

APPENDIX B – CHAPTER 1 HERBICIDE ACTIVE INGREDIENT PROPERTIES

1.0 INTRODUCTION

Intertox was not asked to focus on the fate and transport of chemicals, but we have included a brief summary of information available for the 12 herbicide active ingredients not included in the 1993 EIS: clopyralid, MCPA, bromoxynil, diflufenzopyr, flumioxazin, fluroxypyr, norflurazon, pendimethalin, pyraflufen, sulfentrazone, and tebuthiuron. The information contained in this chapter should not be held to the standards of comprehensiveness that have been outlined for the toxicology and risk assessment components of this report.

2.0 HERBICIDES (ACTIVE INGREDIENTS)

This section has been updated with information regarding the fate, transport, and metabolism of the 12 herbicide active ingredients not included in the 1993 EIS: clopyralid, MCPA, bromoxynil, diflufenzopyr, flumioxazin, fluroxypyr, norflurazon, pendimethalin, pyraflufen, sulfentrazone, and tebuthiuron.

2.1 Clopyralid

2.1.1 Environmental Fate

In soil and water, clopyralid is degraded primarily by microbial metabolism. It is resistant to degradation by sunlight, hydrolysis, or other chemical degradation. It is water-soluble, does not bind strongly with soils, and has the potential to be highly mobile in soils, especially sandy soils. Clopyralid is not highly volatile (Tu *et al.*, 2001).

Soil – Clopyralid is moderately persistent in soils. Because it is degraded entirely by soil microbes, soil conditions that maximize microbial activity (warm and moist) will facilitate clopyralid degradation. The average half-life of clopyralid in soils is one to two months but can range from one week to one year depending on the soil type, temperature, and rates of application (Tu *et al.*, 2001).

Water – Clopyralid is highly water-soluble and will not bind with suspended particles in the water column. Degradation is almost entirely through microbial metabolism in aquatic sediments, but because clopyralid does not bind with sediments readily, it can be persistent in an aquatic environment. The half-life of clopyralid in water ranges from 8 to 40 days (Tu *et al.*, 2001).

2.1.2 Transport

When clopyralid enters the soil through direct spray, runoff from plant foliage, or translocation from the roots of treated plants, it rapidly disassociates to the anion form. The negatively charged anion form is highly water-soluble and has a very low capacity to adsorb to soil particles. Consequently, clopyralid has the potential to be highly mobile in the environment. Clopyralid's chemical characteristics suggest it has a high potential for movement, but most field studies found that it is not as mobile expected. Where clopyralid leaches to lower soil depths, it persists longer than it does at the surface because the

microbial populations generally decrease with soil depth (Tu *et al.*, 2001).

2.1.3 Metabolism

Mode of Action – Clopyralid is an “auxin mimic” or synthetic auxin. This type of herbicide kills the target weed by mimicking the plant growth hormone auxin (indole acetic acid), and when administered at effective doses, cause uncontrolled and disorganized plant growth that leads to plant death. The exact mode of action of clopyralid has not been fully described but it is believed to acidify the cell wall, which results in cell elongation. Low concentrations of clopyralid can stimulate RNA, DNA, and protein synthesis leading to uncontrolled cell division and disorganized growth, and ultimately, vascular tissue destruction. High concentrations of clopyralid can inhibit cell division and growth (Tu *et al.* 2001).

Plant Metabolism – Clopyralid passes rapidly into leaves and roots of plants and is rain-fast within two hours. Once inside the plant, clopyralid is converted to the anion form and transported throughout the plant. It is not readily degraded by the plant and can be persistent, even in non-susceptible species (Tu *et al.*, 2001).

Animal Metabolism – The manufacturer reports that studies found that the majority of clopyralid ingested by mammals was excreted unmetabolized in their urine within 24 hours. Some clopyralid, however, was retained in their livers and kidneys (Tu *et al.*, 2001).

2.2 MCPA

2.2.1 Environmental Fate

Soil – MCPA and its formulations are rapidly degraded by soil microorganisms and it has low persistence, with a reported field half-life of 14 days to 1 month, depending on soil moisture and soil organic matter. Decreased soil moisture and microbial activity, as well as increased soil organic matter, will prolong the field half-life for MCPA (EXTOXNET, 1996).

Water – MCPA is relatively stable to light breakdown, but can be rapidly broken down by microorganisms. In sterilized water, it takes about five weeks for half of the compound to degrade due to the action of sunlight. In rice paddy water, however, MCPA is almost totally degraded by aquatic microorganisms in under two weeks (EXTOXNET, 1996).

