reviewed above.

The only potentially major degradation products of aminopyralid are formed during aqueous photolysis and include two small amino acid analogs, i.e., malonamic acid and oxamic acid, along with four unidentified acid amides of 2-3 carbons in length. EPA concluded that neither of the two identified compounds would be of concern as they are expected to be readily metabolized following uptake and/or rapidly excreted without any significant biological effects. In addition, none of these compounds are expected to be produced to any great extent as aqueous photolysis only occurs up to the depth that sunlight penetrates a water body. Only carbon dioxide and some non-extractable residues were found in amounts over 10% of the applied study residue in all other laboratory degradation studies of aminopyralid, at maximums of 76.2% in aerobic soil metabolism and 15% in aerobic aquatic metabolism.

Summary of Toxicity and Risk Assessment:

Available toxicity information reviewed by the secondary sources cited above all indicate that aminopyralid at environmentally relevant concentrations has low potential toxicity to humans, as well as terrestrial animals and aquatic organisms. This finding is consistent with its mode of action, which is specific to plant biology. A number of systemic mammalian studies as well as aquatic ecotoxicity studies indicate that exposure concentrations of aminopyralid associated with herbicide applications are well below concentrations of concern for these receptors.

In terms of mammalian effects, the weight of evidence indicates that aminopyralid does not produce significant systemic effects. The effects most often seen following exposure to aminopyralid are on the gastrointestinal tract after oral exposure, with cecal effects in rats and stomach effects in dogs and rabbits. In rats, the typical effect is cecal enlargement. Given that cecal enlargement is typically seen with poorly absorbed osmotically active compounds, this effect is categorized by a number of investigators as an adaptive change and/or not toxicologically significant. The significance of cecal effects to humans, which only have a vestigial trace of this organ, is also unclear. The USDA Forest Service considers the effects on the gastrointestinal system as portal of entry effects. The differences in effects are attributed to differences in species anatomy and methods of exposure (i.e., gavage vs. dietary). Another somewhat notable effect in mammals includes the results of an acute oral toxicity study in rats in which bilateral cloudiness and lacrimation of eyes was seen in all rats after one day but not on subsequent days. Cloudiness of eyes is an unusual effect that has not been seen in any other aminopyralid study. The significance of these findings is unclear. Finally, in one developmental study, incoordination in several adult female rabbits was noted but this effect was rapidly reversible.

EPA developed a chronic Reference Dose (RfD) of 0.5 mg a.e.[3]/kg/day for aminopyralid for the general population derived based on a No Observed Adverse Effect Level (NOAEL) of 50 mg a.e./kg/day from a 24-month feeding study in rats. The endpoint, increase in cecal weights at 500 mg a.e./kg/day, may have very little relevance to potential effects in humans. However, the RfD is based on the most sensitive effect for the most sensitive species from the available database for aminopyralid. EPA also derived a Human Health Benchmark for Pesticide (HHBP) concentration of 3500 ug/L (ppb) from this chronic RfD

[3] Because aminopyralid dissociates from its acid form to its anionic form in the environment, aminopyralid application rates and concentrations are reported as "acid equivalents" (a.e.), instead of "active ingredients" (a.i.) because the acid part of the active ingredient salt is the herbicidally active component.

based upon a 70 kg adult who drinks 2 L/day of water and incorporating a Relative Source Contribution (RSC) factor of 20%.

For short-term/intermediate exposures, EPA developed an acute RfD of 1.0 mg a.e./kg/day derived based on a NOAEL of 104 mg a.e./kg/day from a developmental gavage study in rabbits in which decreased maternal food consumption and body weight as well as spontaneous abortion (in one rabbit) and decreased fetal weights were seen at higher doses.

A comparison of predicted short and long-term exposure to aminopyralid following application indicates that exposures are substantially below the above acute and chronic criteria.

Though the potential for aminopyralid to contaminate groundwater is high due to aminopyralid's high solubility and prolonged half-life in soil, both EPA and the U.S. Forest Service concluded that predicted short and long-term concentrations of aminopyralid in groundwater are substantially below concentrations of health concern for people using groundwater as a source of drinking water.

In terms of ecological effects, it appears that birds are more sensitive to aminopyralid administered through gavage than dietary exposure. A series of ecological benchmark toxicity concentrations were developed by both EPA and the US Forest Service for various terrestrial and aquatic wildlife. Though there were some differences in some of these values between the two agencies, the evaluations conducted by both agencies point to the same conclusion, that there is no indication from the available data that aminopyralid will adversely affect mammals, birds, fish, aquatic and terrestrial invertebrates, terrestrial microorganisms and amphibians.

A couple of ecological data gaps remain in the data submitted by the manufacturer of this compound to the U.S. Environmental Protection Agency (USEPA). These include a cyanobacteria growth study, an early life stage study in fathead minnows and an invertebrate lifecycle study in mysid shrimp. Additional information on data that are needed to address uncertainties in risk assessments is available in documents that were issued with the Registration Review of aminopyralid. The Registration Review of aminopyralid was initiated in 2013 and is scheduled to be completed in 2020. Information and notices related to this review will be available in the docket (USEPA, 2013).

An additional quantitative comparison of modeled concentrations of aminopyralid in surface water and groundwater following land application in rights-of-way areas was done by DAR to available ecological and human health benchmarks. This analysis indicated that projected water concentrations resulting from application of aminopyralid are well below concentrations of concern for ecological receptors in surface water as well as for humans who use these waters as sources of drinking water. For additional details on this evaluation as well as on the modeling conducted, please see the companion document to this review, entitled "Exposure Assessment of Aminopyralid in Surface and Ground Water: Review of Modeling Input Parameter, Refined Modeling and Comparison with Benchmarks."

Plants:

Aminopyralid's auxinic mode of action renders it toxic to all terrestrial (dicot) broadleaf plants. It is generally not toxic to terrestrial (monocot) grasses. While aquatic macrophytes have been shown to be more sensitive to aminopyralid than aquatic organisms, this herbicide is generally not toxic to aquatic macrophytes and algae.

Given that aminopyralid has an auxinic mode of action that can affect all terrestrial broadleaf plants, the potential impact to non-target broadleaf plants, particularly plants that are endangered species, is seen as the greatest concern for this herbicide. In addition, effects on non-target plants that might not be endangered species but which might serve as a food source for endangered animal species would be of concern.

