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Attenuation and Effectiveness of Triclopyr and 2,4-D Along Alaska Highway Rights-of-Way in a Continental and a Coastal Subarctic Environment

Final Report

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After more than 20 years of only mechanical brush cutting, ADOT&PF evaluated the use of herbicides to manage vegetation that interferes with line-of-sight and maintenance of the roadway. While researchers have investigated herbicide effectiveness and attenuation in more-temperate climates, little study has focused on cold regions. The purpose of this project was to measure the effectiveness and attenuation of two different selective auxin-type herbicides, 2, 4 dichlorophenoxyacetic acid (2,4-D), and 3,5,6-trichloro-2-pyridinyl acetic acid (triclopyr) in two subarctic climates; an extremely cold continental climate and a maritime climate. Conclusions from this study will aid the ADOT&PF in developing a plan for controlling vegetation along highway rights-of-way in Alaska.

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APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
		AREA		
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yard	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
		VOLUME		
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
		NOTE: volumes greater than 1000 L shall be shown in m^3		
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
		TEMPERATURE (exact degrees)		
^oF	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	^oC
		ILLUMINATION		
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	$candela/m^2$	cd/m^2
		FORCE and PRESSURE or STRESS		
lbf	poundforce	4.45	newtons	N
lbf/in^2	poundforce per square inch	6.89	kilopascals	kPa

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
		AREA		
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.386	square miles	mi^2
		VOLUME		
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	cubic meters	35.314	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3
		MASS		
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
		TEMPERATURE (exact degrees)		
^oC	Celsius	1.8C+32	Fahrenheit	^oF
		ILLUMINATION		
lx	lux	0.0929	foot-candles	fc
cd/m^2	$candela/m^2$	0.2919	foot-Lamberts	fl
		FORCE and PRESSURE or STRESS		
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^2

*SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.
(Revised March 2003)

Executive Summary

After more than 20 years of only mechanical brush cutting, the Alaska Department of Transportation and Public Facilities is currently evaluating the use of herbicides to manage vegetation that interferes with line of sight and maintenance of the roadway. While researchers have put great effort into investigating herbicide effectiveness and attenuation in more-temperate climates, little study has focused on cold regions. The purpose of this project is to measure the effectiveness and attenuation of two different selective auxin-type herbicides, 2,4-dichlorophenoxyacetic acid (2,4-D) and 3,5,6 –trichloro-2-pyridinyl acetic acid (triclopyr), in two subarctic climates: an extremely cold continental climate and a cold maritime climate. Conclusions from this study will aid the Alaska Department of Transportation and Public Facilities in developing a plan for controlling vegetation along highway rights-of-way in Alaska.

Both herbicides are selective, systemic postemergence herbicides, effectively used for control of woody and herbaceous broadleaf plants in forests, grasslands, and croplands and along rights-of-way. Once applied, herbicide attenuation from soil can occur by several different mechanisms including application losses, volatilization, photodegradation, uptake and metabolism in susceptible and non-susceptible plant species, chemical and microbial degradation, and leaching. The relevance of each mechanism to the overall attenuation will be dependent upon such factors as the type of herbicide, soil type, vegetation type, and climatic conditions. Others have studied the attenuation rates of 2,4-D and triclopyr in different climatic zones. Various field studies have shown both herbicides to persist in soil for periods ranging from as few as 14 days to over two years, depending on factors such as climate, soil type, soil moisture, and organic matter.

Two sites representing the two different subarctic climates were chosen. The site representing a subarctic continental climate was located near Delta Junction, Alaska. This area is characterized as a very cold (-2.0°C annual average temperature) and relatively dry (30.3 cm annual precipitation) climate. A site near Valdez, Alaska, was chosen as the cold maritime climate, with an annual average temperature of +3.5°C and 171.2 cm annual precipitation. Each herbicide was applied with a side-mounted broadcast sprayer to two plots, each located in the right-of-way. Herbicide was also applied to a Crop Reserve Program agricultural field in Delta Junction. This field mostly contained the same type of vegetation as the right-of-way study sites located in the same area; however, the agriculture site was mowed (with the cut vegetation left in place) prior to herbicide application. Multiple samples from three depths at each plot were taken at defined intervals up to one-year after application. Samples were solvent extracted, esterfied with boron trifluoride, and analyzed by gas chromatography with mass spectrophotometry. Soil temperature at the three sampling depths was monitored at each site during the study period. Weather data were obtained from established meteorological stations located close to the study sites.

Results from this study indicate that both herbicides are effective at reducing woody vegetation in subarctic continental climates. In addition, the non-woody cover increased in the treated plots in comparison with the non-treated control plots. This result indicates that application of herbicide to reduce the presence of woody vegetation results in increased dominance of non-woody vegetation, slowing the reestablishment of the woody vegetation. Hence, after an application of herbicide to highway rights-of-way, the time until another application will be increased due to the dominance of the non-woody vegetation. Unfortunately, an unscheduled mowing masked the results from the Valdez study site.

Both herbicides persisted in the surface soil for up to or longer than one year, which is longer than the persistence found in most studies (but not all) in more-temperate soils. This result is due primarily to the long period soils are frozen in subarctic climates. Yet, during the growing season, the attenuation rate of both herbicides is comparable with that found by others in warmer climates. The overall persistence of 2,4-D is longer than that of triclopyr, though the amount of 2,4-D on a mass basis found in the soil at any one time was much less than for triclopyr. This result indicates that the attenuation mechanisms for 2,4-D are more effective at reducing the mass of 2,4-D in the soil at these subarctic study sites than triclopyr.

This study provided key information on the attenuation and effectiveness of two selective systemic postemergence-type herbicides in subarctic climates. Owing to the persistence past the one-year study time at each site, further long-term studies on herbicide longevity and vegetation grow-back rate is required. If the State decides to pursue herbicide application to highway rights-of-way prior to further longevity testing, reapplication should be no sooner than two years after initial application. In addition, soil sampling and analysis for presence of the applied herbicide should be conducted prior to reapplication of herbicide until long-term longevity studies are conducted.

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1.0 Introduction

Highway rights-of-way (ROW) are an essential component of the public highway transportation system. Once a highway ROW is established regular maintenance is necessary, chiefly vegetation management, to ensure functionality and integrity of the corridor. Vegetation management on highway ROW is desirable and necessary for a variety of reasons including the promotion of safe and clear line-of-sight distances, visibility of signs and other fixtures, reduction of fire hazard, snow or dust drift control, prevention of icing due to shading and to provide adequate drainage in roadway ditches. As an example of the necessity for ROW maintenance, during the winter of 2003, Alaska drivers hit 1,322 moose. At an average cost of $15,000 in automobile damage per collision, moose/car accidents cost Alaskans over $18 million a year (Stigall, 2005). Sufficient vegetation control removes the food source from the roadside as well as improves driver visibility, thus increasing reaction time when moose are present in a highway ROW, reducing the probability of collision. Vegetation control also aids in maintaining structural integrity of the roadbed and road surface, which can be deteriorated by pervasive root development (Gangstad, 1982).

The primary objectives of vegetation management are prevention, control, and eradication of weeds. In the context of vegetation management weeds are defined as plants that are competitive, persistent, and destructive, and interfere with human activities. Vegetation control on highway ROW can be achieved in various ways including mechanical, chemical, biological, and preventative weed control, used individually or in combination. In practice, most of the emphasis and effort spent on controlling weeds is centered on mechanical and chemical methods (Ross et al., 1985).

The Alaska Department of Transportation and Public Facilities (AKDOT&PF) has expressed interest in implementing chemical vegetation control methods for highway ROW vegetation management. Currently mechanical vegetation control methods are the primary means for managing vegetation along Alaskan highways. Chemical control is a potentially attractive alternative or supplementation, as mechanical control is generally more cost and labor intensive with reduced long-term efficacy (Ross et al., 1985). Many studies have been conducted on attenuation rate (often referred to as persistence in studies examining the potential crop damage from planting a new crop too soon after herbicide application) of the type of herbicides that are effective in controlling weed along rights-of-way. However, prior to engaging in chemical vegetation management, information is needed to evaluate the performance and risks associated with this management tool in Alaska's unique climatic conditions. The purpose of the work presented in this study was to examine the migration and attenuation of two different herbicides, 2,4-D and triclopyr, in two different subarctic regions of Alaska; a continental climatic zone located in Interior Alaska and a maritime climatic zone located in South Central Alaska. The effectiveness of the herbicides on reducing weeds in the right-of-way was also assessed. This part of the study included examining the effectiveness of the herbicide glyphosate as well.

To meet this objective, 2,4-D and triclopyr were applied to four study plots located on a roadside right-of-way measuring 61 m x 4.6 m each: two plots for 2,4-D and two plots for triclopyr. Sixteen additional plots were located in an agricultural field near the roadside plots. Triclopyr was applied to four 2m x 10m study plots; each study plot receiving a different dose of herbicide. These study plots were located approximately 18 miles outside the town of Delta Junction, Alaska (1.5 mile Sawmill Creek Road). The study site near Delta Junction was chosen to represent a very cold continental subarctic environment.

A similar study was conducted along the Richardson highway right-of-way near Valdez, Alaska. This location was chosen due to its coastal subarctic environment. The study plots for the Valdez study measured 30.5 m long by 4.6 m wide. The study was conducted between the three and four highway milepost.

The herbicides were applied by two different methods: sprayed on the vegetation and applied directly to the vegetation as it was been cut with a mower. The second application method is known as wet-blade mowing. Glyphosate was not applied by wet blade mowing in the Valdez study. Attenuation studies were only conducted on the study plots that received herbicide by spray application. Attenuation of glyphosate was not assessed in this study.

After herbicide application, soil samples from three different depths were taken from each study plot periodically for approximately one-year. These samples were analyzed in the laboratory by gas chromatography with mass spectrometry (GCMS). Analyses of the results indicate that both herbicides attenuate during the growing season at a rate similar to results from similar studies presented in the literature for more temperate regions. Though, the persistence for both herbicides appears to be longer most likely due to the relatively long period of time the soil is below a temperature that is conducive to rapid microbial degradation or is frozen. Further the mass of 2,4-D measured in the soil at both study sites during periods the soil was sampled is less than the mass of triclopyr measured during these same periods by as much as a factor of 30.

In Delta Junction, use of the wet blade mower or a broadcast application of triclopyr or 2,4-D are useful for reducing the amount of woody vegetation and increasing the amount of non-woody vegetation a year later along the road ROW. This increase in non-woody vegetation may result in a slowing of the growth rate and reestablishment of the woody vegetation. Herbicide effectiveness was inconclusive at the Valdez study site due to an unscheduled mowing of the site, which masked the results of the study.

2.0 Background

Both 2,4-D and triclopyr are selective systemic postemergence herbicide, effectively used for control of woody and herbaceous broadleaf plants in forests, grasslands, and croplands and along rights-of-way (Ghassemi et al., 1981). Both herbicides used in this study are a hormone-like herbicide. This type of herbicide controls target-weeds or susceptible species by mimicking the plant hormone auxin (indole-2-acetic acid) causing uncontrolled, disorganized plant growth leading to plant death. The precise mode of action within plants has not been completely delineated, however research on triclopyr indicates that at effective doses it tends to acidify and loosen cell walls, allowing cells to expand without typical control and coordination (Tu et al., 2001). Loos (1975) discusses the affect 2,4-D has on cell division and differentiation as well as synthesis of nucleic acids and proteins, which also impact normal plant growth. Rapid uptake or absorption of triclopyr and 2,4-D occurs in both foliar and root tissue, followed by rapid translocation throughout the plant (Gorrell et al., 1988; Loos, 1975; Ghassemi et al., 1981).

Typically, herbicide molecules in their pure chemical form are of limited value in vegetation control applications. To impart practical value and usability to the pure chemical form, most herbicides are combined with appropriate solvents or surfactants to generate a formulation. The term formulation has two meanings in reference to chemical vegetation control. First, a formulation is an herbicide preparation or mixture supplied by the manufacturer for practical use. The formulation includes all contents inside the container including active ingredient (effective chemical) and inert ingredients such as solvents, dilutents and adjuvants (e.g. surfactants, drift control additives, etc.). Second, formulation is also the process carried out by the manufacturer in preparing herbicides for practical use. Herbicides are commercially available as formulations and rarely as pure products. In addition, a given herbicide may be formulated in a variety of differing, application specific formulations. Formulations vary according to the solubility of the herbicide active ingredient in water, oil, and organic solvents, and the manner in which the formulation is applied (Smith, 1995).

Triclopyr is produced in two major formulations: water-soluble and oil-soluble. The active ingredient in the water-soluble form is present as the triethylamine salt of the triclopyr acid. The oil-soluble form is a water emulsifieable ethylene glycol butyl ether ester formulation. There are several formulations of 2,4-D, which include low-volatile esters, high-volatile esters, water-soluble amines, oil-soluble amines, and inorganic salts.

Most herbicides are formulated so they can be applied in a convenient and suitable carrier. A carrier is a gas, liquid, or solid substance used to dilute or suspend an herbicide during application. Most commonly, sprayable formulations are diluted with and applied in water, fertilizer solutions, or diesel consistency oils (Ross et al., 1985).

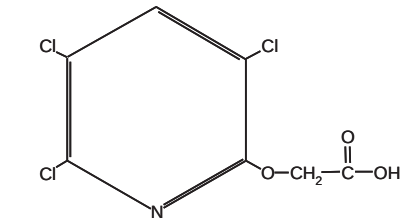
Attenuating processes immediately begin to act on herbicides once they are applied in the environment. In this study, attenuation is defined as a combination of processes that both degrade (breakdown) the parent herbicide and process that disperse the mass of herbicide originally applied. The properties of both herbicides studied and the attenuating processes will be discussed.

2.1 Properties of Triclopyr

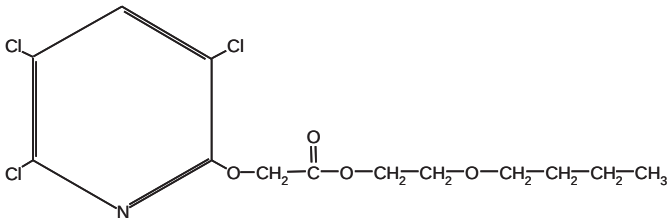
The Chemical Abstracts Service (CAS) name for triclopyr (Figure 2.1) is [(3,5,6-trichloro-2-pyridinyl)oxy]acetic acid and its CAS registration number is 55335-06-3. Triclopyr is marketed under a host of trade names including Garlon™, Crossbow™, Turflon™, Grazon™ and

others. The triclopyr butoxyethyl ester (TBE) formulation (Figure. 2.1) used in this study was Garlon™ 4.

Triclopyr is a substituted acetic acid that has the empirical formula $C_7H_4Cl_3NO_3$ and a molecular weight of 256.5 g/mol. The herbicide is a fluffy white solid with a density of 1.85 g/mL and a melting point of 148-150 °C, thus stable under normal storage conditions. It has an acid dissociation constant (pK_a) value of 2.68 and is therefore a weak acid. The octanol-water partition coefficient (K_{ow}) varies with pH and has been reported as 2.64 (pH 5), 0.36 (pH 7) and 0.11 (pH 9) (Senseman, 2007). Other relevant physical parameters for triclopyr and TBE are summarized in Table 2.1.