2.2.2 Transport

MCPA readily leaches in most soils, but its mobility decreases with increasing organic matter. MCPA and its formulations show little affinity for soil (EXTOXNET, 1996).

2.2.3 Metabolism

Mode of Action – MCPA works by concentrating in the actively growing regions of a plant (meristematic tissue) where it interferes with protein synthesis, cell division and ultimately the growth of the plant (EXTOXNET, 1996).

Plant Metabolism – MCPA is absorbed, translocated, and actively broken down by vegetation. The metabolite found in plants is 2-methyl-4-chlorophenol (EXTOXNET, 1996).

Animal Metabolism – MCPA is rapidly absorbed and eliminated from mammalian systems. Rats eliminated nearly all of a single oral dose within 24 hours, mostly in urine with little or no metabolism. In another rat study, three quarters of the dose was eliminated within two days. All was gone by the eighth day. Humans excreted about half of a 5 mg dose in the urine within a few days. No residues were found after day five. Cattle and sheep fed MCPA in low to moderate doses in the diet for two weeks had no residues from levels less than about 18 mg/kg. The major metabolite of MCPA is 2-methyl-4-chlorophenol in the free and conjugated form, which is formed in the liver (EXTOXNET, 1996a).

2.3 Bromoxynil

2.3.1 Environmental Fate

Soil – Bromoxynil has a low persistence in soil. It is broken down in the environment by photolytic degradation, abiotic hydrolysis and microbial-mediated metabolism under both aerobic and anaerobic conditions. In sandy soil, the half-life is about 10 days. Degradation in clay was slower, with half of the bromoxynil degraded to its metabolites in about a 2-week period at 25°C. The persistence of the compound is also slightly longer in peat field soils than in the sandy soils (EXTOXNET, 1996b; U.S. EPA, 1998a).

Water – Environmental fate studies indicate that bromoxynil (phenol and octanoate) should not persist in surface waters. The aerobic aquatic metabolism study shows rapid degradation with a half-life of <12 hours (U.S. EPA, 1998a).

2.3.2 Transport

Based on the available data, U.S. EPA concluded that the potential for ground water contamination from bromoxynil octanoate is low; it does not exhibit the mobility or persistence characteristics of pesticides that are normally found in ground water (U.S. EPA, 1998a).

2.3.3 Metabolism

Mode of Action – Bromoxynil is a nitrile herbicide that acts by inhibiting photosynthesis in target species of plant. Its primary use is for control of post-emergent broadleaf weeds (EXTOXNET 1996b).

Plant Metabolism – The herbicide works by disrupting the plants ability to produce energy for cell-related activities. It is not readily translocated throughout the plant once it has been absorbed (EXTOXNET 1996b).

Animal Metabolism – No bromoxynil was present in the milk or feces of cows 9 days after exposure to low doses of the herbicide. Less than 20% of the compound was excreted in urine as the parent compound (EXTOXNET 1996b).

2.4 Diflufenzopyr

2.4.1 Environmental Fate

The stability of Diflufenzopyr varies in the environment. In aerobic soil, the half-life ranged from 8-10 days; in an aerobic aquatic environment, the half life ranged from 5-26 days. In an anaerobic aquatic environment, the half-life was 20 days (U.S. EPA, 1999).

2.4.2 Transport

Both the diflufenzopyr and its metabolites are considered very mobile in soil. However, based upon proposed uses, fate characteristics, and model predictions, EPA does not expect diflufenzopyr to reach drinking water resources in significant quantities (U.S. EPA, 1999).

2.4.3 Metabolism

Mode of Action – Diflufenzopyr provides control of postemergent noxious broadleaf weeds by inhibiting the plant's ability to spread auxins, which normally play a key role in plant development and cell growth (BASF, 2003). Diflufenzopyr can enhance the effect of Dicamba when the two herbicides are applied concurrently (U.S. EPA, 1999).

Plant Metabolism – Diflufenzopyr is absorbed through a plant's leaves, roots and shoots and is translocated to the growing parts of the plant (BASF 2003).

Animal Metabolism – In a rat metabolism study, radio-labeled diflufenzopyr administered orally was partially absorbed and rapidly eliminated. By oral administration, 20 to 44 % of the dose was eliminated in urine and 49 to 79 % in feces. Elimination half-life in urine and feces was 5.2-6.9 hours for all single dose groups and 7.7-10.8 hours for all repeat oral dose groups. Total radioactive residues in tissues from rats in all dose groups were <3% of the administered dose. Blood residue levels for all dose groups were <1% of the administered dose at all sampling intervals through 72 hours post-dose. Diflufenzopyr was eliminated in urine, feces and bile primarily as unchanged parent compound. Metabolism of diflufenzopyr was also conducted in laying hens and lactating goats. The data showed diflufenzopyr was rapidly eliminated from the animals (U.S. EPA, 1999).