An important consideration with this compound is that aminopyralid ingested by animals in grasses and other vegetation is excreted largely unchanged. As has been found with two of its predecessor compounds, (i.e., clopyralid, and picloram), use of manure from domesticated animals (that have ingested aminopyralid-treated grasses and vegetation) as compost in gardens can have detrimental effects to sensitive broadleaf plants, including plants in the nightshade family such as potatoes, tomatoes, and legumes. The aminopyralid product label warns that manure from animals that have grazed on aminopyralid-treated vegetation within the previous three days should not be used on land used for growing susceptible broadleaf plants. The three-day warning refers to the time it takes for consumed vegetation containing aminopyralid residues to pass through grazing animals. While this warning does not directly apply to application of aminopyralid on rangeland, it should be considered in scenarios where there is the potential for range vegetation to enter the garden compost stream.

Conclusions/Recommendations:

The information contained in the secondary documents from both EPA and the US Forest Service that were reviewed for this evaluation consistently present the same profile and conclusions on the toxicity, fate and transport of this herbicide. No conflicting information was identified in the literature. In addition, supplemental modeling conducted by DAR for this review consistently point to the same conclusions as those reached by EPA, the US Forest Service and others. Modeled concentrations of aminopyralid in environmental media following application as specified in product labels are well below toxicity levels of concern for humans, as well as terrestrial and aquatic wildlife.

Sensitive non-target plant species have been identified as the organisms of concern. Given that herbicides are designed to control plants, this is not surprising. This information, coupled with the fact that aminopyralid is very mobile and persistent in the environment strongly suggests that application of aminopyralid should be targeted as much as possible to avoid impacts on non-target plants. Measures that minimize drift should be used in applying this product. In addition, as with any application, a preliminary field survey should be conducted prior to application to identify any plants on the endangered species list and/or any other plant species that are important to that ecosystem.

Based upon the available database for aminopyralid, use of this herbicide in sensitive areas of rights-of-ways should be acceptable if it is applied in a manner that is consistent with the product label, the above recommendations and the Massachusetts Sensitive Areas of Rights-of-Way Regulations.

Reference:

Durkin, P. R. (2007). Aminopyralid Human Health and Ecological Risk Assessment – FINAL REPORT. SERA TR-052-04-04a. Report prepared for USDA/US Forest Service. Fayetteville, NY, Syracuse Environmental Research Associates, Inc. .

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USEPA, 2013. Aminopyralid Registration Review; Docket ID: EPA-HQ-OPP-2013-0749; Accessed at: www.regulations.gov.

USEPA, 2014. Registration Review; Preliminary problem formulation for environmental fate, ecological risk, endangered species, and human health drinking water exposure assessments for aminopyralid. USEPA, Environmental Fate and Effects Division. February 12, 2014. Accessed at: http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPP-2013-0749-0011.

Exposure Assessment of Aminopyralid in Surface and Ground Water: Review of Modeling Input Parameter, Refined Modeling and Comparison with Benchmarks

1. Introduction

Aquatic exposure modeling has been used to estimate aminopyralid residue concentrations in surface water and ground water to support human health and ecological risk assessments. The USDA Forest Service document, "Aminopyralid-Human Health and Ecological Risk Assessment-FINAL REPORT", prepared by Syracuse Environmental Research Associates, Inc. (SERA) (Durkin 2007) describes the modeling that was used to estimate the concentrations of aminopyralid that may occur in surface and ground water. The risk assessment also reviews environmental fate input parameters and summarizes results from other modeling efforts conducted by USEPA and DOW AgroSciences (DAS).

The present document reviews these modeling data and also provides the results of additional modeling conducted by DAR, utilizing more recent modeling information and environmental fate input parameters, to complement and refine existing modeling results. All of these modeled concentrations in surface and ground water were assessed by comparing them to benchmark toxicity values for aquatic life and human health established by USEPA.

2. Review of Modeling Data in SERA Risk Assessment

The SERA risk assessment (Durkin 2007) notes that modeling results are sensitive to the input parameter value for soil half-life. The range of input values for aerobic soil metabolism half-life used in the various modeling efforts is related to the limitations and uncertainty in the data that were available for this parameter at the time modeling was conducted. SERA used a slightly higher value for half-life time of 343 days compared to 310.5 days by USEPA. The value used by USEPA was based on a single study result of 103.5 days. USEPA multiplied that half-life value by 3 to account for the uncertainty associated with using only a single study result.

SERA notes that the soil binding parameter (i.e., soil-water partitioning coefficients K_{OC} and K_D) is variable and not closely related to organic carbon content of the soil. Model input values for this parameter used in GLEAMS modeling were refined by using specific values associated with the type of soil. Values used for K_{OC} ranged from 0.87 in clay to 8.91 mL/g in loam; K_D values ranged from 0.39 in sand to 0.63 mL/g in clay. The parameter values used in modeling by USEPA was K_D of 0.03 mL/g and DOW AgroSciences used a K_{OC} value of 0.81mL/g.

The input parameter values used in the modeling described in SERA were considered to be the most conservative and resulted in the highest estimates for concentrations in surface water. The modeling results for selected scenarios that are most representative for Massachusetts are

included in Table 1 for comparison with other modeling results. The SERA report notes that the central estimate for surface water exposure based on GLEAMS modeling is similar to the value estimated by USEPA based on the PRZM/EXAMS modeling. The GLEAMS modeling data were the basis for the concentrations used in the SERA risk assessment.

SERA did not conduct modeling of concentrations in groundwater, but considered groundwater modeling results from USEPA and DAS (see also Table 2). The drinking water exposure assessment described by SERA is based on modeling results for surface water. As noted in SERA, modeling results for concentrations in surface water are higher than modeling results in groundwater.

3. Recent Information Related to Environmental Fate Characteristics and Model Input Values

As noted in the section above, the model input values for soil half-life and soil binding were found to be important parameters in modeling of aquatic exposure. Recent assessments by USEPA (2014A) and the European Union (EFSA, 2013) provide updated information for these properties of aminopyralid.