3,5,6-trichloro-2-pyridinyloxyacetic acid



butoxyethyl ester

Figure 2.1. Molecular structure of triclopyr and triclopyr butoxyethyl ester.

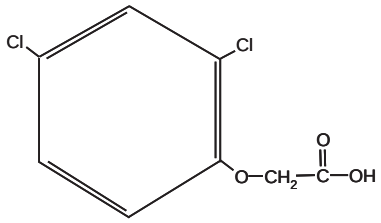
Table 2.1: Physical Parameters for triclopyr and TBE from Cessna et al., 2002

Triclopyr	Water solubility (mg/L)	Vapor pressure (mPa)	Henry's Law constant ($atm \cdot m^3/mol$)	Field half-life (days)	K_{oc} (L/kg)
Acid[a]	430	0.17	9.65×10^{-10}	32	20
TBE	23	0.48	2.47×10^{-7}	1.1[b]	780

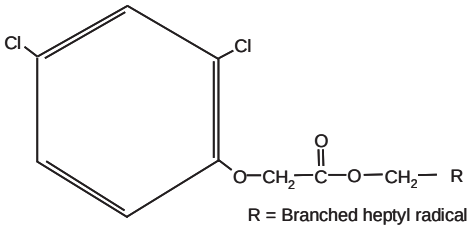
[a]Occurs as anionic form at pH values (5-9) typical of natural waters; [b]TBE is rapidly hydrolyzed to the acid in all mediums.

2.2 Properties of 2,4-D

The Chemical Abstracts Service (CAS) name for 2,4-D is 2,4-dichlorophenoxyacetic acid and its CAS registration number is 94-75-7. The chemical structure of 2,4-D is shown in Figure 2.2. Several different formulations of 2,4-D are available: low and high volatile esters, water soluble amines, and oil soluble amines (Ghassemi et al., 1981). The formulation used in this study was the low volatile 2-ethylhexyl ester (isooctyl ester, Figure 2.2) sold under the trade name 2,4-D LV6. The pKa for 2,4-D acid is equal to 2.73 (Roberts et al., 1998). Other pertinent properties of 2,4-D acid and the isooctyl ester formulation are provided in Table 2.2.



2,4-dichlorophenoxyacetic acid



2-ethylhexyl ester

Figure 2.2. Molecular structure of 2,4-D acid and 2,4-D isooctyl ester (2-ethylhexyl ester).

Table 2.2: Physical parameters for 2,4-D acid and 2,4-D isooctyl ester from

2,4-D Formulation	Water solubility (mg/L)	Vapor pressure (Pa)	Henry's Law constant ($atm \cdot m^3/mol$)	Field half-life (days)	K_{oc} (L/kg)
Acid	20,031 [(1)]	1.29×10^{-5} (20^oC) [(1)]	1.78×10^{-12} (25^oC, pH 7) [(1)]	14 [(1)]	60 [(2)]
Isooctyl ester	0.07 [(3)]	-	4.6×10^{-5} (25^oC) [(4)]	2-3 [(3)]	25,000 – 68,000 [(3)]

[(1)] USDA, 1996
[(2)] Tomlin, 1994
[(3)] Howard, 1991
[(4)] Syracuse Environmental Research Associates, 1999

2.3 Mechanisms of Herbicide Attenuation

Once applied, herbicide attenuation from soil can occur by several different mechanisms. The relevance of each mechanism to the overall attenuation will be dependent upon such factors as the type of herbicide, soil type, vegetation type, and climatic conditions. A conceptual model of the attenuation process first presented in Edwards (1966) is illustrated in Figure 2.3. Each of these attenuation processes will be discussed.

2.3.1 Application Losses and Volatilization

Application losses predominantly include spray drift of the liquid as the herbicide is sprayed onto vegetation and vapor drift. Spray drift can be divided into two categories: droplet drift and vapor drift. Droplet drift is not dependent on the herbicide formulation; rather it is caused by low output nozzles or applications under high wind conditions. These losses can be minimized using chemical additives, spraying during low wind conditions, and by adjusting the application boom height and release pressure. Another means of controlling droplet drift is by applying the herbicide using a special mechanical mower that applies herbicide from the blades onto the cut stems as the vegetation is cut. These mowers are known as wet blade mowers. Vapor drift, however, is dependent on the herbicide formulation and is caused by volatilization,

generally from foliage or soil surfaces (Piper, 1997). Gile (1983) though reports volatilization of 2,4-D from the soil is unlikely. Using C_{14} labeled butyl ester he showed that 2,4-D related materials could not be extracted from the top 2 cm of soil indicating that volatilization from this media was unlikely.

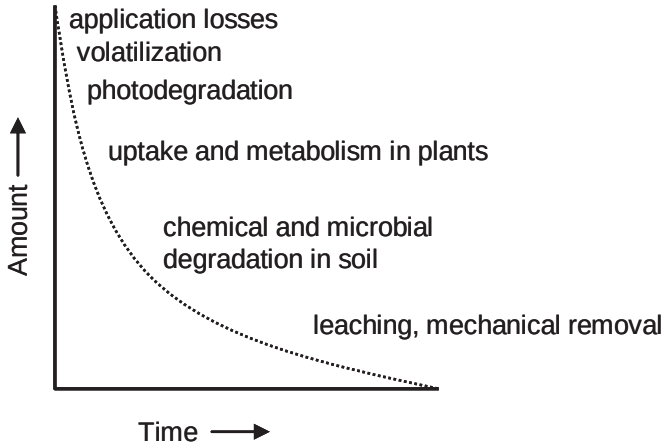


Figure 2.3. Mechanisms of herbicide attenuation from soil. Conceptual model shows approximate relative time at which different possible attenuation mechanisms are prevalent and the amount of herbicide remaining as a function of time.

Gile (1983) investigated volatile losses of 2,4-D esters (iso-octyl ester and butyl ester) in controlled laboratory studies. He found that the majority of herbicide loss through drift and volatilization mechanisms occurred in the first two to four days after the application.

Grover et al. (1985) conducted a study to investigate the typical magnitude of droplet and vapor drift. The researchers applied 2,4-D iso-octyl ester to wheat fields under wind speed conditions of 2.6 m/s. Air samples were collected at six heights during the application at a temporary location downwind of the treated area. The resulting concentrations, the sum of droplet and vapor drift during the application process, represented less than 0.2% of the total amount applied.

In another study, slight spray drift was observed downwind of two Ontario power line rights-of-way after the areas were treated with 2,4-D tri-isopropaolamine salt (Meru et al., 1990). These researchers placed Petri dishes in or near brush at intervals of 0.1, 2, 4, 6, and 10 meters downwind of both application areas. Immediately following the herbicide application, the Petri dishes were collected and analyzed in the laboratory. One site had trace amounts of 2,4-D tri-isopropaolamine salt present 2 meters downwind of the application area, while the other had trace amounts present at 10 meters downwind (Meru et al., 1990).

Herbicide volatility is variable among the different classes and types of herbicides. Cessna et al. (2002) notes that the low vapor pressure of triclopyr acid and the rapid hydrolysis of TBE to triclopyr acid indicates that it is unlikely for volatilization to be an important attenuation mechanism. Likewise, the 2,4-D iso-octyl ester formulation used in this study is considered to be a low volatile herbicide as is the acid form of the herbicide.

Studies show that 2,4-D esters can volatilize for several days after an application. Grover et al. (1985) collected air samples at two-hour intervals for six days following an herbicide application from several heights above the crop canopy at a location near the center of the treated

area. The highest vapor densities occurred between 2 ½ and 6 ½ hours after the spray. Diurnal patterns were observed for the first two days, with the minimum vapor densities occurring in the early morning when the surface temperatures were lowest. The diurnal fluxes appeared to be from the crop canopy, which intercepted 52% of the applied herbicide, given 2,4-D ester was still present in the soil even after little to no additional ester concentrations were detected in the air or canopy. Distinct concentration gradients were also observed for the first four days, with the highest concentrations being recorded at the lowest height. By the fifth day, the cumulative losses of 2,4-D iso-octyl ester through volatilization were 20.8% of the total amount applied (Grover et al., 1985).

2.3.2 Photodegradation

Most photodegradation studies focus on degradation in surface water; however, there is some relationship between rates found in surface water and rates that would be measured in water found on a leaf surface. McCall and Gavit (1986) used artificial sunlight (laboratory) as well as field conditions to estimate photolysis half-lives of triclopyr and TBE in pH 5 phosphate buffer solutions. These researchers measured a half-life for triclopyr of 2.1 hr and 12.5 hr for TBE. Limitations imposed by laboratory conditions were the neglected effects of cloud cover, which may reduce sunlight intensity by 50% in overcast conditions, turbid water, which reduces photolysis rates, and the effect of dissolved organics, which can act as sensitizers to enhance rates of photolysis.

Calculated photolysis half-lives of triclopyr and TBE in natural waters at 40° N latitude ranged from 2.8 to 14.1 hr, respectively, in the summer season. Photolysis of triclopyr was approximately five times faster than that of TBE (McCall and Gavit, 1986). In general, photodecomposition occurs rapidly and may significantly reduce the initial broadcast- applied mass of triclopyr, prior to transport into the soil environment.

Aly and Faust (1964) first showed the irradiation of aqueous solutions of 2,4-D compounds with ultra violet light from a mercury lamp. Breakdown of 2,4-D resulted in the production of 2,4-dichlorophenol in their study. Crosby and Tutass (1966) found rapid photodecomposition of 2,4-D acid in aqueous solutions under artificial and natural sunlight. These researchers propose a mechanism for the breakdown of 2,4-D in dilute solutions. Following this mechanism, the ether bond is first cleaved to produce 2,4-dichlorophenol, which is dehalogenated to 4-chlorocatechol and finally to 1,2,4 benzenetriol.

2.3.3 Uptake and Metabolism in Plants

Both herbicides are primarily brought into the plant by adsorption through leaves. However, stems and roots do play a role in uptake. Leaf interception and retention of the herbicide is the first step for leaf uptake of the applied herbicide. Devine and Vanden Born (1991) provide a good review of these processes.

A substantial amount of applied herbicide is likely intercepted by vegetation. Morton et al. (1967) recovered from 28% to 102% of applied herbicide (2,4-D and 2,4,5-T) from vegetation one hour after application. When 2,4-D butoxy-propyl ester was applied to two study sites in California, the results showed that 20.7% of the amount applied was intercepted by chamise brush and another 25.2% was intercepted by grass and forbs (Radosevich and Winterlin, 1977). Only 0.1% of the applied amount was accounted for in the soil immediately following application. After thirty days, 5.6% of the total 2,4-D applied was detected in the chamise, 2.0% remained in the grass and forbs, and 0.07% was present in the soil.

Due to a lack of precipitation at the site within the first thirty days following the 2,4-D application, Radosevich and Winterlin (1977) hypothesized that the decrease in concentration may have been caused by volatility losses. After a year, 2,4-D was no longer present in the grass and only 0.01% of the original amount applied remained in the brush (Radosevich and Winterlin, 1977).

Once in the plant the herbicide is translocated throughout the plant. Metabolism or biotransformation of organic herbicides in plants is recognized as a significant process influencing the activity, selectivity and, more importantly to this study, ultimate fate of these chemicals following their introduction into the environment (Hatzios, 1991). In general, plant species tolerant to auxin herbicides (monocotyledons) such as grasses can detoxify a given concentration of herbicide fast enough to avoid an accumulation to phytotoxic levels in the tissue, while auxin herbicide susceptible plants (dicotyledons) such as broad-leafed species cannot achieve sufficient detoxification (Devine et al., 1993). Owing to the conversion of the herbicide to other products, plant metabolism into water-soluble conjugates and insoluble "terminal" residuals that remain in the plant during its life, plant metabolism is a mode of attenuation for these herbicides; though Hatzios (1991) discusses that the identity and subsequent fate of bound residuals are poorly understood.

Detoxification of toxic substances is commonly conceptualized into a three-phase process. This concept was first presented by Williams (1959a and 1959b) and further addressed by Parker and Williams (1969). Hatzios (1991) summarizes this concept in the context of herbicide toxicity to plants (phytotoxicity). The primary (Phase I) reactions that take place during the detoxification process include mainly oxidation, reduction, and hydrolysis. The result from this initial step are metabolites with reduced or modified phytotoxicity, increased polarity, and possibly predisposes the parent molecules to further metabolism in Phase II. Conjugation of xenobiotics (synthetic reactions) occurs in Phase II resulting in the formation of metabolites with greatly reduced or no phytotoxicity. In metabolism, conjugation is a biochemical process in which a substance is bound to a sugar or amino acid, thereby deactivating its biological activity (Devine et al., 1993). The compounds are also characterized with higher water solubility and are typically less mobile in the plant. Herbicide conjugates formed in Phase II are converted in Phase III to secondary conjugates or insoluble bound residuals such as lignin biopolymers, which are essentially non-phytotoxic. Hence, herbicides biotransformation in higher plants involves a combination of reactions in which through a series of intermediate reactions results in the formation of insoluble residues of herbicides. Yet, as Hatzios (1991) notes, in this process aromatic and heterocyclic rings of most herbicides are somewhat stable in plants and they are rarely, if not at all, oxidized completely to CO_2.

Devin et al. (1993) conceptualize the metabolic behavior of herbicides in plants as shown in Figure 2.4. The detoxification steps shown in the conceptualization are a key step in the degradation of these herbicides in the environment. Hydrolysis is the first important step in conversion of the ester formulation of each herbicide to the acid formulation. The hydrolysis of esters and amides is enzymatic. These enzymes split ester or amide substrates with the addition of water to yield the corresponding acids. Carboxylic acid esters (such as triclopyr butoxyethyl ester and 2,4-D isooctyl ester) are readily hydrolyzed to their free acid forms in plants (Hatzios, 1991). This step has been reported to be relatively rapid for both triclopyr and 2,4-D and corresponds to phase I in the metabolism processes discussed above (Lewer and Owen, 1990; Grover et al. 1985). Once in the acid form triclopyr and 2,4-D follow metabolic pathways. The

resulting residuals formed through these metabolism processes are typically insoluble with limited mobility (Schimabukuro, 1985).