2.5 Flumioxazin

2.5.1 Environmental Fate

Flumioxazin is unstable in the environment with a half-life ranging from 0.01-5 days depending upon pH. The data indicates hydrolysis is probably the primary pathway for degradation. Flumioxazin is unstable in the presence of light with a one day half-life in water and 3-8 day half-life on soil. The aerobic soil metabolism studies observed a moderate rate of metabolism with a half-life of 5-19 days depending on the soil type. The anaerobic soil metabolism study with a saturated soil observed a half-life of less than one day. Terrestrial field dissipation of flumioxazin in loam and sandy soils ranged from 10-42 days. The high value was thought to be due to a lack of rainfall or irrigation during the sampling period (CalEPA, 2003).

2.5.2 Transport

Available data indicate that flumioxazin is relatively unstable and its potential to leach to groundwater is low. However, the potential for the degradation products APF and THPA to leach to groundwater is high. These residues may persist in the environment and may leach to groundwater. Flumioxazin could potentially reach surface water via spray drift or runoff under certain environmental conditions (U.S. EPA, 2001).

2.5.3 Metabolism

Mode of Action – Flumioxazin is a selective control herbicide used to control preemergent and postemergent grasses and broadleaf weeds. Flumioxazin interferes with heme and chlorophyll biosynthesis, resulting in a buildup of photo-toxic porphyrins (U.S. EPA, 2001).

Animal Metabolism – After oral administration in rats, gastrointestinal tract absorption of flumioxazin was greater than 90% at 1 mg/kg and up to 50% at 100 mg/kg. At least 97% was recovered in feces and urine 7 days after dosing. In addition to the untransformed parent compound, 7 metabolites were identified in urine and feces (38-46% for low dose and about 71% at high dose) (U.S. EPA, 2001).

2.6 Fluroxypyr

2.6.1 Environmental Fate

Fluroxypyr is resistant to photolysis in water with a half-life of 197 to 429 days at pH 5. In soil, the half-life due to photolysis is 119 days. It is also stable to hydrolysis with an estimated half-life of 454 days at pH 7. In soil, the half-life from bacterial metabolism under aerobic conditions was 23 days. Metabolism under aerobic and anaerobic aquatic conditions resulted in a half-lives of 14 and 8 days, respectively (U.S. EPA, 1998b).

2.6.2 Transport

U.S. EPA's evaluation of laboratory studies suggests that fluroxypyr is mobile to very mobile in soil. Field studies, however, suggest that potential hydrolysis and microbial degradation act to limit its leaching potential and persistence (U.S. EPA, 1998b).

2.6.3 Metabolism

Mode of Action – Fluroxypyr is a selective herbicide used to control annual and perennial broadleaf weeds and woody brush post emergence. Fluroxypyr binds to auxin receptor sites causing inhibition of plant growth and cellular processes. It also interferes with the processes of enzyme production and nitrogen metabolism in target plants (EPA 1998b).

Animal Metabolism – Radio-labeled fluroxypyr administered to rats showed the principal route of excretion being expired CO₂, followed by urine and feces. It was extensively absorbed and rapidly eliminated (U.S. EPA, 1998b).

2.7 Norflurazon

2.7.1 Environmental Fate

Norflurazon is a persistent and mobile compound. Norflurazon's primary route of dissipation appears to be photodegradation in water and on soil to desmethyl norflurazon with a half-life of 2-3 days and 12-15 days, respectively. Norflurazon is stable to hydrolysis and degrades slowly in aerobic soil with a half-life of 130 days. In an aerobic aquatic study, norflurazon degraded to desmethyl norflurazon with a half-life of 6-8 months. Under anaerobic conditions, norflurazon is persistent with a half-life of approximately 8 months. The degradate, desmethyl norflurazon, is also persistent under aerobic and anaerobic conditions (U.S. EPA 1996a).

2.7.2 Transport

Norflurazon is mobile to highly mobile in soil. The mobility of desmethyl norflurazon (a major degradate of norflurazon), in soils other than high organic peat, has not been adequately defined. Fish accumulation data have shown that norflurazon has a low potential to bioaccumulate in bluegill sunfish. There is a concern that norflurazon may contaminate surface water at application via spray drift and runoff. Substantial amounts of applied norflurazon could be available for runoff several months postapplication. Norflurazon exhibits some of the properties and characteristics of chemicals that have been detected in groundwater. Data suggest that norflurazon leaches to groundwater as a result of normal agricultural use (U.S. EPA, 1996a).