USEPA (2014A) considered the data from eight soils. The soil half-life values ranged from 31 to 193 days, with an average of 103.7 days. The K_D values ranged from 0.03 to 0.29 mL/g for soils with pH values of 6.1 to 7.8; K_D values of acid soils were in the range of 0.15 to 0.72 mL/g. The K_{OC} values for soils with near-neutral pH values were in the range of 1.05 to 7.54 mL/g and for acidic soils the values were in the range of 19.95 to 24.3 mL/g. In general, K_{OC} values increase with decreasing pH. USEPA (2014A) indicated that these data on soil half-life and soil binding (soil-water distribution coefficient data) are acceptable for use in exposure modeling and risk assessment.

In addition to the USEPA assessment, aquatic exposure modeling conducted as part of a European risk assessment (EFSA, 2013) was reviewed to provide additional data and information. The model input value for soil half-life geometric mean of 54.8 days was lower than the values used in the SERA risk assessment and the values used by USEPA. The model input value for soil binding parameter (mean K_{FOC} of 6.64 mL/g) was within the range of values used in the other modeling efforts reviewed above. The EFSA modeling results are included in Table 1.

Consideration of the data from the recent USEPA and EFSA assessments indicates that the input parameter values used in the GLEAMS modeling described in the SERA risk assessment were conservative values. In the refined modeling described below, DAR considered the recent information with the selection of input parameter values.

4. Additional Aquatic Exposure Modeling

For the purpose of this review, DAR conducted additional modeling using updated input parameter values to complement the existing data with refined exposure modeling results. The modeling conducted by DAR was done with recently released EPA water exposure models (see Appendix 1 and 2.

The model input parameter values for soil half-life and soil binding were based on the environmental fate information and data provided in the recent assessment by USEPA (2014A). The average value for soil half-life of 103.5 day and the lowest value for soil binding parameter K_D of 0.03 mL/g were used for model input. The application rate was the maximum labeled rate of 0.11 lbs of aminopyralid per acre. For surface water modeling, the watershed scenarios modeled were the EPA standard pond, the EPA index reservoir and a custom small pond scenario. Further details on model input can be found in Appendix 1.

The results of DAR modeling are presented below and compared with the modeling data summarized in the SERA risk assessment (Durkin, 2007) and EFSA (2013).

4.1. Surface Water Modeling

Additional modeling of surface water concentrations was conducted to complement the existing modeling data that were generated with EPA standard scenarios using modeling data that are more representative for Massachusetts ROW. The model scenario that was developed for surface water exposure assessment of herbicide components in ROW areas (Wijnja, 2010), was used in the modeling here with the latest version of the EPA surface water exposure model (see Appendix 1). The latest version of the EPA surface water exposure model also allows the modeling of a custom watershed scenario. For the purpose of this assessment, DAR developed a custom small pond scenario. More detailed information on the model input and modeling results can be found in Appendix 1.

The modeled surface water concentrations are summarized and compared with other modeling results in Table 1. To facilitate comparison of modeling results, results from other modeling were scaled, if necessary, to the value representative of an application rate of 0.11 lbs/acre.

The modeling results generated with the MA-specific ROW scenario by DAR show the highest concentrations for the custom small pond scenario. These higher concentrations are attributed to the smaller dimensions of the watershed, including a shallower pond, compared to the EPA standard pond and reservoir.

Comparison of the most conservative refined modeling results (ROW scenario and custom small pond) with the concentrations used in the SERA risk assessment indicate that the results are similar to the central values used in SERA risk assessment.

The results for the MA-specific ROW scenario with standard pond and index reservoir watersheds are lower than the concentration generated by EPA modeling for the same type of watersheds. This is likely the result of difference in the land use scenarios (ROW versus range land or a generic scenario) and weather input data. The results for the ROW scenario and custom small pond watershed resulted in higher concentrations compared to the EPA standard pond and EPA Index Reservoir water bodies.

Table 1. Modeling results for surface water concentrations of aminopyralid. The results are representative of an application rate of 0.11 lbs/acre.

Agency/Org.	Model/Scenario	Concentration (µg/L or ppb)		Source/Notes
		Peak	Longer-term	
DAR	MA ROW scenario with:			
	SWCC, EPA Standard Pond	0.612	0.477	Appendix 1A
	SWCC, EPA Index Reservoir	1.93	1.45	Appendix 1B
	SWCC, Custom Small Pond	12.1	3.32	Appendix 1C
SERA				Durkin, 2007:
	GLEAMS Standard, Pond	3.34 - 14.3	2.21 - 7.76	Table 6; 50 inch rainfall and rate of 0.11 lbs/acre
	GLEAMS-Driver, Pond	8.8 - 34.1	4.4 – 19.8	Table 9, 10; average rainfall and for rate of 0.11 lbs/acre
EPA				Durkin, 2007:
	PRZM/EXAMS, Reservoir	10.01	1.936	Table 11, rate of 0.11 lbs/acre
	GENEEC, EPA Standard Pond	6.38	5.39	″
DOW				Durkin, 2007:
	GENEEC	6.16	3.96	Table 11; rate of 0.11 lbs/acre
				″
SERA	Conc. used for Risk Assess.			Durkin, 2007:
	Central	11	4.4	Table 12, rate of 0.11 lbs/acre
	Lower	0.23	0.11	″
	Upper	66.0	28.6	″
EFSA				EFSA, 2013: Annex A
	FOCUS Step 1	20.4	20.1	Screening-level Assessment
	FOCUS Step 3	0.052	0.049	Late Spring Application, Pond D4 Scenario
	FOCUS Step 3	0.332	0.042	Late Spring Application, Stream Scenario D4

DAR modeling with ROW-scenario also evaluated the sensitivity of the results for the input value of the soil aerobic metabolism half-life. The model results did not change significantly for simulations with a soil aerobic metabolism half-life of 310.5 d compared to 103.5 d (Table 1 in Appendices 1A, 1B and 1C). The 310.5 d value was used in earlier modeling by EPA (see Section 2); the value of 103.5 d was more recently recommended for use in risk assessment (see Section 3).

Modeling data generated by the European EFSA agency show screening-level assessment concentrations that are higher than the DAR custom pond values, but concentrations for specific scenarios are lower than modeling results for all other scenarios included in Table 1.

4.2. Groundwater modeling results

Additional groundwater modeling was conducted with EPA models SCIGROW and PRZM-GW (Water Models | Pesticides | US EPA: http://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/about-water-exposure-models-used-pesticide).