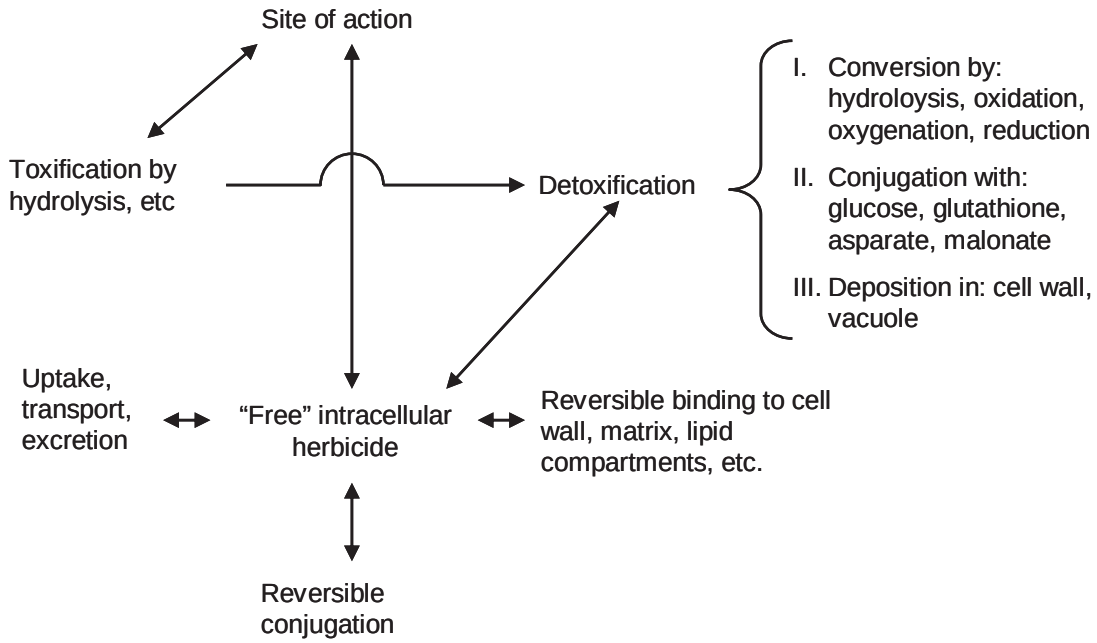


Figure 2.4. Metabolic behavior of herbicides in plants (after Devin et al., 1993).

Metabolism of 2,4-D in plants has been well studied by several (Feung et al., 1971; Feung et al. 1972; Feung et al., 1973; Feung et al., 1974; Feung et al., 1976; Feung et al., 1978, Loos, 1971). The proposed metabolic pathway is shown in Figure 2.5. 2,4-D is metabolized in the plant by side chain hydroxylation of the ring structure (NIH shift shown in Figure 2.5), conjugation of 2,4-D with plant constituents (sugar and amino acid conjugation), formulation of metabolites, ring cleaveage, or side chain lengthening (Loos, 1975). Plants resistant to 2,4-D convert the herbicide into inactive, nontoxic carbohydrate conjugates. Susceptible plants convert 2,4-D into amino acid conjugates, which obstruct normal nucleic acid metabolism and protein synthesis, resulting in death of the plant (Ghassemi, 1981). Results from two studies performed by Scheel and Sandermann (1981a,b) indicate that there is a tendency toward more metabolism of 2,4-D via hydroxylation in tolerant species and more conjugation to amino acids in susceptible species. From these results it appears that metabolism in tolerant grasses is primarily to irreversible detoxification products, while that in susceptible species is primarily to reversible conjugates.

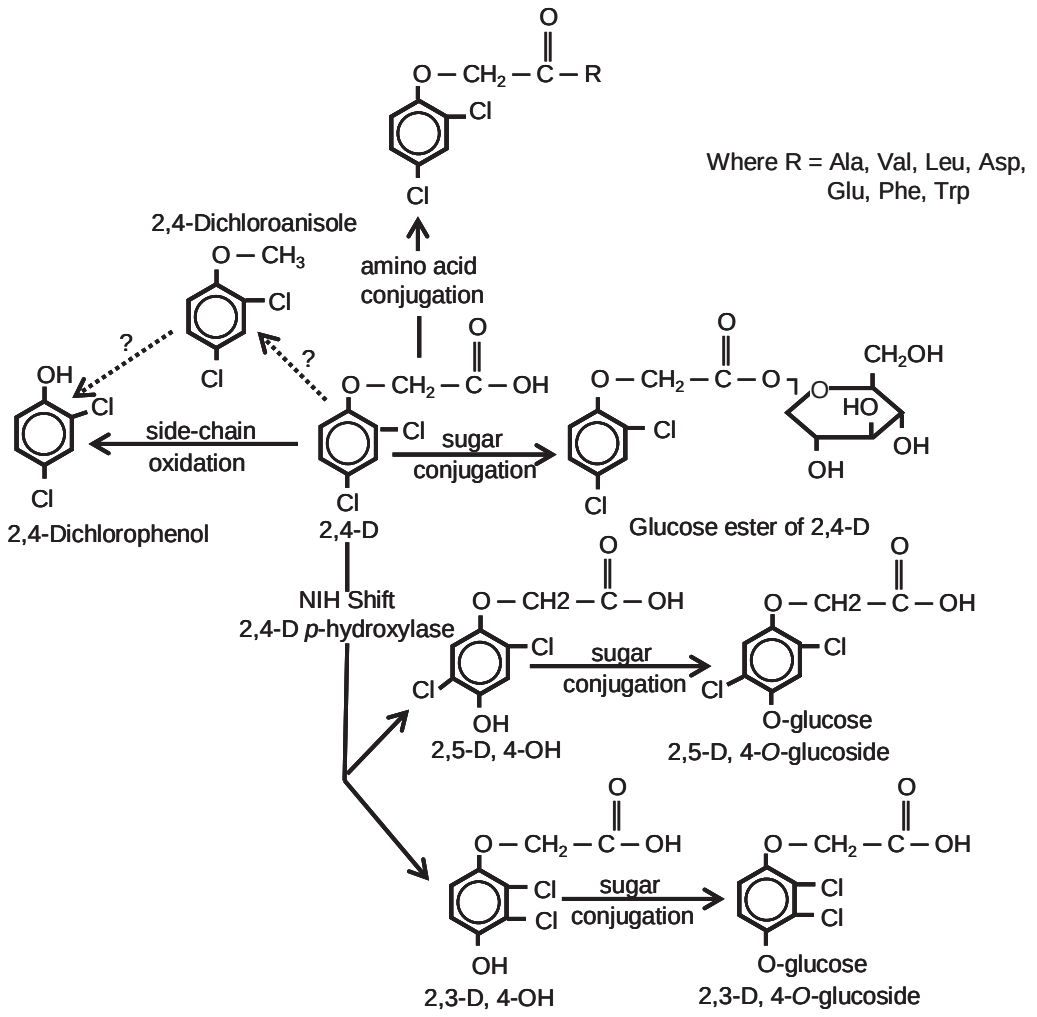


Figure 2.5. Biotransformations and metabolic pathways of 2,4-D in higher plants (adopted from Hatzios and Penner, 1982).

In comparison to 2,4-D, triclopyr metabolism in plants is not as well understood. Lewer and Owen (1989) investigated the uptake and metabolism of radiolabeled triclopyr in soybean cell suspension cultures. Seven days after treatment, these researchers found two major metabolites resulting from amino acid conjugation, identified as asparate and glutamate amide conjugations, which were not released from the cell. In a more extensive study on triclopyr metabolism in wheat (tolerant species), barley (moderately tolerant species), and chickweed (susceptible species), Lewer and Owen (1990) again showed the formation of triclopyr asparate in chickweed and possibly in wheat. As in the studies conducted on 2,4-D, Lewer and Owen (1987) found a tendency toward more metabolism via hydroxylation in tolerant species and more conjugation to amino acids in susceptible species. Other major metabolites found in wheat and barley by Lewer and Owen (1990) were complex mixtures of compounds having the properties of sugar esters; however, none was specifically identifiable. In susceptible plants, a slower metabolism of triclopyr has been measured in comparison to non-susceptible plants (Lewer and Owen, 1990). A well-defined metabolic pathway for triclopyr in higher plants has not been

reported. The best information to date shows triclopyr metabolism to trichloromethoxypyridine (TMP) and trichloropyridnol (TCP).

2.3.4 Chemical and Microbial Attenuation in Soils

There are fundamental similarities and differences between plant and microbial metabolism of herbicides. Many of the biotransformation processes are the same: hydrolysis, oxidation, and reduction. However, unlike herbicide metabolism in plants, cleavage of aromatic and heterocyclic rings is possible allowing for oxidation to CO_2 under favorable conditions. Several studies have been conducted on microbial metabolism of both herbicides; the metabolic byproducts produced, the favorable conditions for metabolism, and the resulting degradation rates produced during microbial metabolism of the herbicides.

The first step in microbial metabolism is hydrolysis of the ester form of the herbicide to the acid form. The rate of this reaction has been measured to be relatively rapid for both herbicides. Stewart and Gaul (1977) saw complete hydrolysis of the iso-octyl ester one day after applying 2,4-D at a rate of 7.8 kg/ha in Nova Scotia, well above the 2.2 kg a.e./ha application rate at the Delta Junction and Valdez study sites. These researchers note that high application can increase the time required for complete hydrolysis of the ester form to the acid. Grover et al. (1985) found that 70% of the 2,4-D iso-octyl ester that was applied at a rate of 0.5 kg/ha had hydrolyzed after five days at a study site in Saskatchewan. Hydrolysis of the remaining fraction was not complete until 34 days after treatment. These researchers note that field conditions such as humidity, soil temperature, soil moisture content, soil type, and air temperature likely contribute to the time necessary for the complete hydrolysis of the active compound to the parent acid. Petty and Gardner (discussed in Cessna et al., 2002) report a half-life for triclopyr 2-butoxyethyl ester of approximately 1.1 days.

As with metabolism of phenoxyacetic herbicides by plants, microbial degradation of 2,4-D has been studied more extensively than that of triclopyr. Metabolism by A*rthrobacter* sp. of 2, 4-D was extensively investigated at Cornell University (Loos et al., 1967a; Loos et al., 1967b; Loos et al., 1967c; Bollag et al., 1967; Helling et al., 1968; Bollag et al., 1968a; Bollag et al., 1968b; Tiedje et al., 1969; Duxbury et al., 1970). Following this metabolic pathway, the side chain is first removed to yield the corresponding phenol. Ring cleavage follows with the phenol further metabolized by ortho-hydroxilation to 3,5 diCl catechol and finally to succinic acid.

Metabolism of 2,4-D by *Pseudomonas* sp. was studied extensively in the past by others (Evans and Smith, 1954; Evans et al., 1961; Brown and McCall, 1955; and Fernley and Evans, 1958). As in metabolism of 2,4-D by *Arhrobacter* sp., these researchers found side chain removal to 2,4-diCl-phenol followed by ring cleavage. The end product detected in these laboratory studies was α-chlor-muconic acid. Ellis et al. (2008) propose the degradation pathway shown in Figure 2.6.

Crespin et al. (2001) note that the intermediate phenol compounds, specifically 2,4-dichlorophenol (Syracuse Environmental Research Associates, 1999), produced during microbial degradation are more hazardous to human health than the parent herbicide in the acid form and are included in the lists of priority pollutants for both the European Community and the US EPA (Crespin et al., 2001).

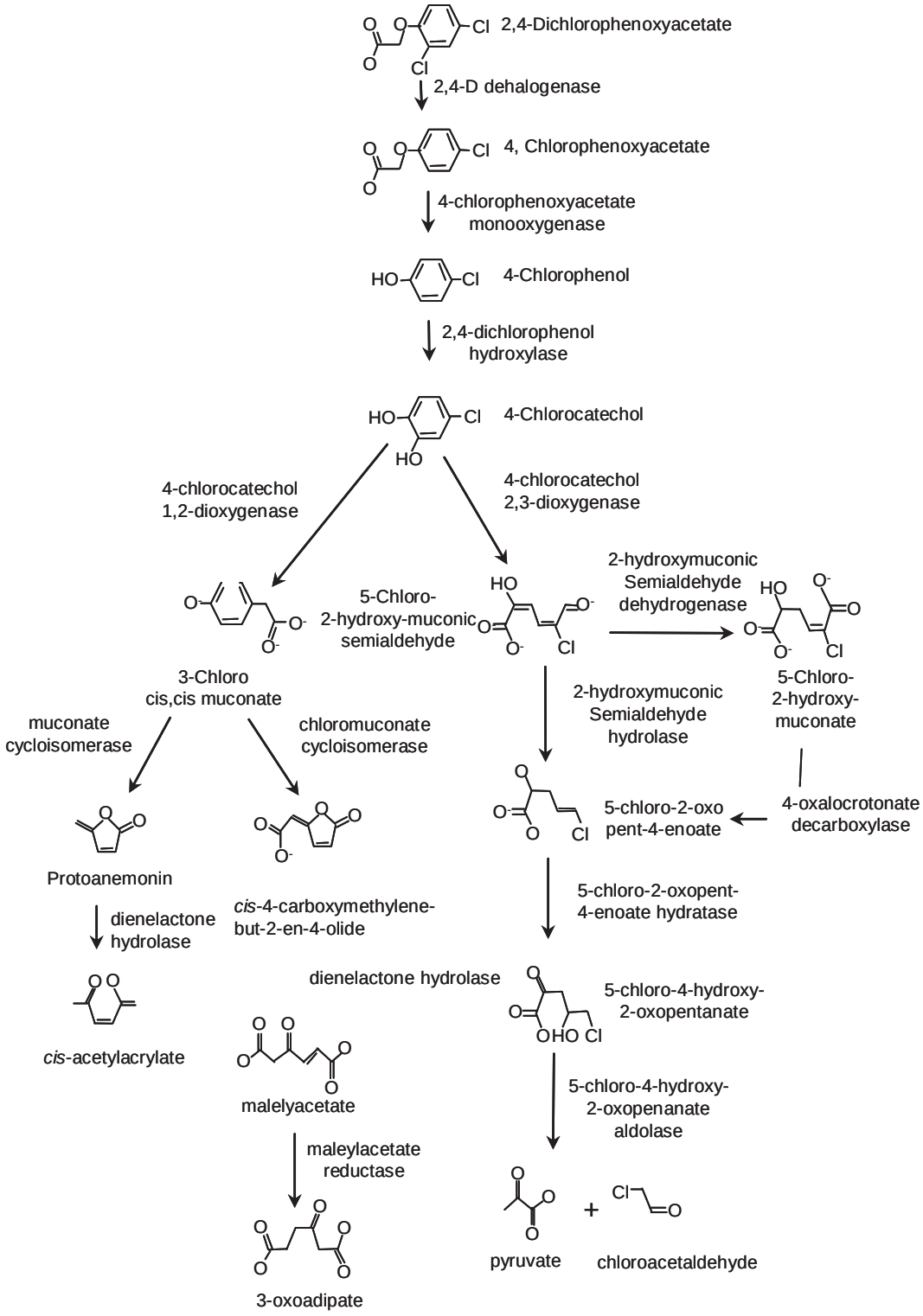


Figure 2.6. Proposed microbial degradation pathway of 2,4-D (Ellis et al., 2008).