2.8 Metabolism

Mode of Action – Norflurazon is a selective herbicide; it suppresses the production of carotenoids through uptake of pesticide in the root system (U.S. EPA, 1996b).

Plant Metabolism – Norflurazon is translocated to the foliage, ears, and grain of corn, the roots of carrots, the foliage and nuts of peanuts, the foliage, heads, and grain of wheat, and the seeds and foliage of cotton. Norflurazon is absorbed from the soil by citrus, soybean, and cotton. Conjugated and free forms of norflurazon and its desmethyl metabolite were identified in these plants at maturity (U.S. EPA, 1996b).

Animal Metabolism – In rats administered Norflurazon orally and by i.v., between 18.5-28.4% of the administered dose was eliminated in urine by 96 hours post-dose, and between 65.3-79.5% of the administered dose was eliminated in feces. Thirteen metabolites of norflurazon were isolated. There appear to be 4 pathways for norflurazon metabolism: N-demethylation; displacement of the chlorine atom by glutathione; glutathione attack on the aromatic ring; and replacement of the chlorine atom by hydrogen (U.S. EPA, 1996b).

2.9 Pendimethalin

2.9.1 Environmental Fate

Soil – Pendimethalin is moderately persistent, with a field half-life of approximately 40 days. It does not undergo rapid microbial degradation except under anaerobic conditions. Slight

losses of pendimethalin can result from photodecomposition and volatilization (EXTOXNET, 1996c).

Water – Pendimethalin is stable to hydrolysis, but may be degraded by sunlight in aquatic systems. Pendimethalin may also be removed from the water column by binding to suspended sediment and organic matter. It is rapidly degraded under anaerobic conditions once precipitated to sediment (EXTOXNET, 1996c).

2.9.2 Transport

Pendimethalin is strongly adsorbed by most soils. Increasing soil organic matter and clay is associated with increased soil binding capacity. It is practically insoluble in water, and thus will not leach appreciably in most soils, and should present a minimal risk of groundwater contamination (EXTOXNET, 1996c).

2.9.3 Metabolism

Mode of Action – Pendimethalin is a selective herbicide used to control annual grasses and certain broadleaf weeds at both preemergent and early post emergent stages (EXTOXNET 1996c). The mechanism of action is microtubule disruption (EPA 1997a).

Plant Metabolism – Pendimethalin is absorbed by plant roots and shoots, and inhibits cell division and cell elongation. Once absorbed into plant tissues, translocation is limited and pendimethalin breaks down via oxidation. Pendimethalin is not absorbed by the leaves of grasses, and only very small amounts are taken up by plants from the soil. Residues on crops at harvest are usually below detectable levels (0.05 ppm) (EXTOXNET, 1996c).

Animal Metabolism – Pendimethalin is largely unabsorbed from the gastrointestinal tract, and excreted unchanged in the feces. Pendimethalin, which does become absorbed into the bloodstream from the gastrointestinal tract, is rapidly metabolized in the kidneys and liver and is then excreted as metabolites via urine. One day after administration to rats, 90% of a 37 mg/kg dose was recovered in feces and urine. After 4 days this figure was 96%. Lower doses resulted in almost 100% excretion within 4 days. Tissue burdens of the compound were on the order of 0.3 mg/kg, with slightly higher concentrations in the body fat (EXTOXNET, 1996c).

2.10 Pyraflufen

2.10.1 Environmental Fate

The environmental fate data indicate that pyraflufen-ethyl is stable in the environment under acidic conditions (pH 5), with an estimated half-life of 267 days. However, the chemical is rapidly hydrolyzed with neutral or alkali conditions with a half-life of 11 days (pH 7) and 6 hours (pH 9). Pyraflufen-ethyl is readily degraded by sunlight with a half-life of 1.25 days in water and 2.2 days on soil. With aerobic soil conditions, the half-life of pyraflufen-ethyl was less than one day. Similarly, in water with anaerobic soil conditions the chemical's half-life was also less than one day (CalEPA, 2004).

2.10.2 Transport

Pyraflufen-ethyl has low mobility in the soil. This physical property was evaluated with a soil column leaching study utilizing radioactively labeled pyraflufen-ethyl. The majority (95%) of the radioactivity remained in the top 10 cm of soil indicating low mobility in soil. Soil dissipation of pyraflufen-ethyl in the field was evaluated in California and Washington. The results indicate pyraflufen-ethyl rapidly dissipates from the soil surface with a half-life of only a few hours (CalEPA, 2004).