SCI-GROW (Screening Concentration in Groundwater) as a screening-level tool to estimate drinking water exposure concentrations in groundwater resulting from pesticide use. As a screening tool, SCI-GROW provides conservative estimates of pesticides in groundwater. It is a generic model that provides peak estimates of compound concentrations in groundwater based on a given application rate, number of applications, and standard environmental fate parameters of soil aerobic half-life and soil binding constant.

The PRZM-GW (Pesticide Root Zone Model – Ground Water) model has the capability to consider variability in leaching potential of different soils, weather (including rainfall), cumulative yearly applications or depth to aquifer. The conceptual model is based on a rural drinking water well beneath an agricultural field (a high pesticide use area), which draws water from an unconfined, high water-table aquifer. Processes included in the conceptual model that influence pesticide transport through the soil profile include water flow, chemical specific dissipation and transportation parameters (i.e., degradation and sorption), and crop specific factors, including transpiration, pesticide interception and management practices.

Six different scenarios were developed for the PRZM-GW model. The modeling for the review presented here used was based on the Delmarva Sweet Corn - Evesboro Loamy Sand scenario. Delmarva Peninsula sweet corn scenario is one of the six PRZM-GW standard scenarios that fall within regions where groundwater is highly susceptible to nitrate contamination. The six scenarios are expected to provide reasonable upper bound estimates for pesticide concentrations for vulnerable groundwater sources (USEPA, 2015).

The Delmarva Corn scenario most closely represents the Virginia Coastal Plain spatially and characteristically. In the Delmarva Corn scenario, the vadose zone ends and the aquifer begins 9 meters (29.5 feet) below the land surface. It has been reported that 26 of 29 Virginia Coastal Plain counties have at least one domestic well with a depth to the bottom of the well screen of 30 feet or less. Using this example, it follows that modeling with PRZM-GW provides estimated drinking water concentrations (EDWCs) that represent a subset of a broadly distributed population relying on shallow, private drinking water wells.

The scenario characteristics for vegetation were adjusted to be representative of ROW vegetation. Weather input data were representative for Eastern Massachusetts. This model simulation can be considered to be representative of behavior at a vulnerable site given the loamy sand soil profile and the absence of a buffer zone around the well.

Details on the SCI-GROW and PRZM-GW modeling can be found in Appendices 2A and 2B. The modeling results are summarized in Table 2 and compared with the other ground water modeling data.

Table 2. Comparison of groundwater modeling results for concentrations of aminopyralid for maximum application rate of 0.11 lbs/acre.

Agency/Org.	Model/Scenario	Concentration (µg/L or ppb)		Source/Notes
		Peak	Longer-term	
DAR	SCIGROW	5.17		Appendix 2A ; K_{OC}:1.05; soil half-life: 103.5 d
	PRZM-GW	12.6	10.5	Appendix 2B; K_{OC}:1.05; soil half-life: 103.5 d
EPA				Durkin, 2007: Table 11
	SCI-GROW	0.627		Application rate of 0.11 lbs/acre; K_{OC}: 1.05; soil half-life: 38.7 d
DOW				Durkin, 2007:
	SCI-GROW	1.65		Table 11, for application rate of 0.11 lbs/A; K_{OC} of 7.1 and soil half-life of 88.6 d
	SCI-GROW	0.121		Rate: 0.11 lbs/acre; K_{OC} of 7.1; soil half-life of 30 d
				″
EFSA				EFSA, 2013: Annex A
	FOCUS PEARL	0.116		Annual application of 0.053 lbs ai/acre; field dissipation half-life of 14.1 d; K_{foc}: 5.14 mL/g

Modeling results from DAR show the highest concentrations due to the use of conservative values for soil adsorption constant and soil half-life input parameters. These input values are the most recent values that EPA recommends for use in risk assessment (see section 3).

It should be noted that the soil defined in the Delmarva Sweet Corn - Evesboro Loamy Sand scenario represents a sandy soil profile with relatively low organic matter content. Such a soil profile is considered to favor leaching of substances into the profile. In the model scenario, the soil is definedto have low organic matter (highest is 0.52 % organic carbon in top layers and 0.1 – 0.20 % in deeper soil layers). Percentage of sand in the soil layers is greater than 90 % and clay content is between 2 and 5%. These soil particle size distributions are similar to values for sandy soils that occur in southeastern Massachusetts and Cape Cod. For example, the Carver soils are sandy soils with clay content of 1 to 5 % and organic matter content in the ranges of 0.1 – 1.0 %. (Soil Survey for Barnstable County: http://nesoil.com/barnstable/index.htm).

4.3. Groundwater Monitoring Data

The ground water modeling results can further be evaluated by considering results from monitoring studies. At the time of this review, two studies were located that were publicly available (online) that included aminopyralid as a target analyte.

A groundwater monitoring study conducted in Wyoming by the US Geological Survey (USGS) included aminopyralid as a target analyte. Aminopyralid was not detected (Eddy-Miller et al., 2013).

In a monitoring study in the Bitterroot Valley, MT, aminopyralid was detected at a level of 0.1 µg/L in one of 46 samples from 23 wells (Schmidt and Mulder, 2009).

USGS pesticide use data indicate that there was substantial use of this herbicide in both Montana and Wyoming (Fig. 1).

These monitoring study results show low detection frequencies of aminopyralid in areas where this herbicide was used. When detected, the level was much lower than the ground water modeling data presented in section 4.2.