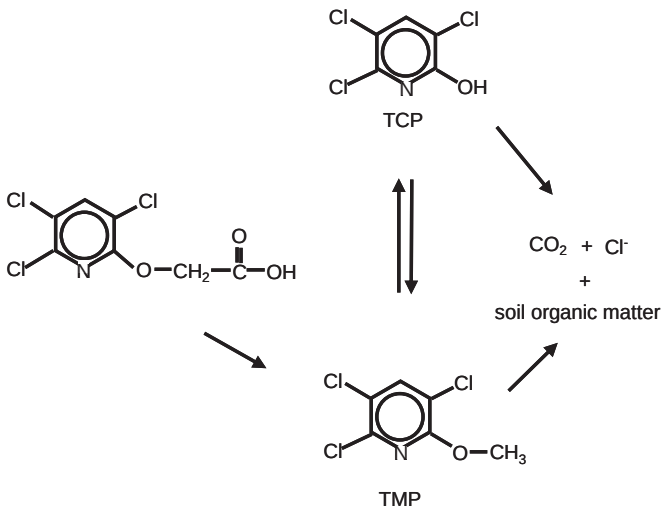


Figure 2.7. Triclopyr degradation pathway (Cessna et al. 2002).

As with any chemical, microbial metabolism of 2,4-D and triclopyr are dependent on soil temperature, moisture, and organic matter content of the soil. Han and New (1994) found in a laboratory study that the effects of water availability on 2,4-D degradation by microorganisms in soil is related to the activity and survival of different 2,4-D degrading microbial communities at various moisture contents (soil-water potentials). For the soils studied by these researchers, the optimum soil-water potential corresponded to field capacity. It is interesting to note that in the results discussed in Han and New (1994), 2,4-D degrading microorganisms were appreciably more sensitive to moisture content than other heterotrophic organisms enumerated in the soil.

The dependency of soil moisture content on 2,4-D and triclopyr microbial degradation rates was also measured by Johnson et al. (1995) in soil column studies. As in the study conducted by Han and New (1994), Johnson et al. (1995) found a dependency of degradation rates on moisture content. Grover et al. (1985) investigated the dissipation of 2,4-D iso-octyl ester in a wheat field near Regina, Saskatchewan, Canada and found that the ester losses from soil occurred only when the soil surface was moist. The researchers note that deposition of dew in the early morning contributed sufficient amounts of moisture to the soil to detect ester losses.

In a study discussed in USDA (1984), triclopyr applied to soil persistence for one to two years was attributed to the cold climate of the study site. Bidlock (1977) found relatively more rapid degradation in a loam soil and a silty clay loam soil under partially saturated conditions (aerobic) as opposed to water-logged conditions (anaerobic).

In controlled soil column studies, Johnson et al. (1995) detected a dependency of microbial degradation rates on temperature with the degradation rates of both 2,4-D and triclopyr being relatively higher at 30^{o}C in comparison to 15^{o}C. Further, the influence of temperature on degradation rates was greater for triclopyr than for 2,4-D.

2.3.5 Leaching and Mechanical Removal

Leaching and mechanical removal (removal in runoff water) of herbicides do not decrease the overall mass initially applied to a soil in any particularly setting; these attenuation mechanisms only displace mass downgradient. Leaching of herbicides is strongly dependent on

adsorption capacity of a given soil, which in turn is a function of the soil organic matter and pH of the soil.

As expected, rainfall and irrigation rates play a dominant role in the vertical transport of 2,4-D in soil. In several studies, simulated irrigation caused 2,4-D to move to lower layers within the soil profile. In the study conducted by Crespín et al. (2001), during the first eight days following the application, 2,4-D was not detected deeper than 10 cm in a soil profile that was composed of primarily clay with some sand and silt. The site was irrigated with 17 mm of water 8 days after the application, causing the herbicide to leach into the soil profile, where it was detected to a depth of 30 cm the following day. After the site was irrigated a second time, the herbicide was detected at a depth of 30 cm to 40 cm (Crespín et al., 2001). Concentrations in the subsurface were always lower than those observed at the surface, with concentration decreasing with increasing depth (Crespín et al., 2001).

While the results were not as immediate as those found by Crespin *et al.* (2001), a study conducted in Washington found that 16 mm of simulated rainfall was enough to cause 2,4-D to leach into a silt loam soil profile (Wilson and Cheng, 1976). In Wilson and Cheng's study, simulated rainfall was applied to the treated fields one day following the herbicide application. Two days after the simulated rainfall, 2,4-D was present at a depth of 24 cm. After four days, the herbicide had leached to a depth of 40 cm (Wilson and Cheng, 1976). The herbicide continued to move downward in the soil for 30 days after application. For the most part, 2,4-D concentrations decreased as the depth increased. The surface soil samples always had the highest concentrations of 2,4-D, though as the time after treatment increased, the subsurface soil samples often saw an increase in concentration with increasing depth (Wilson and Cheng, 1976).

Sorption of the herbicide onto soil organic matter can potentially limit the mobility of triclopyr and 2,4-D, particularly in organic rich surface soil layers. A number of studies indicate that triclopyr and 2,4-D are largely confined to the upper 30 cm to 40 cm of the soil column when significant organic content exists (Aly and Faust, 1964; Wiese and Davis, 1964; Frissel and Bolt, 1962; Grover 1977; Plumb et al., 1977; Radosevich and Winterlin, 1977; Lee et al., 1986; Norris et al., 1987; McCall et al., 1988; Woodburn et al., 1988; Newton et al., 1990; Stephenson et al., 1990; Hermosin and Cornejo, 1991; Racke and Lubinski, 1992; Johnson et al., 1995; Newton et al., 2008).

Several studies have been conducted on the factors influencing mobility of 2,4-D and triclopyr. Wiese and Davis (1964) compared the leaching of different 2,4-D formulations into columns packed with silty clay loam. These researchers found significant differences between the depth the amine formulation of 2,4-D reached compared to the ester formulation, with the amine formulation reaching a greater depth. They attributed the difference to the comparatively greater solubility of the amine formulation. Using laboratory columns, Grover (1977) showed an inverse relationship between soil organic matter content and mobility of 2,4-D in five Canadian soils. In addition, Grover (1977) noted that 2,4-D was more mobile in soils with higher pH, however no correlation between mobility and clay content was found. Frissel and Bolt (1967) studied adsorption of 2,4-D on montmorillonite and illite and found little if any adsorption capacity for 2,4-D on these clays at pH greater than 4 and 7, respectively. Aly and Faust (1964) quantified the adsorption of 2,4-D and ester derivatives (including iso-octyl ester) on kalonite, bentonite and illite and found very low adsorption capacities. Hermosin and Cornejo (1991) found high organic matter and free iron in soils favored adsorption of 2,4-D. Further, the authors of this study found high pH, large surface area, and the presence of phyllosilicates as essential clay components decreased adsorption capacity.

Johnson et al. (1995) performed batch adsorption/desporption studies with triclopyr and 2,4-D in silt loam and silty clay soils under various pH conditions. They found triclopyr sorption on these soils to be slightly greater than 2,4-D sorption and sorption of both herbicides increased with decreasing pH and increasing organic matter. These researchers conclude that at lower pH, both the herbicide and the functional groups in the soil are in a less polar form, resulting in increased sorption through hydrogen bonding, protonation of the acid groups on the herbicides by a proton from the functional groups in the soil, and partitioning of the herbicide molecules onto the organic phase of the soil. Sorption of both herbicides was found to be greatest in the silt loam soils in each trial regardless of pH. Desorption depended on the herbicides, soil type, and initial concentration with the amount desorbed increasing with increasing initial concentration. These researchers further concluded that specific binding sites on the soil become saturated at higher herbicide concentrations. Moreover, weaker binding sites are responsible for retaining the herbicides at higher herbicide concentrations.

Triclopyr is generally characterized as not strongly adsorbed and its adsorption potential varies with soil organic matter, clay content and soil pH (Senseman, 2007). TBE has displayed a greater adsorptive behavior compared to that of triclopyr. Five-minute batch adsorption trials on four sand and silt loam soils showed that TBE was strongly adsorbed by each soil, with an average K_{oc} value of 1200 L/kg (McCall et al., 1988). Conversely, triclopyr and its primary metabolite TCP were shown to have comparatively weak adsorptive behavior. Woodburn et al. (1988) reported an average triclopyr K_{oc} value of 59 L/kg for sand, silt and clay loam soils. Racke and Lubinski (1992) calculated an average K_{oc} value of 159 L/kg for TCP in 26 sand, silt and clay loam soils.

To investigate movement and fate of triclopyr and TBE in soils Lee et al. (1986) packed glass columns with soil containing either triclopyr or TBE at a triclopyr concentration equivalent to a 5.6 kg/ha application. Soils were obtained in a cedar-hemlock forest (34% organic matter, 8.3% clay, 45.4% sand, 46.3% silt, pH 3.4) from the wet coastal biogeoclimatical zone of British Columbia. Sand with equivalent concentration of triclopyr and TBE were packed into separate columns. Water was passed through the column for 54 days. Samples were obtained of the eluates from each column over the duration of the test. Results from controlled column studies conducted by Lee et al. (1986) on triclopyr show preferential sorption of TBE and triclopyr along with the metabolites 3,5,6-trichloro-2-pyridinol and 2, methoxy-3,5,6-tricloropyridine to soil organic matter in the highly organic near surface soil layer.

Results from a number of laboratory and field studies conducted under a variety of application conditions also indicate a limited potential for 2,4-D and triclopyr leaching. In separate studies Plumb et al. (1977) and Radosevich and Winterlin (1977) detected minimal leaching of 2,4-D into course soils past approximately 20 cm. Both study sites were located in areas characterized as having moist cool winter followed by six months of hot dry conditions. Adsorption to soil particles was proposed by the authors of both studies as the mechanism that kept leaching of the herbicides into the soil column minimal.

In brush fields of southwest Oregon Newton et al. (1990) aerially applied TBE and 2,4-D propylene glycol butyl ether ester to shallow, rocky, clay loam soils and subsequently sampled various depths in the soil column up to 60 cm periodically for 325 days. Relatively high concentrations of triclopyr and 2,4-D, on the order of 0.8 mg/kg were observed initially in the upper 15 cm of the soil column, followed by decreases of up to two orders of magnitude over time. Low concentrations of approximately 0.005 to 0.03 mg/kg for triclopyr and 0.009 to 0.021 mg/kg for 2,4-D were consistently observed from 30 to 60 cm depth in the soil column after 365

days, in spite of extreme precipitation events typical of the study location. The low relative proportions recorded at depth suggest that limited vertical movement occurred and that a comparatively large proportion of the applied triclopyr and 2,4-D were both degraded biologically and adsorbed to organic matter in the upper section of the soil column (Newton et al., 1990).

In a similar study, Norris et al. (1987) aerially applied a triclopyr isopropylamine salt (IPA) formulation to silty clay loam soils with organic matter content ranging from 2 to 5%, on two hillside pastures in western Oregon. Soils were subsequently analyzed at numerous depths up to 90 cm over the course of one year. Triclopyr residues at both locations remained in the top 30 cm of the soil column with negligible or no residues detected below 30 cm after one year. Triclopyr metabolites TCP and TMP were also detected mainly in the top 30 cm of the soil column with TMP detected in the smallest concentrations.

At a northern Ontario forest site Stephenson et al. (1990) applied TBE to sand and clay loam soils with varying amounts of vegetative cover. Seven days after application, triclopyr leaching was observed in response to heavy rainfall however, triclopyr residues at a depth of 25-30 cm never exceeded 0.006 mg/kg when present. Even after continued significant rainfall events over the following months, approximately 90% or more of the triclopyr residues were present in the upper organic soil layers, with 97% being recovered in the upper 15 cm of the soil column. Limited vertical mobility was attributed to high organic matter content (averaging 25%) in the upper 15 cm and relatively low soil pH of approximately 5 (Stephenson et al., 1990).

Wilson and Cheng (1976) measure leaching of 2,4-D past 40 cm and discuss the possibility of a fraction of the applied herbicide leaching to greater depths. Though the concentrations of 2,4-D at 40 cm measured by these researchers are on the same order of magnitude (0.001 to 0.1 mg/kg) as those measured by Newton et al. (1990). In summary, as shown by these studies, for both 2,4-D and triclopyr a majority of the applied mass will most likely be retained in the upper soil horizon and eventually be decayed by microbial metabolism. However, a fraction of the herbicide will most likely leach past the upper soil horizon, the amount being dependent upon the hydraulic and chemical properties of the soil as well as the rate of microbial decay.

2.3.6 Overall Attenuation Rates

Various field studies have shown both herbicides to persist in soil for periods ranging from as low as 14 days to over 2 years, depending on factors such as climate, soil type, soil moisture, and organic matter. In a controlled field study Lavy et al. (1973) measured rapid microbial degradation of 2,4-D in soils located at 15, 40, and 90 cm depths. At these three depths, 2,4-D treated soils obtained from the three depths were buried in containers that were open to the soil atmosphere (to monitor aerobic degradation) and closed to the soil atmosphere (to measure anaerobic degradation). Both sets of containers were protected against infiltrating water such that leaching of the herbicide was not a factor in measured attenuation. Dissipation of 2,4-D was measured by bioassay. After 41 days, the herbicide treated soil at 40 and 90 cm showed no phytotoxicity to soybean and only slight phytotoxicity at 15 cm.

Wilson and Cheng (1976) applied 2,4-D ester to soil under winter wheat and in fallow at two different doses; 1.1 and 11.2 kg/ha. The upper 24 and 40 cm of soil at each application site and for each application rate was sampled at 0, 3, 8, 14, 29, 43, and 175 days. After 175 days there was little difference in residual 2,4-D concentration between the different application sites in both soil depths. Slight differences in concentration were measured between the sites with

different doses in the upper 24 cm. Concentration of 2,4-D at both sites (cropped and fallow) receiving 11.2 kg/ha was measured to be 0.11 and 0.12 ppm at 24 cm, while the sites receiving 1.1 kg/ha had a residual concentration of 0.01 and 0.03 ppm. At 40 cm after 191 days, there was essentially no difference in concentration between the two different doses and the two different sites with the concentration at this time ranging between 0.03 and 0.04 kg/ha.

Stewart and Gaul (1977) found trace amounts of 2,4-D in soils at a depth of 0-10 cm (up to 0.10 ppm) 265 days after application at field sites located in a humid temperate climate. Subsequent sampling at 385 days resulted in no detectable amounts of 2,4-D in the surface soils. Concentrations in subsurface soils (10-20 cm) were not detectable after 70 days. Application doses in this study were much higher than typically would be applied in an agricultural setting (up to 22.4 kg/ha). Similarly in a contrasting environment, arid climate with 6 months of hot dry conditions, Radosevich and Winterlin (1977) and Plumb et al. (1977) both measured only residual amounts in soils after 360 days and 379 days, respectively. Radiosevich and Winterline (1977) found only 0.01% of the original applied mass in near surface soils (0-5 cm). In this study no detectable levels of 2,4-D were found below a depth of 5 cm. Plumb et al. (1977) found 0.04 ppm at a depth of 0-10 cm after 279 days and 0.02 ppm at a depth of 10-20 cm as well as 20-30 cm.