2.10.3 Metabolism

Mode of Action – Pyraflufen-ethyl is a protoporphyrinogen inhibitor that inhibits protoporphyrinogen IX oxidase causing cell membranes to become necrotic and die (CalEPA, 2004).

Plant Metabolism – The metabolism of pyraflufen-ethyl has been studied in cotton, wheat, and potato. Metabolism in the plant involves ester hydrolysis, de-methylation on the pyrazole ring and further degradation of the phenoxycetate moiety to bound polar metabolites (U.S. EPA, 2002).

Animal Metabolism – Pyraflufen-ethyl is rapidly absorbed, metabolized, and excreted to feces and urine, with greater than 90% of the administered dose excreted within 24 hours in rats. Based on metabolism studies with goats, hens, and rats, there is no reasonable expectation that measurable pyraflufen-ethyl-related residues will occur in meat, milk, poultry, or eggs from the proposed use (U.S. EPA, 2002).

2.11 Sulfentrazone

2.11.1 Environmental Fate

Based on the current environmental fate data base, sulfentrazone has the following characteristics: 1) moderately soluble, 2) not susceptible to hydrolysis, 3) extremely susceptible to direct photolysis in water, 4) very stable to photolysis on soil, 5) aerobic half-life of 1.5 years, 6) anaerobic half-life of 9 years, 7) very high mobility in soil (average $K_{oc} = 43$, $K_d < 1$), and 8) low volatility from soils and water (U.S. EPA, 1997b).

2.11.2 Transport

With the above properties, it appears that sulfentrazone is highly mobile and persistent, and has a strong potential to leach into groundwater and move offsite to surface water. The primary routes of dissipation are through direct aqueous photolysis and leaching. Direct photolysis would only be an effective dissipation pathway in clear shallow waters because sulfentrazone is stable to hydrolysis and biodegradation. Low soil/water partitioning indicates that most sulfentrazone runoff is through dissolution in runoff water, as opposed to adsorption to eroding soil. It also indicates that most sulfentrazone will be partitioned in the water column instead of in the suspended and bottom sediments (U.S. EPA, 1997b).

2.11.3 Metabolism

Mode of Action – Sulfentrazone acts by inhibiting protoporphyrinogen oxidase (PPO). Following soil application, sulfentrazone is primarily taken up by plant roots. Contact with leaves causes desiccation and necrosis of plant tissue. Treated plants become necrotic and die following exposure to light (U.S. EPA, 1997b).

Animal Metabolism – A metabolism study in rats resulted in the administered dose and nearly all radioactivity excreted in the urine, indicating nearly complete absorption. Most of the test article was eliminated by urine and feces within 72 hours, and appeared to be independent of dose and sex (U.S. EPA, 1997b).

2.12 Tebuthiuron

2.12.1 Environmental Fate

Soils – Tebuthiuron is highly persistent in soil. Reported field half-lives are from 12 to 15 months in areas with over 40 inches annual rainfall, with longer half-lives expected in drier areas or in soils with high organic matter content. Tebuthiuron is broken down slowly in the soil through microbial degradation. Photodecomposition, or breakdown by sunlight, is negligible, as is volatilization (or evaporation from the soil surface) (EXTOXNET, 1996d).

Water – Tebuthiuron is resistant to photodegradation in water. In continuously irradiated water, Tebuthiuron did not degrade in 33 days. U.S. EPA has concluded that Tebuthiuron is persistent in both aerobic and anaerobic aquatic environments (U.S. EPA 1994).

2.12.2 Transport

Tebuthiuron is poorly bound to soil, suggesting high mobility. In field studies, however, little or no lateral movement has been seen in soils with appreciable clay or organic matter content. Neither tebuthiuron nor its degradation products have been detected below the top 24 inches of soil in field studies. It was found in some groundwater samples in Western states (Texas, California, Missouri, Oklahoma, and Washington) at levels up to 3.8 µg/L (EXTOXNET, 1996d).

2.13 Metabolism

Mode of Action – Tebuthiuron produces its effect by inhibiting photosynthesis, the process by which plants receive light from the sun and convert it into energy (EXTOXNET, 1996d).

Plant Metabolism – Tebuthiuron is readily absorbed through roots and translocated to other plant parts (EXTOXNET, 1996d).

Animal Metabolism – In rats, rabbits, dogs, mallards, and fish, tebuthiuron is readily absorbed into the bloodstream from the gastrointestinal tract, rapidly metabolized, and then excreted in the urine. Tests indicate that the herbicide is broken down and excreted within 72 hours, primarily as a variety of urinary metabolites (EXTOXNET, 1996d).

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