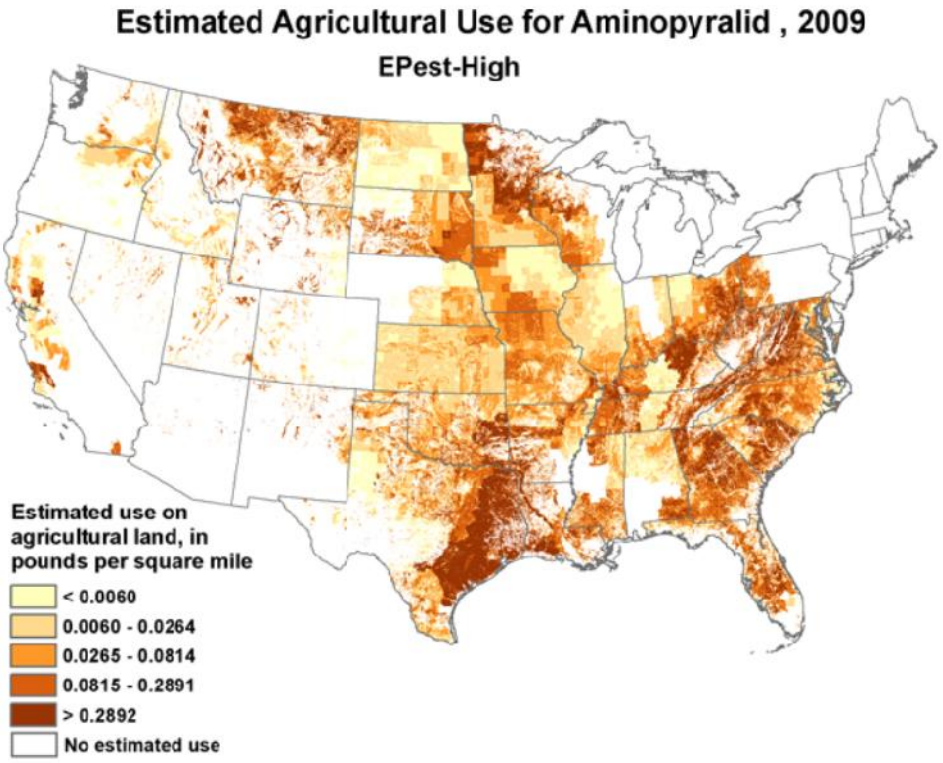

Figure 1 Estimated Agricultural use of Aminopyralid in the US during 2009. Accessed at: USGS NAWQA: The Pesticide National Synthesis Project

5. Comparison of Modeled Concentrations with Aquatic Life and Human Health Benchmarks

EPA developed benchmarks that can assist with the assessment of monitoring and modeling data. Surface water modeling data were compared with aquatic life bench mark to assess the potential for ecological effects in aquatic systems.

Comparison of modeled surface water concentrations with Aquatic Life Benchmarks for Aminopyralid (Table 3) can be helpful to assess risk to aquatic life (USEPA, 2014B). Comparison of the modeled concentrations in Table 1 (DAR data for peak 0.612 – 12.1 µg/L and chronic 0.477 to 3.32 µg/L) with the benchmarks in Table 3 shows levels well below benchmark values. This comparison indicates minimal risk to aquatic life.

Table 3. Aquatic life benchmarks for aminopyralid

Species	Acute (µg/L or ppb)	Chronic (µg/L or ppb)
Fish	>5,000	1360
Invertebrates	>49,300	10200
Non-vascular plants	18,000	
Vascular plants	>88,000	

Comparison of the modeled concentrations with human health benchmark values for aminopyralid can further assist with assessment of potential for human health effects.

The chronic or life-time human health benchmark (HHBM) value for aminopyralid is 3500 ppb (US EPA, 2014C). An acute HHBM value has not been established. The EPA risk assessment notes that aminopyralid is of low acute toxicity and therefore no acute reference dose was identified for any population.

Comparison of the modeled aminopyralid concentrations in groundwater and the HHBM indicates that there is no concern for effects on human health from drinking water containing residues of aminopyralid following application per label specifications..

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Appendix 1A: Summary of Water Modeling of Aminopyralid and the USEPA Standard Pond

Estimated Environmental Concentrations for aminopyralid are presented in Table 1 for the USEPA standard pond with the RightOfWay_MA_PAX field scenario. A graphical presentation of the year-to-year peaks is presented in Figure 1. These values were generated with the Surface Water Concentration Calculator (SWCC Version 1.106) (Water Models | Pesticides | US EPA)[1]. The SWCC model estimates pesticide concentrations in water bodies that result from pesticide applications to land. The SWCC is designed to simulate the environmental concentration of a pesticide in the water column and sediment and is used for regulatory purposes by the USEPA Office of Pesticide Programs (OPP). The SWCC uses PRZM version 5.0+ (PRZM5) and the Variable Volume Water Body Model (VVWM), replacing the older PE5 shell (last updated November 2006), which used PRZM3 and EXAMS.

Critical input values for the model are summarized in Tables 2 and 3. This model estimates that about 1.1% of aminopyralid applied to the field eventually reaches the water body. The main mechanism of transport from the field to the water body is by runoff (53.3% of the total transport) followed by spray drift (46.7%).

In the water body, pesticide dissipates with an effective water column half-life of 68.2 days. (This value does not include dissipation by transport to the benthic region; it includes only processes that result in removal of pesticide from the complete system.) The main source of dissipation in the water column is photolysis (effective average half-life = 71 days) followed by metabolism (1744.3 days) and volatilization (1.866018E+10 days).

In the benthic region, pesticide dissipation is negligible (1744.3 days). The main source of dissipation in the benthic region is metabolism (effective average half-life = 1744.3 days). The vast majority of the pesticide in the benthic region (92.5%) is in the pore water rather than sorbed to sediment.

Table 1. Estimated Environmental Concentrations (ppb) for aminopyralid.

	Soil half-life 103.5 d	Soil half-life 310.5 d
Peak (1-in-10 yr)	0.610	0.612
4-day Avg (1-in-10 yr)	0.596	0.598
21-day Avg (1-in-10 yr)	0.552	0.553
60-day Avg (1-in-10 yr)	0.476	0.477

[1] USEPA Water Models Pesticides: http://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/about-water-exposure-models-used-pesticide