Grover et al. (1985) found the dissipation of 2,4-D from soil to be highly dependent upon soil moisture content. These researchers measured the dissipation of the both the ester formulation and 2,4-D acid in air, crop, and soil compartments in a wheat field following application. Concentration of 2,4-D ester declined rapidly in the first two-days after application with a slow but continuous decline up to seven days after application. Up to two days after application there was no change in the 2,4-D acid concentration in the upper 7.5 cm of soil in this study. Following a rainfall event on day three the acid concentration in the soil started to slowly decline over the next 14 days. Subsequent rainfall events resulted in dissipation of the herbicide with no detectable total 2,4-D (acid and ester) remaining in the soil after 34 days. Conversely, detectable levels of 2,4-D acid remained in the crop compartment after 34 days.

At a forest site located in Oregon characterized by hot dry summers and cold wet winters Newton et al. (1990) found rapid initial decrease in 2,4-D concentration during summer months followed by slow dissipation during winter. At 325 days after application residual concentrations (0.009 mg/kg to 0.021 mg/kg) were detected at the three depths investigated (0-15 cm, 15-30 cm, and 45-60 cm). Similar results were found for triclopyr (non-detect to 0.028 mg/kg).

In a study to investigate the usage of 2,4-D on power line rights-of-way, Meru et al. (1990) found no detectable residuals after eight weeks at one study site and 11 weeks at another study site. The site with the most rapid dissipation was characterized as having coarse textured sandy loam soil, while the site with the relatively slower dissipation rate consisted of sand clay loam. The authors hypothesized that given the somewhat permeable soils, 2,4-D may have leached below the soil horizon sampled (15 cm) resulting in the relatively rapid dissipation in comparison to other studies.

In a comprehensive dissipation study of 2,4-D ethylhexyl ester and 2,4-D dimethylamine salt over 30 different sites comprising seven different US States, Wilson et al. (1997) found relatively short half-lives of 2,4-D acid. These researchers applied each formulation to either corn crops, wheat crops, pasture, turf, or bare soil. Half-lives ranged from 1.7 days (ester applied to turf in North Carolina) to 27.5 days (ester applied to pasture in California). The North Carolina site consisted of sand with 0.77 to 1.43% organic matter. Soil at the study site in California was characterized as sandy loam to loamy sand with 0.7 to 3.9% organic matter.

Residuals were measured in the soil past 120 days with the shortest span from application to non-detect residual amounts being 14 days. Consistent with the extensive results generated by Wilson et al. (1997), Crespin et al. (2001) measured a 4.9 day half-life for 2,4-D applied to agricultural clayey soils (47 to 60% clay) in a temperate region.

Torstensson and Stark (1982) applied 2,4-D buthoxiethyl ester at a rate of 2.0 kg a.e./ha to eight plots in three regions of Sweden including the northern region. Only the upper 5 cm of the soil was sampled. Three out of the eight sample locations, which were all located in the same region, had measurable concentrations (> 0.05 μg/sample) of 2,4-D three hundred days following the application.

Several additional studies on triclopyr attenuation rates have been conducted. In an Idaho forest several woody species were foliarly treated with TBE, and it was reported that triclopyr in terminal branch and leaf segments continuously decreased with time (Whisenant and McArthur, 1989). Foliar applications of ^{14}C-triclopyr were made to various plant species including big leaf maple, tan oak, snowbush ceanothus and bean and barley seedlings. Four days after treatment, recovery of triclopyr ranged from 63% to 87% in these five species (Radosevich and Bayer, 1979). In Southwestern Oregon, foliarly applied TBE dissipated relatively slowly in tan oak with a reported half-life of 73.5 days (Newton et al., 1990).

In New Zealand TBE was applied to pasture grass and the triclopyr dissipation half-life was reported as approximately 30 days over a 249 day period (Wilcock et al., 1991). In a western Oregon hill pasture a similar triclopyr dissipation half-life of approximately 40 days over a 365 day period was observed in grasses, with rapid initial dissipation over the first two weeks, followed by a much slower rate of loss over the remainder of the year (Norris et al., 1987). In forest grasses, Whisenant and McArthur (1989) also observed rapid initial dissipation of triclopyr and reported a half-life of approximately 3 days.

Torstensson and Stark (1982) also investigated triclopyr persistence in the same eight soils in Sweden. Triclopyr euthyleneglycolbuthylether ester was applied to the soil at a dose of 2.2 kg a.e./ha. Unlike 2,4-D, measureable concentrations were detected in all soils three hundred days and as much as two years following the application (Torstensson and Stark, 1982). The relatively longest persistence occurred in the northern field sites.

Mulkey (1990) investigated the persistence of triclopyr at six sites in Alaska along the railroad corridor: Fort Wainwright, Clear, Seward, Chulitna, Birchwood, and Firecreek. Residual triclopyr concentrations were found at all six sites after approximately one year. These concentrations ranged from a high of 1.12 ppm at Clear to a low of 0.02 ppm.

Newton et al. (2008) applied triclopyr to soils located near Fairbanks, Alaska. The dose used in the study was 2.2 kg/ha. Results from this study indicate that triclopyr in soil at this subarctic location dissipated at approximately the same rate during the summer months as more temperate locations. However, dissipation during the winter months halted. After 476 days triclopyr was non-detectable in the soil depths sampled (0-15 cm and 15-45 cm). Soils at the site were characterized as well-drained silt. These researchers also applied triclopyr to soils located at Windy Bay, Alaska (on the Southern tip of the Kenai Peninsula) at a dose of 2.2 kg/ha. Results from this study indicate triclopyr was still measurable at 456 days; however, the concentration appears to be low (less than 0.1 ppm).

3.0 Methodology

In the continental study three different field tests were conducted in Delta Junction, Alaska: triclopyr attenuation in roadside right-of-way (ROW) soils, 2,4-D attenuation in roadside ROW soils, and triclopyr attenuation in agricultural soils. The overall methodology for each field test was similar; herbicide was applied to the site-specific soil after which soil samples were taken with time and analyzed for the specific herbicide. However, minor differences in the methodology exist for each field test. Four different application dose amounts were applied to multiple field plots in the agricultural field study allowing for comparison of herbicide effectiveness as a function of the amount applied. In contrast, only one dose amount was applied to the ROW sites. While the vegetation on the ROW sites was left untouched prior to herbicide application, the vegetation on the agricultural field plots was mowed prior to herbicide application.

The coastal study conducted in Valdez, Alaska consisted of two field sites located along the Richardson Highway right-of-way. One site was treated with triclopyr (2 plots) and one site was treated with 2,4-D (2 plots). The methodology was the same as used in the Delta Junction ROW study. Each study site will be described followed by description of the field and laboratory procedures.

3.1 Continental Region Right-of-Way Site Description

The continental ROW field site was located on a right-of-way at mile 1.5 Sawmill Creek Road, approximately 18 miles southeast of Delta Junction, Alaska. Situated in the central Tanana Valley the site rests upon alluvial plain deposits, bounded by the Alaska Range to the south and the rolling hills of the Yukon-Charley Rivers National Preserve to the north. Relatively recent development in the region includes large-area land clearing, suitable for agricultural uses such as small grain and vegetable production and forages. The local climate is classified as sub-arctic boreal continental, characterized by short warm summers and long cold winters. Mean annual temperature ranges from -4.4° C to -2.2° C with the warmest month, July, recording a mean high temperature of 21° C and the coldest month, January, recording a mean low temperature of -26° C. Mean annual precipitation ranges from 230 mm to 330 mm, with approximately one third of the total received as snow (Western Regional Climate Center, 2008). Annual precipitation values in this range qualify the region as a sub-arctic desert.

Due to logistical complications, daily on-site precipitation and air temperature measurements were not possible. As a result, these data were collected at the nearest meteorological station operated by the National Weather Service. The station used was Delta Junction 20 SE, located approximately 5 km from the study site. Precipitation observations were made once daily at 7:00 AM, measured to the hundredth of an inch. Air temperature was reported as daily maximum and minimum (Figure 3.10. Precipitation amounts for the study period are shown in Figures 3.2.

Four plots (two plots per herbicide) at the Delta Junction site were selected for sample collection and analysis. Each plot was 60.7 m long and 4.6 m wide and consisted of a diverse mix of densely vegetated areas and bare ground with low grasses and small diameter gravel (<1.3 cm). The majority of the study plots displayed little to no slope. Vegetation at the site included Balsam Poplar (*Populus balsimifera*), Paper Birch (*Betula papyrifera*), Felt-leaf Willow (*Salix alaxensis*), Little-tree Willow (*Salix arbusculoides*), Quaking Aspen (*Populus tremuloides*), Fireweed (*Epilobium angustifolium*), Horsetail (*Equisetum arvense*), Golden Rod (*Solidago sp.*),

Yarrow (*Achillea millefolium*), and Lowbush Cranberry (*Vaccimium vitus*). The vegetation was not cut prior to the broadcast spray application.

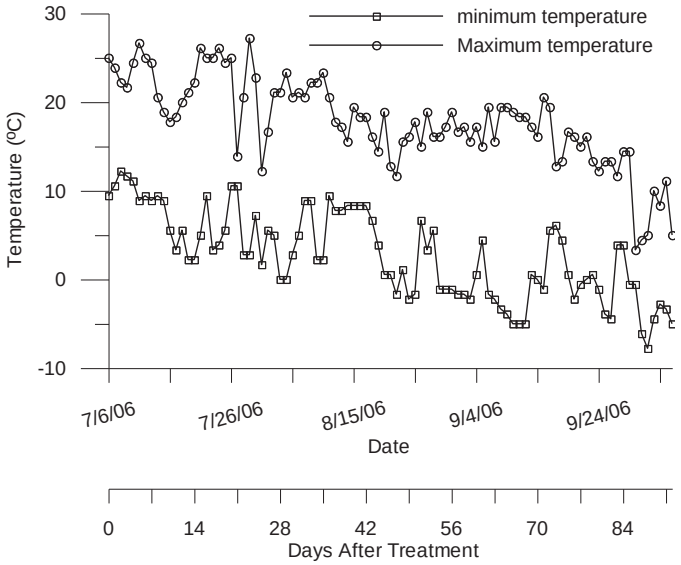


Figure 3.1. Minimum and maximum air temperatures vales for the study period measured at Delta Junction 20SE weather station.

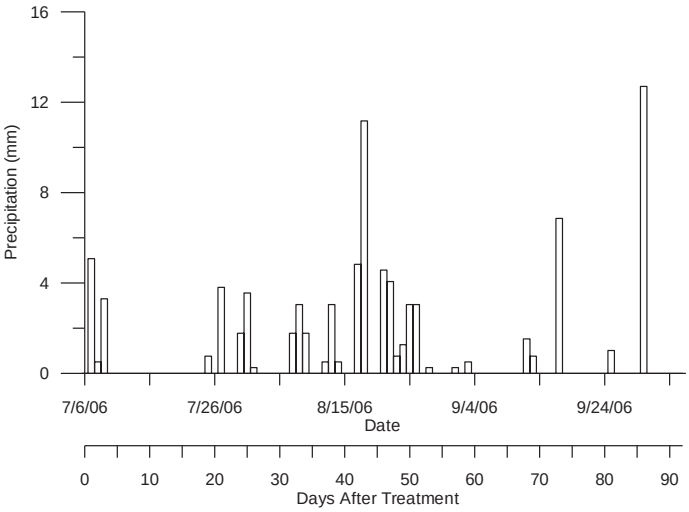


Figure 3.2. Precipitation amounts for the study period measured at Delta Junction 20SE weather station.

A regional soil classification developed by the Natural Resources Conservation Service (NRCS) provides a general description of the soil horizons considered at the Delta Junction area field site (Moore et al., 2007). It should be noted that due to the close proximity of the study area relative to the roadside and power line right-of-way, minor variation between the NRCS description and the actual conditions at the study location might be present. Nonetheless, based on qualitative observation and quantitative soil classification tests (to be discussed), there is general agreement between the NRCS description and the soils that comprise the study area.

To measure soil temperature thermistor probes were placed at three representative soil depths including 0-5 cm, 10-18 cm and 30-38 cm, coupled with a data logger for continuous data collection. Temperature was recorded every two hours. The data logger was weatherized with multiple plastic bags and encapsulated in a plastic container, which was sealed with silicon to prevent moisture infiltration. The excavation required for thermistor probe placement was carefully backfilled and compacted to reestablish the undisturbed condition. Soil temperatures for the study period are shown in Figure 3.3

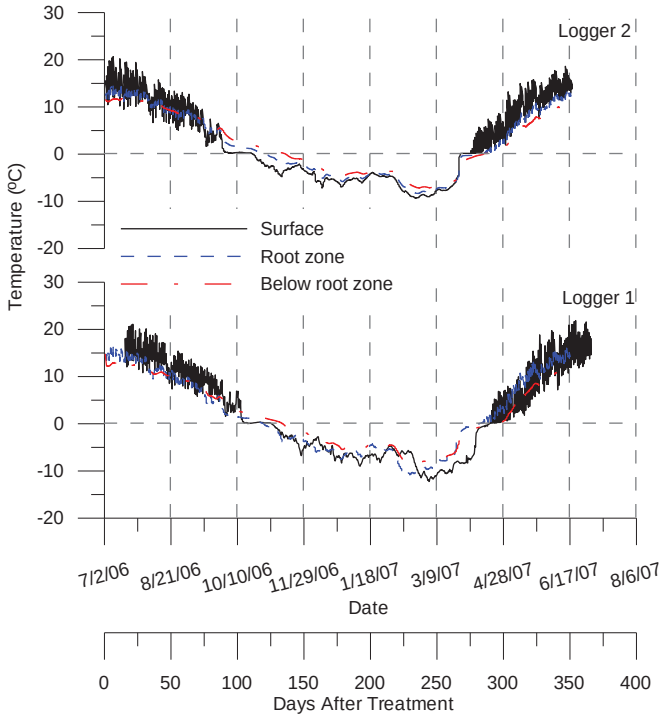


Figure 3.3. Soil temperatures at the Delta Junction study site measured in two locations at the three sampling depths during the duration of the study. The soil froze approximately 110 days after application (11/03/06) and thawed approximately 276 days after application (4/18/07).

Soils from 0 to 5 cm depth consist of a dark brown silt loam to very-fine sandy loam and slightly decomposed plant material. High densities of both very fine and coarse roots are present at this depth. The soil pH is acidic with a values ranging from 4.0 to 4.8 (EPA method 9045D). Sparse distributions of pebble to cobble sized particles occur in this layer and are likely relic materials from road construction and maintenance. Soils in the 10 to 18 cm depth range consist of dark grayish-brown silt loam. Very fine and coarse roots are present at this depth; however, their occurrence is less pervasive than in the 0 to 5 cm depth. Soil pH is less acidic in the range of 5.3 to 5.6. Soils at 30 to 38 cm depth consist of dark yellowish-brown silt loam stratified with loamy very fine sand. At this depth, roots occur infrequently or not at all. Soil pH is yet less acidic falling in the 5.6 to 6.0 range (Moore et al., 2007). Particle size analyses for each soil depth are shown in Figure 3.4. Particle size distribution was determined using ASTM D 6913-04 (2004).

Soil moisture was measured only during sampling events. A standard test method was employed to determine the soil moisture by mass. The moisture content was calculated as the

mass of water divided by the bulk sample mass. Results are shown in Figure 3.5. Soil pH was measured using Method 9045D (US EPA, 2004): Soil and Waste pH. Soil organic matter content was determined using AASHTO T 267-86 (2004): Determination of Organic Content in Soils by Loss on Ignition. Hydraulic conductivity of the soil was measured by flexible wall permeameter according to ASTM D 5084 (2003). Relevant soil properties for the Delta Junction site are provided in Table 3.1.

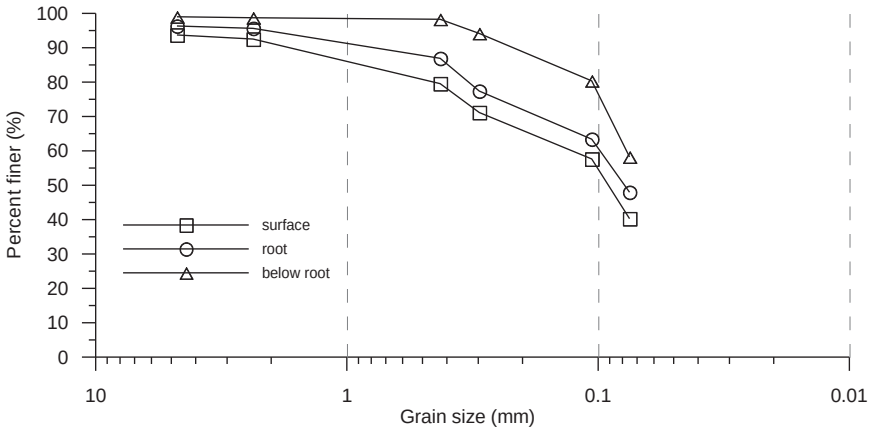


Figure 3.4. Grain-size distribution for surface soil, root zone soil, and below root zone soil at the Delta Junction site.

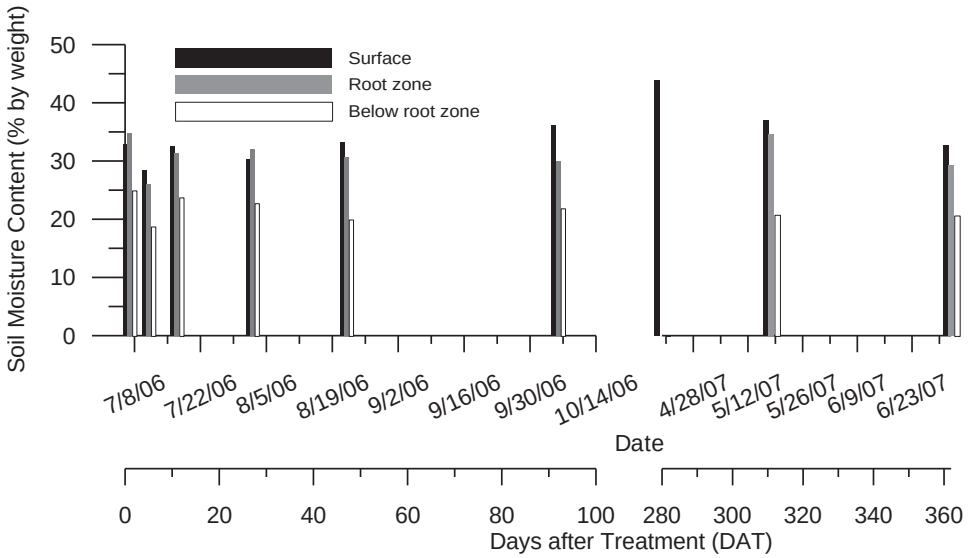


Figure 3.5. Soil moisture content for each sampling depth at the time of each sampling event.

Table 3.1: Delta Junction area field site soil properties

Soil Depth (cm)	Soil pH	% Organic Matter	Soil Type	Saturated Hydraulic Conductivity (cm/s)
0-5	4.5	7.5	Silt Loam[a]	$2.11 \times 10^{-5} \pm 8.0 \times 10^{-7}$ [b]
10-18	5.5	6.5		
30-38	5.8	6.1		

[a,b]Soil type and saturated hydraulic conductivity are representative of all depths.

3.2 Coastal Region Right-of-Way Site Description

The coastal ROW field site was located near Valdez, Alaska, on a right-of-way at 3.5 mile Richardson Highway. Four plots (two plots per herbicide) at the Valdez site were selected for sample collection and analysis. Valdez is located near the head of a deep fjord in the northeast section of the Prince William Sound, surrounded by the heavily glaciated Chugach Mountains. Geologically the surrounding area is composed of an accumulation of sediments including silts, sands, and gravels derived from both deltaic and alluvial fan processes. Sediments lie atop irregular ridges of greywacke bedrock and scattered till deposits (Palmer, 1982). At Valdez the major woody species were Salmon berry (*Rubus spectabilis*), Willow (*Salix* sp.), Alder (*Alnus* sp.), Poplar (*Populus balsamifera*), and Currants (*Ribes* sp.) and the major non-woody species were grasses, Ferns (Pteridophyta sp.), Fireweed, (*Epilobium angustifolium*), Horsetail (*Equisetum arvense*), Yellow rattlebox (*Rhinanthus minor*), Pushki (*Heracleum lanatum*), Dandelion (*Taraxacum officinale*), and Delphinium (*Delphinium* sp.).

The local climate is characterized by short cool summers and comparatively long wet, mild winters moderated by the Gulf of Alaska. Mean annual temperature is approximately 2.2°C with the warmest month July, recording a mean high temperature of 16°C and the coldest month, January recording a mean low temperature of -12°C. Total mean annual precipitation is approximately 1.6 m including 5.6 m received as snowfall (Western Regional Climate Center, 2008). Precipitation amounts and temperature values were recorded at the Valdez WSO weather station (Figures 3.6 and 3.7).

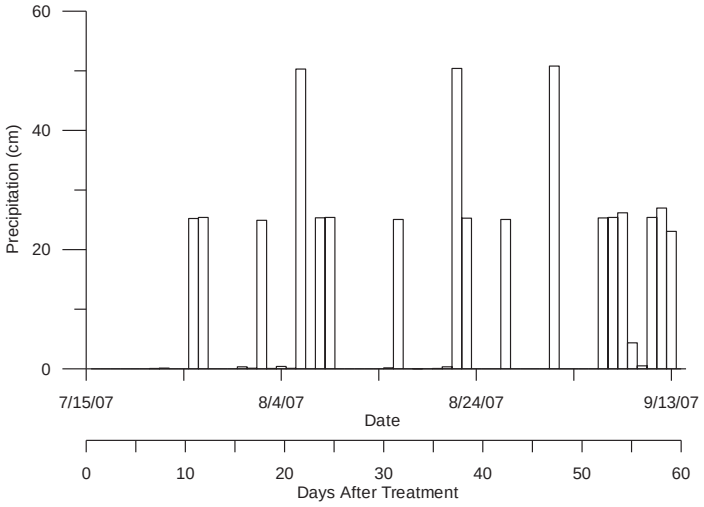


Figure 3.6. Precipitation amounts for the study period measured at Valdez WSO weather station.

Regional soil classification documentation was not available for the Valdez area field site. However, a number of soil characteristics were determined in this study including soil pH, organic matter content, particle-size distribution, and hydraulic conductivity. The same methods as were used at the Delta Junction study site were used to obtain these data. However, particle size distribution was determined from a well-mixed combination of soils obtained from the three depths (surface, root and below root). Figure 3.8 and Table 3.2 provide these relevant properties. Soil temperatures at the Valdez study site are shown in Figure 3.9

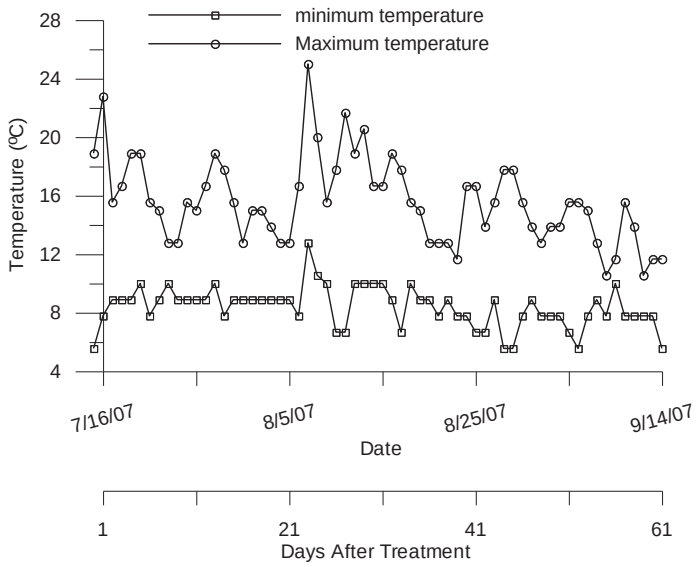


Figure 3.7. Minimum and maximum air temperature values for the study period measured at Valdez WSO weather station.

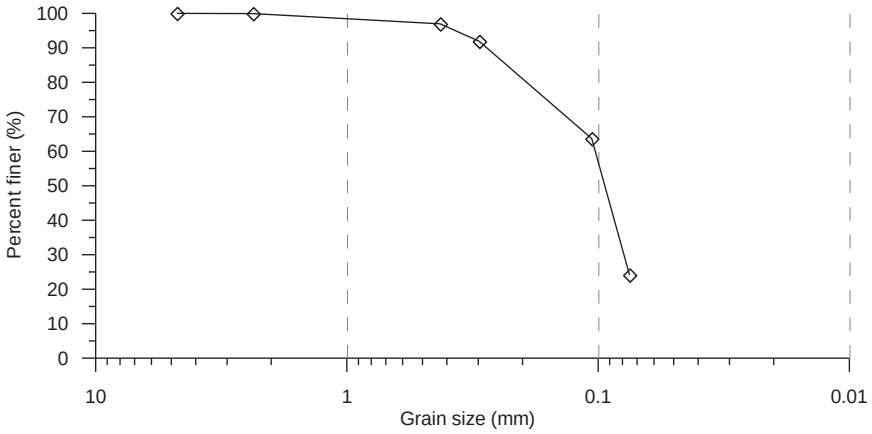


Figure 3.8. Grain-size distribution for a well-mixed combination of surface soil, root zone soil, and below root zone soil at the Valdez site.

Table 3.2: Valdez area field site soil properties

Soil Depth (cm)	Soil pH	% Organic Matter	Soil Type	Saturated Hydraulic Conductivity (cm/s)
0-5	4.9	7.2	Silty Sand[a]	$2.54 \times 10^{-4} \pm 7.34 \times 10^{-5}$ [b]
10-18	5.9	1.6		
30-38	6.0	0.93		

[a,b]Soil type and saturated hydraulic conductivity are representative of all depths.

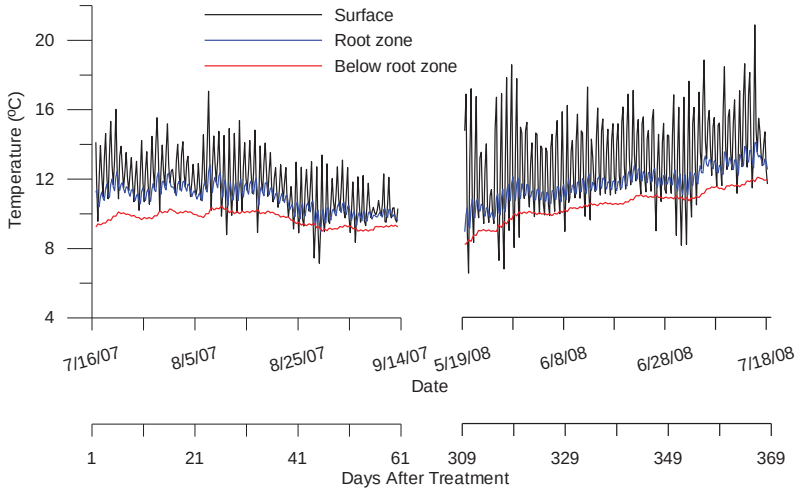


Figure 3.9. Soil temperatures at the Valdez study site measured in one location at the three sampling depths during the duration of the study,

3.3 Herbicide Application on Right-of-Way Field Sites

When applying herbicides various factors are considered such that upon application, maximum efficacy is attained within the vegetation while minimal herbicide concentrations are introduced into the environment. The effectiveness of the herbicide is largely related to appropriate timing with respect to vegetation growth rates. When growth rates are high, maximum uptake and translocation of the chemical will occur within the plant, which is relevant to both the effectiveness of the herbicide and the attenuation. Typically, maximum growth rates are observed in late spring to early summer. For this study, it was determined that optimal conditions for herbicide application occur within a range from late June through mid-July.

Other factors such as wind speed and precipitation are also considered prior to broadcast application. If wind speed exceeds a threshold value of 9 mph, significant off-site drift is possible and non-target plant species may be affected (Smith, 1995). Furthermore, off-site drift decreases the quantity of herbicide intended for the target area and vegetation may be less effectively controlled, as previously discussed. Precipitation or even the presence of excess moisture on leaf surfaces is undesirable for broadcast application as well. Excess moisture results in dilution of the herbicide solution after it is deposited on the leaf surface. Precipitation tends to wash the herbicide off the leaf surfaces, ultimately to the ground (Ross et al., 1985). Again, these factors can lead to a reduction in product effectiveness.

The spray-truck used for broadcast application was supplied and operated by the Salcha-Delta Soil and Water Conservation District (Figure 3.1). The truck delivered 2.2 kg a.i./hectare (active ingredient, triclopyr), proportioned with 30 gallons/acre water containing a 0.25% (volume/volume) non-ionic surfactant. Non-ionic surfactants function to reduce surface tension in the solution, improve spreading upon the leaf surface, and enhance herbicide absorption. To orchestrate a constant dose amount with variable truck speed the truck was equipped with a Raven SCS 4400 controller system (console), which served as an interface between a frame-mounted Doppler radar unit and pump/spray system.

Figure 3.10. Spray-truck used in this study applying herbicide to vegetation at the Delta Junction study site.

The pump and spray system mixes and sprays the chemical and water solution in the correct proportion based on vehicle speed and spray area. A Boom Buster Model 187 side delivery nozzle was used in place of the traditional extended boom system. The nozzle was angled to produce a 15-foot stream perpendicular to the direction of travel, corresponding to the short dimension of the study plot. Stream spray width is measured to the inch, so that spray area can be calculated and programmed into the console. Doppler radar is then utilized to acquire vehicle speed independent of its speedometer. With vehicle speed and spray area known, the console can instantaneously calculate the area/second covered. The console is then programmed to dispense 280.6 liters/hectare (30 gallons/acre) water with 2.2 kg a.i./hectare (active ingredient). As vehicle speed varies, the system adjusts fluid pressure accordingly such that a constant flow rate is maintained. The Doppler radar, water-flow meter and chemical injection chamber are calibrated prior to operation.