365-day Avg (1-in-10 yr)	0.145	0.146
Entire Simulation Mean	0.726E-01	0.727E-01

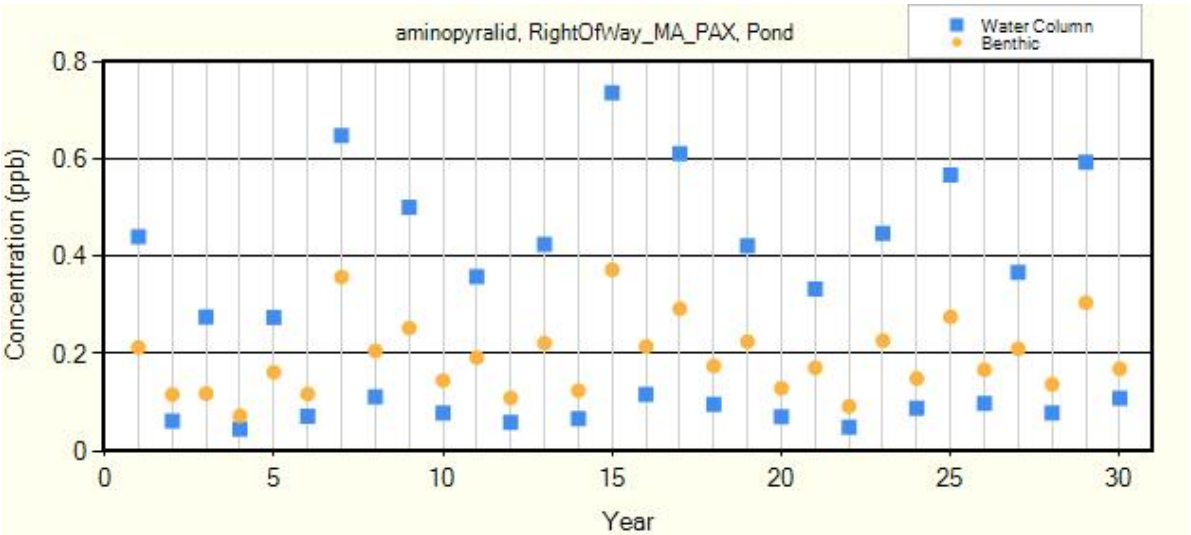
Table 2. Summary of Model Inputs for aminopyralid.

Scenario	RightOfWay_MA_PAX
Cropped Area Fraction	1
K_D (ml/g)	0.03
Water Half-Life (days) @ 20 °C	1073.6
Benthic Half-Life (days) @ 20 °C	1073.6
Photolysis Half-Life (days) @ 42 °Lat	0.6
Hydrolysis Half-Life (days)	0
Soil Half-Life (days) @ 20 °C	103.5
Foliar Half-Life (days)	
Molecular Wt	207
Vapor Pressure (torr)	7.4e-11
Solubility (mg/l)	2480

Table 3. Application Schedule for aminopyralid (every two years)

Date (Mon/Day)	Type	Amount (kg/ha)	Eff.	Drift
07/01	Foliar	0.11	0.95	0.05

Figure 1. Yearly Peak Concentrations


aminopyralid, RightOfWay_MA_PAX, Pond
Water Column
Benthic
Concentration (ppb)
0.8
0.6
0.4
0.2
0
0
5
10
15
20
25
30
Year

Appendix 1B: Summary of Water Modeling of aminopyralid and the USEPA Standard Reservoir

Estimated Environmental Concentrations for aminopyralid are presented in Table 1 for the USEPA standard reservoir with the RightOfWay_MA_PAX field scenario. A graphical presentation of the year-to-year peaks is presented in Figure 1. These values were generated with the Surface Water Concentration Calculator (SWCC Version 1.106). Critical input values for the model are summarized in Tables 2 and 3.

This model estimates that about 0.72% of aminopyralid applied to the field eventually reaches the water body. The main mechanism of transport from the field to the water body is by runoff (78.9% of the total transport) followed by spray drift (21.1%).

In the water body, pesticide dissipates with an effective water column half-life of 53.4 days. (This value does not include dissipation by transport to the benthic region; it includes only processes that result in removal of pesticide from the complete system.) The main source of dissipation in the water column is photolysis (effective average half-life = 97.3 days) followed by washout (126.8 days), metabolism (1744.3 days), and volatilization (2.556444E+10 days).

In the benthic region, pesticide dissipation is negligible (1744.3 days). The main source of dissipation in the benthic region is metabolism (effective average half-life = 1744.3 days). The vast majority of the pesticide in the benthic region (92.5%) is in the pore water rather than adsorbed to sediment.

Table 1. Estimated Environmental Concentrations (ppb) for aminopyralid.

	Soil Half-life 103.5 d	Soil Half-life 310.5 d
Peak (1-in-10 yr)	1.11	1.11
4-day Avg (1-in-10 yr)	1.08	1.08
21-day Avg (1-in-10 yr)	0.985	0.989
60-day Avg (1-in-10 yr)	0.792	0.794
365-day Avg (1-in-10 yr)	0.223	0.224
Entire Simulation Mean	0.938E-01	0.941E-01

Table 2. Summary of Model Inputs for aminopyralid.

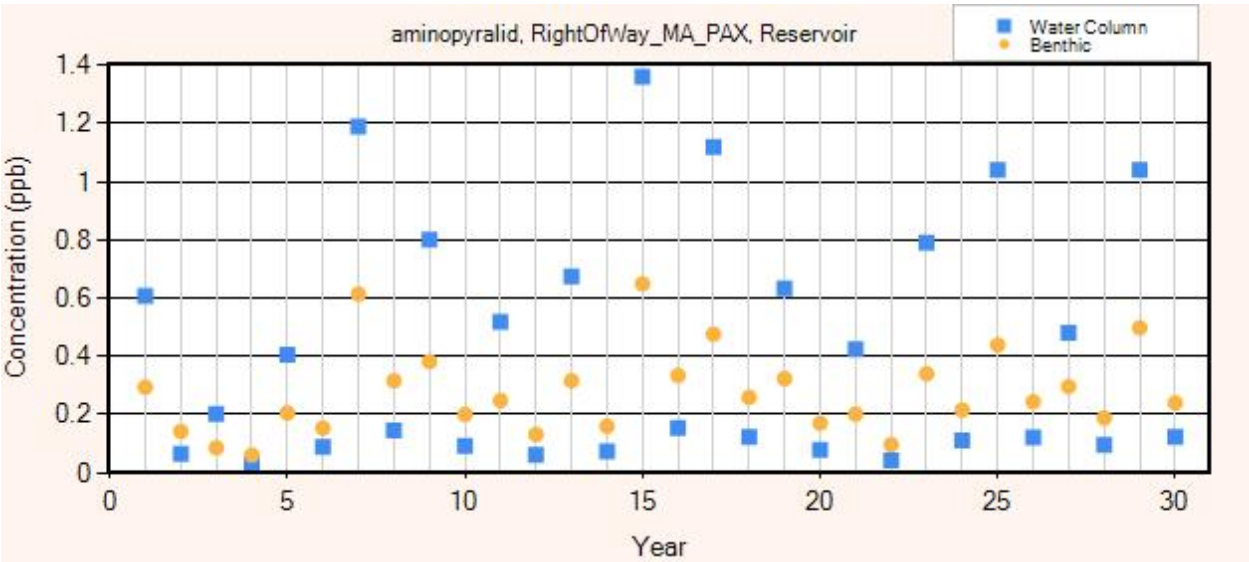
Scenario	RightOfWay_MA_PAX
Cropped Area Fraction	1.0
K_D (ml/g)	0.03