3.4 Field Sampling on Right-of-Way Field Sites

The sampling plan was designed to balance various factors including travel logistics, sample-processing time in the laboratory and minimum sample number suitable for statistical analysis, while providing adequate representation of chemical dissipation and migration processes. Travel time from UAF to the Sawmill Creek RD and Valdez field sites from Fairbanks was 2.5 and 7 hours, respectively, and was a limiting factor with respect to sampling frequency. To guide the sampling frequency schedule, first-order decay was assumed and modeled such that half of an initial concentration dissipated in 30 days. A 30-day chemical half-life was chosen based on the triclopyr and 2,4-D literature average.

Two plots at each field site were treated via broadcast application and sampled, using a simple random-sampling method. Constrained by plot dimensions, random numbers were generated to provide random sample coordinate locations. For one sampling event (i.e., day one) four locations were generated for each plot, totaling eight sample locations per event. At each location three sample depths were considered including surface (0-5 cm depth), root zone (10-18 cm depth) and below root zone (30-38 cm depth) for each field plot. Therefore, for each field study, 24 total samples from two treated plots were collected per sample event.

For the Sawmill Creek Road field site, nine sampling events were conducted over the course of one year following herbicide application. The sampling frequency reported in days

after application (DAT) was 1, 5, 11, 27, 47, 92, 288, 316, and 362. For the Valdez field site, six sampling events were conducted over the course of ten months following a schedule of 1, 2, 8, 2, 60, and 309 DAT.

Samples were collected using stainless steel trowels, stainless steel soil probes, steel hand-powered soil augers, and 4 oz. amber glass jars. Using a stainless steel trowel, vegetation, and surface litter was removed and an 8 cm by 8 cm by 7.6 cm cube was removed from the ground. Soil was then removed from the cube and placed in a labeled surface sample amber glass jar. Root zone samples were collected using a stainless steel soil probe that was inserted into the soil column at the same location where the surface sample had been removed. Soil was then removed from the soil probe, excluding the top inch that was discarded to prevent cross-contamination, and placed in a labeled root zone sample jar. Soil augers were used to remove the root zone portion of the soil column. Once this was removed, a soil probe was used to collect the below root zone samples. Again, the top inch was removed and the rest of the soil core was placed into a labeled below root zone amber glass jar. The three samples from each location were placed in a cooler with ice to prevent further biological and photodegradation and for transport to the UAF lab. During a sample event, a total of eight samples were collected from each depth at the study sites, excluding any site condition that prevented sample collection, such as large pebbles in the subsurface.

In the field, several steps were taken to prevent cross contamination. All equipment was washed and sterilized prior to collecting each sample. After a sample was collected, the equipment was rinsed with water and any remaining soil would be removed with a brush. The equipment was then rinsed with acetone and de-ionized (DI) water. Each piece was then hand dried with a clean paper towel and placed in a clean garbage bag to prevent contamination from vegetation treated with 2,4-D at the study site. All samples were collected using nitrile gloves that were replaced after each sample was collected.

In addition, samples were collected for pre-application testing, soil moisture determination and soil characterization. Pre-application testing was performed to ascertain the presence or absence of triclopyr and 2,4-D within the study area prior to broadcast treatment. Pre-application samples were collected in the same manner as post-application samples and received the same analytical treatment in the laboratory (to be discussed). Chromatographic results from ten random locations within the two study plots at each field site indicated that there were no detectable levels of triclopyr or 2,4-D present. Thus, any herbicide quantified from post-application samples was assumed to have originated from the broadcast treatment.

For soil moisture determination, one location was generated per treated plot, adjacent to the plot boundary outside the treated area. The three respective depths sampled at this location were used to represent soil moisture for the entire plot. For soil characterization, three five-gallon buckets were filled with soil from each depth. These samples were collected for particle size analysis, soil organic matter content, soil pH, and soil hydraulic conductivity.

3.5 Herbicide Application and Field Sampling on Agricultural Field Sites

For each site, an experiment was set up with four dilutions of the herbicide triclopyr (2.2, 1.1, 0.55, and 0.275 kg/ha) with four replicates for each rate in a Latin Square experimental design. The control treatments were placed outside of the plots to prevent contamination from the herbicide (Figure 3.11). The dimensions for each plot were 2 m by 10 m, with 0.5 m of space between the plots to avoid spray overlap. The vegetation on the experimental area was mowed to a height of 15 cm and left on the plots prior to herbicide application. Herbicide was applied with

a log step CO_2 backpack sprayer and a 1.8 m boom with four spray nozzles at a height of approximately 30 cm. Twelve soil samples were taken at depths of 0-5 cm, 5-15 cm, and 15-30 cm randomly throughout each plot with a 2 cm diameter corer. The soil corer was cleaned with acetone between the sampling of each plot. Soil samples were taken from each plot 1, 3, 7, 21, 35, 283, and 365 days after treatment (DAT). Soil samples were kept frozen until analysis.

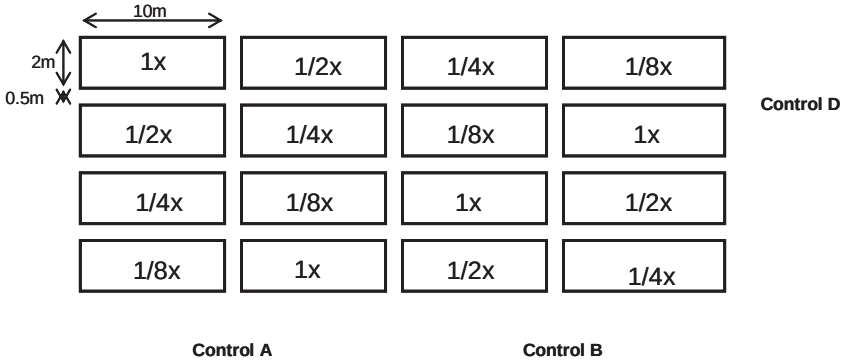


Figure 3.11. Latin Square site map for the agricultural field study.

3.6 Analytical Methods

The laboratory analysis was performed in the Water and Environmental Research Center (WERC) at the University of Alaska, Fairbanks. Triclopyr and 2,4-D were quantified with a gas chromatograph mass spectrometer (GCMS). Initially, soil samples were extracted with organic solvent and subsequently esterified with boron trifluoride to enable analysis by GCMS. Standards were prepared and analyzed to facilitate analyte quantification and selected ion monitoring (SIM) method development. Various quality control and quality assurance methods were practiced throughout the analysis to confirm instrumental integrity and validate data acquisition. All methods were practiced consistently throughout the duration of the study.

GCMS was selected for the analysis. The instrumental system consisted of an Agilent Technologies 6890N Gas Chromatograph equipped with a 7683 Series Injector and Autosampler and a 5973 Network Mass Selective Detector. Pertinent operational parameters and conditions used throughout the analysis are listed in Table 3.3.

As previously discussed, triclopyr ester and 2,4-D ester are relatively rapidly converted to their respective acid forms. In this state the herbicides exhibits high polarity and low volatility characteristic of chlorophenoxy acid herbicides, and cannot be successfully analyzed by gas chromatography. Consequently, triclopyr and 2,4-D acids must be derivatized to a methyl ester through an esterification procedure. After esterification, the methyl ester is readily volatilized under gas chromatographic conditions and quantification may be achieved. The soil extraction and esterification procedure employed was a modification of the method used by Mulkey (1990), which was adapted from Tsukioka (1985). Minor modifications were made so that available equipment and materials could be utilized. A brief description of the extraction and esterification processes follows. A more detailed description is provided in Appendix A.

Table 3.3: GCMS operating conditions

Component	Parameter	Value
Oven:	Initial Temperature (C°)	60
	Maximum Temperature (C°)	325
	Initial Time (min)	1.00
	Equilibration Time (min)	0.50
	Run Time (min)	36.4
Front inlet:	Mode	Splitless
	Initial Temperature (C°)	280
	Pressure (psi)	2.49
	Total Flow (mL/min)	103.1
	Gas Type	Helium
Front injector:	Injection Volume (μL)	2.0
	Syringe Size (μL)	10.0
Capillary Column:	Model #	Agilent 19091S-443 HP-5MS
	Dimensions (diameter, length, film thickness)	[0.25 mm] X [30 m] X [0.25 μm]
	Maximum Temperature (C°)	350
	Initial Flow (mL/min)	0.6
	Average Velocity (cm/sec)	27.0

Initially five grams of soil is weighed into an Erlenmeyer flask and mixed with deionized water and potassium hydroxide solution. The addition of alkaline solution serves to deprotonate the herbicide acid, forcing the compound into its hydrophilic, organic salt. At this point, a surrogate standard is introduced to the solution as well. The basic soil solution is shaken and centrifuged repeatedly to achieve separation between the soil particles and liquid such that the particles may be discarded. Next, diethyl ether (ether) is added and mixed vigorously resulting in an emulsion, followed by centrifugation separating the two fractions so that ether may be discarded. At this stage, ether's function is to remove ether soluble compounds that may be present in the soil, which may introduce matrix interference upon gas chromatography, while leaving the herbicide salt unaffected in the aqueous solution. Following this clean up step, the solution is acidified with sulfuric acid forcing the herbicide into the organic acid, which is readily soluble in ether. The acid is then extracted from the water fraction by successive ether washes, which are collected and eventually taken to dryness in a glass test tube. The remaining residue is ready for esterification. The esterification procedure involves the reaction of the residue with boron trifluoride (BF_3) in methanol, which acts as a catalyst in the formation of the methyl ester. Following the BF_3 reaction, the methyl ester is extracted with hexane and adjusted to a final volume suitable for GCMS analysis. All solvents and chemicals used in the procedure were analytical grade.

Standards were prepared and combined into a single solution that was utilized for various purposes including analyte identification, quantification, extraction efficiency determination and metabolite identification. Four different standards for triclopyr were used throughout the study including triclopyr acid, 2,4-dichlorophenylacetic Acid (DCAA), 1,4-Dichlorobenzene (DCB) and 3,5,6-trichloro-2-pyridinol (TCP). The standard DCAA was used for 2,4-D. After each standard's retention time and mass spectral fingerprint were confirmed, a selected ion monitoring (SIM) method was created. Each standard with the exception of DCB was prepared in a manner similar to that of the soil extraction and esterification procedure. This step was necessary because

as purchased, the standards were present as organic acids and had to be converted to their methyl esters for GCMS analysis.

The first use of the standard solution was to locate retention times and ion fragmentation patterns unique to each compound. This step was accomplished by injecting a relatively high concentration standard solution into the GCMS under a total ion chromatogram program, scanning for all ion fragments from 50 to 500 mass to charge ratio (m/z). Four prominent peaks were produced and subsequently delineated by summing the molecular weights of the ion fragments comprising the individual peaks, and comparing each peak sum with the given molecular weights of the various compounds. After positively identifying each item, the SIM method was developed. SIM allows the mass selective detector to monitor a specified number of ions eluting from the gas chromatographic column, eliminating the detection of ions not useful for the analysis thus reducing background noise in the signal. Six major ions for each compound were chosen for SIM monitoring.

Following SIM development, the internal instrument calibration was performed so that a quantifiable relationship could be established between standard (DCB) and the analyte standard. A series of triclopyr and 2,4-D standard solutions of varying concentration from 500 ppb to 5 ppm were analyzed to confirm instrumental linear response. With linearity established a one-point linear calibration curve between both herbicides and DCB was devised for quantification of environmental samples. DCB also functioned to indicate potential instrumental drift or change in sensitivity over time as it represented a constant concentration in all samples and standards.

DCAA functioned as the surrogate standard used to determine the soil extraction efficiency. In the first steps of the soil extraction procedure, a known quantity of DCAA was injected into each soil/water solution. DCAA is then carried through the extraction and esterification procedure and quantified with the GCMS. The extraction efficiency for a given sample is calculated as the mass ratio of DCAA present upon analysis vs. the original mass injected into the sample. Total extraction efficiency for the procedure is taken as the average of the individual sample recoveries.

TCP is recognized as the major metabolite of triclopyr found in a soil matrix (Ganapathy, 1997). However, in the esterification procedure TCP is converted to 3,5,6-trichloro-2-methoxypyridine (TMP). For the purpose of this analysis, if TMP was detected in the environmental sample it could be concluded that TCP was likely present and some form of microbial degradation was occurring.

Various measures were taken to ensure quality assurance and quality control including the use of continuous calibration verification (CCV), blanks, augmented samples, air/water checks and instrumental auto tune. CCV solutions were composed of the various standards mentioned in the previous subsection. Blank solutions included only the internal standard, DCB, and solvent. CCV and blank standards were injected prior to, and after every ten environmental sample injections to ensure instrumental consistency and data reliability. CCV solutions were also used to establish a detection limit for the analysis, defined as three times the standard deviation of the lowest concentration triclopyr and 2,4-D standard. With the average and standard deviation of 10 standards considered, the detection limit was calculated as 15 ppb.

Periodically environmental samples were augmented to confirm analytical accuracy. Duplicate environmental samples were prepared and prior to analysis one was injected with a known quantity of triclopyr and 2,4-D standard. The percent increase in analyte concentration measured between the sample and the augmented sample was then assessed. All augmented samples fell within the acceptable range of ± 30% of the expected value.

3.7 Herbicide Effectiveness Assessment Procedure

Before treatment application, the cover of each plant species was measured. All treatments were measured in the autumn of the application year and the following year. Before treatments could be measured in Valdez in the first autumn, the plot area was mowed, so measurements could not be made. The following autumn in Valdez, the plots were measured, but the previous years unplanned for mowing of all treatments made comparisons with of among treatments and comparisons with results in Delta Junction impossible.

4.0 Results from Continental Study Sites

The results consist of data collected and analyzed for triclopyr and 2,4-D from the Delta Junction, Alaska, area sites (rights-of-way and agricultural field) over the course of two field seasons. The data from the 2,4-D study will be presented first followed by the data from the triclopyr ROW study. Results from the triclopyr application to the agricultural soils will be discussed last.

4.1 2,4-D Concentration in Continental Right-of-Way Field Site Soil

A summary of 2,4-D concentrations in soil measured at the Delta Junction site are provided in Table 4.1. Non-parametric comparison of the median concentration at each sample time for each site is shown in Figure 4.1. A comparison of the median concentrations at each sample time for each of plot that received 2,4-D showed no distinct concentration differences, therefore the data results from the two plots were combined to determine the median, upper and lower quantile (Table 4.1). Concentration values for each sample location and depth can be found in Appendix B. The reader should note that the results reflect only 2,4-D acid (2,4-D) concentrations and do not include 2,4-D iso-octyl ester concentrations, which were not extracted from the soil samples and analyzed.