Water Half-Life (days) @ 20 °C	1073.6
Benthic Half-Life (days) @ 20 °C	1073.6
Photolysis Half-Life (days) @ 42 °Lat	0.6
Hydrolysis Half-Life (days)	0
Soil Half-Life (days) @ 20 °C	103.5
Foliar Half-Life (days)	
Molecular Wt	207
Vapor Pressure (torr)	7.4e-11
Solubility (mg/l)	2480

Table 3. Application Schedule for aminopyralid (every two years)

Date (Mon/Day)	Type	Amount (kg/ha)	Eff.	Drift
07/01	Foliar	0.11	0.95	0.05

Figure 1. Yearly Peak Concentrations



Appendix 1C: Summary of Water Modeling of aminopyralid in a Custom Small Pond Scenario

Estimated Environmental Concentrations for aminopyralid are presented in Table 1 for the custom small pond with the RightOfWay_MA_PAX field scenario. A graphical presentation of the year-to-year peaks is presented in Figure 1. These values were generated with the Surface Water Concentration Calculator (SWCC Version 1.106). Critical input values for the model are summarized in Tables 2 and 3.

The custom watershed characteristics were made to be more representative of a ROW scenario by considering a smaller catchment area-to-pond area/volume; it was adapted from the TOXSWA scenario: http://www.pesticidemodels.eu/toxswa/eu-registration . The depth of the pond was chosen to be 0.33 m initial depth and 0.67 m maximum depth. The applications occurred every two years.

This model estimates that about 0.62% of aminopyralid applied to the field eventually reaches the water body. The main mechanism of transport from the field to the water body is by runoff (96.8% of the total transport) followed by spray drift (3.24%).

In the water body, pesticide dissipates with an effective water column half-life of 11.6 days. (This value does not include dissipation by transport to the benthic region; it includes only processes that result in removal of pesticide from the complete system.) The main source of dissipation in the water column is photolysis (effective average half-life = 11.7 days) followed by metabolism (1744.3 days) and volatilization (3.078929E+09 days).

In the benthic region, pesticide dissipation is negligible (1744.3 days). The main source of dissipation in the benthic region is metabolism (effective average half-life = 1744.3 days). The vast majority of the pesticide in the benthic region (92.5%) is in the pore water rather than sorbed to sediment.

Table 1. Estimated Environmental Concentrations (ppb) for aminopyralid.

	Soil Half-life 103.5 d	Soil Half-life 310.5 d
Peak (1-in-10 yr)	12.2	12.3
4-day Avg (1-in-10 yr)	10.6	10.7
21-day Avg (1-in-10 yr)	6.63	6.66
60-day Avg (1-in-10 yr)	3.46	3.47
365-day Avg (1-in-10 yr)	0.598	0.600
Entire Simulation Mean	0.218	0.219

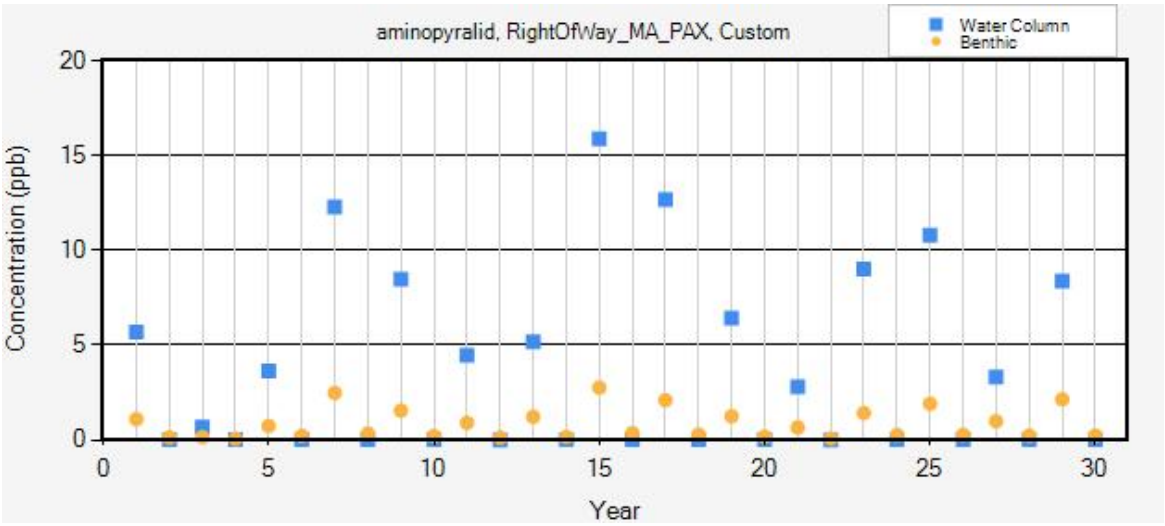
Table 2. Summary of Model Inputs for aminopyralid.

Scenario	RightOfWay_MA_PAX
Cropped Area Fraction	1.0
K_d (ml/g)	0.03
Water Half-Life (days) @ 20 °C	1073.6
Benthic Half-Life (days) @ 20 °C	1073.6
Photolysis Half-Life (days) @ 42 °Lat	0.6
Hydrolysis Half-Life (days)	0
Soil Half-Life (days) @ 20 °C	103.5
Foliar Half-Life (days)	
Molecular Wt	207
Vapor Pressure (torr)	7.4e-11
Solubility (mg/l)	2480

Table 3. Application Schedule for aminopyralid (every two years)

Date (Mon/Day)	Type	Amount (kg/ha)	Eff.	Drift
07/01	Foliar	0.11	0.99	0.01

Figure 1. Yearly Peak Concentrations



Appendix 2A: Groundwater Modeling with SCIGROW

SCI-GROW (Screening Concentration in Groundwater) is a screening-level tool to estimate drinking water exposure concentrations in groundwater resulting from pesticide use. As a screening tool, SCI-GROW provides conservative estimates of pesticides in groundwater. It is a generic model that provides peak estimates of compound concentrations in groundwater based on a given application rate, number of applications, and standard environmental fate parameters of soil aerobic half-life and soil binding constant. SCI-GROW is an empirical model based on a linear best fit through 13 single-application groundwater studies. These studies were typically two to three year studies. SCI-GROW is a screening level risk assessment tool that has been used to evaluate the effect of pesticide use on groundwater. More information on the SCI-GROW model is available at EPA website for water models: Water Models | Pesticides | US EPA [2]

Model input and output is given below.

```
SCIGROW

                    VERSION 2.3
          ENVIRONMENTAL FATE AND EFFECTS DIVISION
               OFFICE OF PESTICIDE PROGRAMS
           U.S. ENVIRONMENTAL PROTECTION AGENCY
                      SCREENING MODEL
              FOR AQUATIC PESTICIDE EXPOSURE


 SciGrow version 2.3
 chemical:Aminopyralid
 time is  2/20/2015  12: 4:28
 ------------------------------------------------------------------------
  Application      Number of       Total Use    Koc      Soil Aerobic
  rate (lb/acre)  applications   (lb/acre/yr)  (ml/g)   metabolism (days)
 ------------------------------------------------------------------------
      0.110           1.0           0.110      1.05E+00      103.5
 ------------------------------------------------------------------------
 groundwater screening cond (ppb) =   5.17E+00
 ************************************************************************
```

[2] USEPA Water Models: http://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/about-water-exposure-models-used-pesticide

Appendix 2B: Groundwater Modeling with PRZM-GW model

Analysis for Aminopyralid and the DELMARVA Sweet Corn - Evesboro Loamy Sand Scenario in the PRZM-GW model system

PRZM-GW (Pesticide Root Zone Model – Ground Water) was developed as the harmonized tool for assessing pesticide concentrations in groundwater. This model has the capability to consider variability in leaching potential of different soils, weather (including rainfall), cumulative yearly applications or depth to aquifer. The conceptual model is based on a rural drinking water well beneath an agricultural field (a high pesticide use area), which draws water from an unconfined, high water-table aquifer. Processes included in the conceptual model that influence pesticide transport through the soil profile include water flow, chemical specific dissipation and transportation parameters (i.e., degradation and sorption), and crop specific factors, including transpiration, pesticide interception and management practices.

Six different scenarios were developed for the PRZM-GW model. The modeling for the review presented here was based on the Delmarva Sweet Corn - Evesboro Loamy Sand scenario. Delmarva Peninsula sweet corn scenario is one of the six PRZM-GW standard scenarios that fall within regions where groundwater is highly susceptible to nitrate contamination. The six scenarios are expected to provide reasonable upper bound estimates for pesticide concentrations for vulnerable groundwater sources (USEPA, 2015)[3].

The Delmarva Corn scenario most closely represents the Virginia Coastal Plain spatially and characteristically. In the Delmarva Corn scenario, the vadose zone ends and the aquifer begins 9 meters (29.5 feet) below the land surface. It has been reported that 26 of 29 Virginia Coastal Plain counties have at least one domestic well with a depth to the bottom of the well screen of 30 feet or less. Using this example, it follows that modeling with PRZM-GW provides estimated drinking water concentrations (EDWCs) that represent a subset of a broadly distributed population relying on shallow, private drinking water wells.

Weather data were representative of Eastern Massachusetts and scenario characteristics for vegetation were adjusted to be representative of ROW vegetation. Vegetation height, root zone depth were set at values that were used in ROW model scenario used of surface water modeling (Wijnja, 2010). Model simulation can be considered to be representative of behavior at a

[3] USEPA, 2015.Implementation of the Pesticide Root Zone Model Groundwater (PRZM-GW) for Use in EPA's Pesticide Exposure Assessments. USEPA, Office of Pesticide Program, Environmental Fate and Effects Division (EFED), September 8, 2015. Accessed at: http://www.epa.gov/sites/production/files/2015-11/documents/attachment_1_-_implementation_report_of_przm-gw_final.pdf

vulnerable site given the loamy sand soil profile and the absence of a buffer zone around the well.

Estimated groundwater concentrations and breakthrough times for aminopyralid are presented in Table 1 for the DELMARVA sweet corn - Evesboro loamy sand groundwater scenario. A graphical presentation of the daily concentrations in the aquifer is presented in Figure 1. These values were generated with the PRZM-GW (Version 1.07). Critical input values for the model are summarized in Tables 2 and 3.

Table 1. Groundwater Results for aminopyralid and the DELMARVA sweet corn - Evesboro loamy sand Scenario for ROW in Massachusetts

	Soil half-life 103.5 d	Soil half-life 310.5 d
Peak Concentration (ppb)	12.6	19.6
Post-Breakthrough Mean Concentration (ppb)	10.5	15.8
Entire Simulation Mean Concentration (ppb)	7.52	11.3
Average Breakthrough Time (days)	3013.025	3013.025
Throughputs	3.63754	3.63754

Table 2. Chemical Properties for Groundwater Modeling of aminopyralid.

Koc (ml/g)	1.05
Surface Soil Half Life (days)	103.5 (310.5)
Hydrolysis Half Life (days)	0
Diffusion Coefficint Air (cm2/day)	0.0
Henry's Constant	0.0
Enthalpy (kcal/mol)	0.0

Table 3. Pesticide application scheme used for aminopyralid. This application scheme was applied once every 2 years of the simulation.

Application Date (Month/Day)	Application Method	Application Rate (kg/ha)
07/01	Above canopy application	0.11

Figure 1. Aquifer Breakthrough Curve for aminopyralid and the DELMARVA Sweet Corn - Evesboro Loamy Sand Scenario. Groundwater depth is 10 m and application of 0.11 lbs/acre occur every 2 years. Results shown are for simulation with soil half-life of 103.5 d.