Extraction efficiencies were determined to be 70.22% ± 11.53% for the samples taken at the Delta Junction site. Extraction efficiencies are not based on all samples due to soil matrix interference with the DCAA. In several samples, the soil matrix interference with the DCAA caused peak collusion with unidentified soil compounds that had the same ions and a similar retention time, making it impossible to analyze areas under the extracted ion chromatogram peaks and determine extraction efficiency. While slight variations in soil composition and organic matter existed between samples, the overall extraction efficiency for each sample location is representative as sample extraction methods were not altered during the study period. Sample concentrations have not been adjusted to reflect the extraction efficiencies. Thus, concentration values presented in Table 4.1 and Figure 4.1 are measured concentration values and have not been adjusted for recovery rate.

While some areas in the study plots may have received no 2,4-D due to interception of the spray stream by tall vegetation (to be discussed), it is impossible to determine if samples with non-detectable levels of 2,4-D never actually received 2,4-D, or if the 2,4-D concentrations were below the GCMS detection limits. Therefore, median concentrations presented in the figures and tables are based on all samples, including those without detectable concentrations, which were assigned a value of zero.

As Table 4.1 and Figure 4.1 shows, the first notable result is the relatively low concentrations measured in the surface and subsurface soils at the Delta Junction site (note concentration values are presented in units of micrograms per kilogram, μg/kg), which is consistent with the findings of Radosevich and Winterlin (1977) discussed previously. The median surface concentration values show a general downward trend over time (Figure 4.1 and Figure 4.2) as expected, though a slight increase in median concentration is noted at 5 DAT, at 47 DAT, and again at 288 DAT. The highest median surface concentration occurred during the second sample event at 5 DAT. However, the highest observed surface concentration during the study period occurred 1 DAT and is shown in Table 4.1. Hydrolysis of the 2,4-D ester to the acid form may partially explain why the highest median concentration of 2,4-D acid occurred five days after the application. Others have reported similar reaction times (Stewart and Gaul, 1977;

Grover et al., 1985). Another likely contributor to increase in concentration at 5 DAT is wash-off of the herbicide from the vegetation.

Table 4.1 2.4-D concentration (μg/kg) summary for the Delta Junction field site. Root zone and below root zone samples were not collected at 288 DAT because those soil layers were still frozen at that time.

Sample Date	DAT	No. of Samples	Median	Low	High	Lower Quantile	Upper Quantile
Surface							
7/7/06	1	8	23.2	ND	252.6	6.48	62.17
7/11/06	5	7	33.4	44.1	139.6	21.80	37.82
7/17/06	11	7	10.4	30.4	91.1	9.05	18.51
8/2/06	27	8	7.5	9.5	31.5	5.41	13.28
8/22/06	47	8	19.7	30.0	90.8	11.22	32.88
10/6/06	92	6	15.0	8.6	29.7	12.29	21.89
4/20/07	288	8	28.2	38.1	128.7	18.83	47.61
5/18/07	316	7	8.2	10.9	32.2	7.69	16.64
7/3/07	362	7	3.1	1.9	6.8	1.92	4.55
Root Zone							
7/7/06	1	8	1.0	ND	9.2	0.78	2.32
7/11/06	5	6	1.5	ND	11.5	0.83	1.80
7/17/06	11	8	4.4	ND	6.8	0.00	5.93
8/2/06	27	7	5.1	4.1	10.4	4.64	5.62
8/22/06	47	8	3.5	2.7	7.9	2.79	4.61
10/6/06	92	6	2.1	ND	2.6	0.41	2.55
4/20/07	288	NT	NT	NT	NT	NT	NT
5/18/07	316	5	0.6	0.4	0.7	0.46	0.61
7/3/07	362	8	ND	ND	ND	ND	ND
Below Root Zone							
7/7/06	1	8	2.1	ND	3.6	0.50	2.78
7/11/06	5	7	0.5	ND	1.2	ND	1.05
7/17/06	11	7	0.0	ND	4.7	ND	3.77
8/2/06	27	8	3.2	1.2	3.9	2.84	3.32
8/22/06	47	7	2.6	1.6	5.2	2.02	3.76
10/6/06	92	6	1.2	ND	1.7	0.22	1.59
4/20/07	288	NT	NT	NT	NT	NT	NT
5/18/07	316	8	0.2	ND	0.5	ND	0.41
7/3/07	362	8	ND	ND	ND	ND	ND

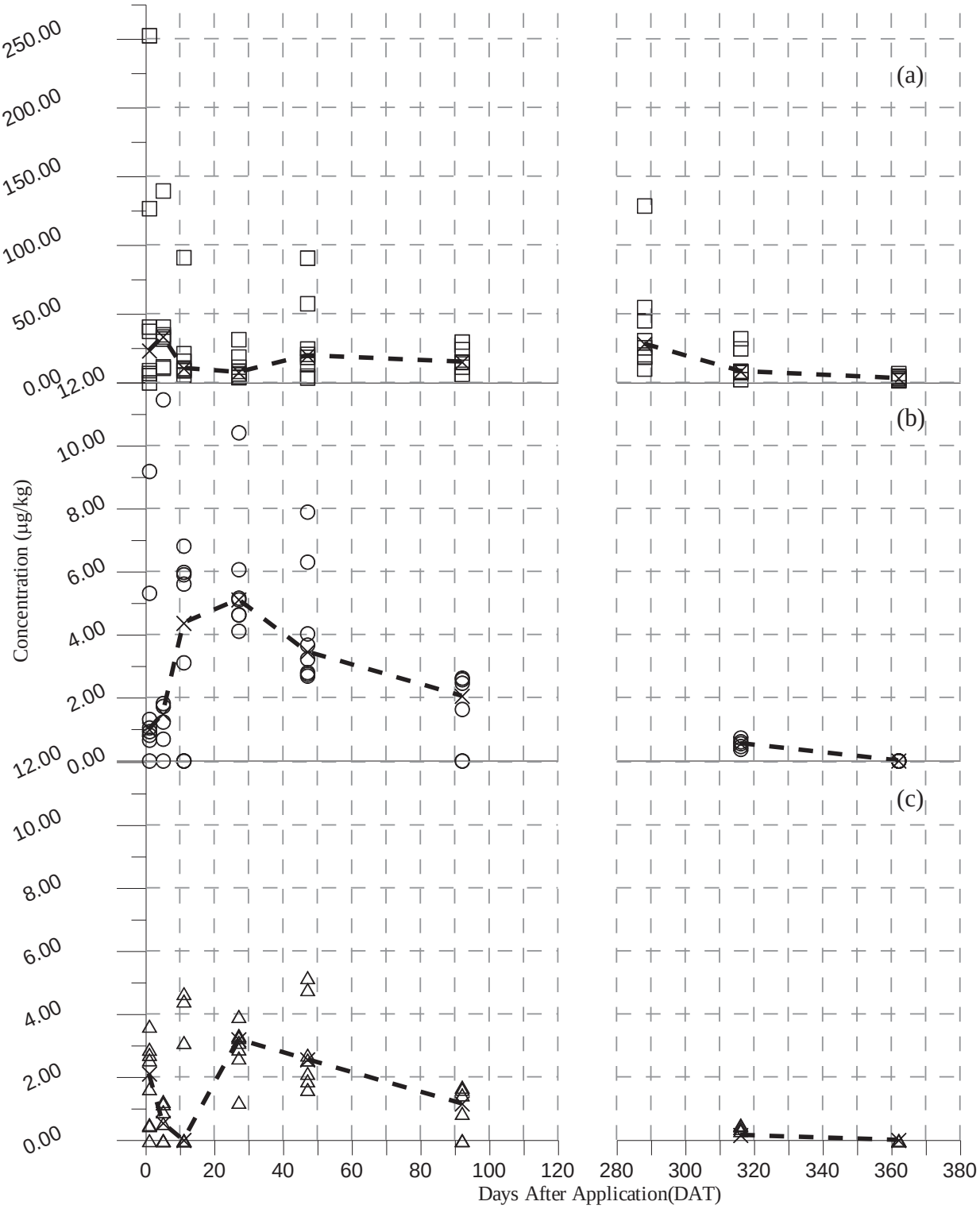


Figure 4.1. 2,4-D concentration measured in surface (a, 0-7.5 cm), root zone (b, 10-30 cm), and below root zone (c, 36-60 cm) soil at the Delta Junction site. The trend lines in each plot represent the median sample concentration. Herbicide was applied to the site on July 6, 2006. The soil froze approximately 120 days after application and thawed approximately 286 days after application. The break in the ordinate axis represents this frozen period. Note the concentration scale difference between (a) and both (b) and (c).

Vegetation interception played a primary role in the surface concentrations in soils collected during the week following the 2,4-D application. Affects include variability in concentration measured in the soil as noted in Figure 4.1. This variability is due in part to direct application on bare soil in some areas and interception by vegetation resulting in little-to-no herbicide contacting soil on the lee side of the vegetation that is blocking the mostly horizontal flow stream as it is ejected from the sprayer. Interception of the herbicide by relatively tall vegetation may also result in concentrating the relatively greater mass in some areas as opposed to others. If a sufficient amount of herbicide impacts the vegetation fluid that is not retained on the plant matter will flow down the plant stem and concentrate at the base of the plant. In addition, some herbicide may be reflected back onto relatively bare soil following impact. As discussed, a fraction of the herbicide that is retained on the plant will be taken up into the plant. The remaining herbicide will be degraded by photooxidation, volatilize into air, and eventually wash off of the leaves after heavy dew or a rainfall. Herbicide that is washed off of the plant will contribute to increases in herbicide concentration measured in the soil.

Variability in the individual surface sample concentrations decreases by day 27. Microbial degradation and sorption most likely contribute to this decrease; however leaching into subsurface soil also likely decreases the surface concentration variability. Leaching into subsurface soil is evidenced by the increase in root zone and below root zone 2,4-D concentration at 27 DAT. Concentrations of 2,4-D in the surface soil at 27 DAT then is most likely the fraction that is sorbed to the organic matter in these near surface soils. Since the organic matter content is most likely somewhat uniform throughout these near surface soils providing a fairly even distribution of sorption sites in the soil, a relatively more consistent concentration is measured. Quantities of 2,4-D not sorbed to soil will leach further down into the soil column as shown by the increases in subsurface 2,4-D concentrations. These results are consistent with those found by Johnson et al. (1995). As previously discussed (Section 2.3.5) these researchers found that specific binding sites for 2,4-D (and triclopyr) in soil are limiting. A relatively greater amount of herbicide is desorbed from the soil as the initial herbicide concentration increases. Relating these findings to the results of this study, the relatively greater mass of 2,4-D found in several of the samples taken at 11 DAT most likely resulted in desorption of the herbicide and downward leaching resulting in the increase in concentration found in the root zone at 27 DAT.

In addition to vegetation interception, drift losses, which transport a herbicide to other regions of the site or to locations that are off-site, can also account for some of the variability at a study site. Though, Grover et al. (1985) found that droplet and vapor drift losses accounted for less than 0.2% of the total amount of 2,4-D iso-octyl ester applied. Applications of 2,4-D tri-isopropaolamine salt in Ontario caused trace amounts to be detected up to 10 meters from the study area (Meru et al., 1990). While drift losses were not measured at the Delta Junction site, these studies suggest that it is unlikely drift loss accounts for the variability observed in the sample concentrations, especially considering that the application was conducted under low wind conditions.

The increase in concentration found in the surface soil 47 DAT closely followed a rain event of 11.2 mm and is shown in Figure 4.2. Other rain events occurred prior to day 47, but none generated more than 5 mm of precipitation and did not result in increased surface soil concentrations. In addition, the increase was not observed in the root zone or below root zone samples, though an increase could have occurred prior to sample collection on day ninety-two as the herbicide leached through the soil profile (Figure 4.1).

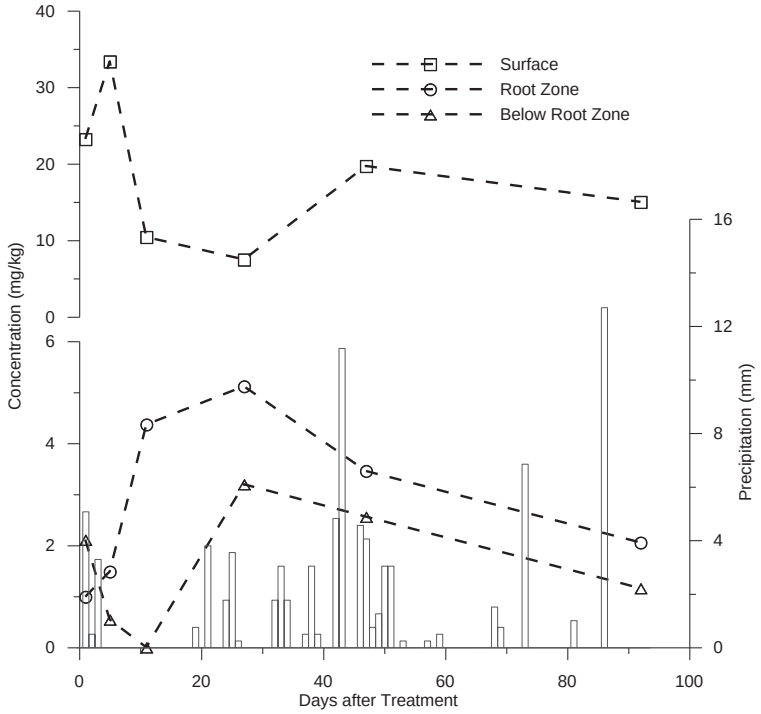


Figure 4.2. Median 2,4-D concentrations at the Delta Junction site and daily precipitation amounts measured at the Delta Junction 20 SE weather station for the first 92 days after treatment.

Several possible explanations can be hypothesized as to why the 2,4-D concentrations increased in the surface soil and detected at day 47. The rain event may have caused surface wash-off from the vegetation and contributed to the concentration increase, though the majority of the herbicide was likely removed from the foliage surface prior to day 47 through the processes of plant uptake, volatilization, photodegradation, and wash off. Other processes such as reverse conjugation in the roots of susceptible species from amino acids to the free acid form may have contributed to the increase, allowing the free acid to be leached from the roots to the soil by the precipitation (Davidonis et al., 1980). Stewart and Gaul (1977) propose a similar mechanism in their study on 2,4-D and 2,4,5-T persistence in a humid, temperate climate.

The increase in soil moisture following the rain event may have caused additional hydrolysis of the ester sorbed to organics or contained in vegetation matter contained in the surface soil to the acid form, which then would cause a release of additional 2,4-D to the soil surface. Grover et al. (1985) found that the hydrolysis process appeared to be positively affected by increased moisture contents. Morton et al. (1967) measured 2,4-D acid and 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) concentrations in several growing non-susceptible grasses and in dead grass vegetation litter over 16 week periods. Results from their study showed an increase in 2,4-D concentration in the dead litter tissue following a relatively significant rainfall that occurred approximately 3 ½ weeks after application. Further, these researchers also measured changes in concentrations of amine esters and butoxyethyl ester of 2,4-D and 2,4,5-T following rain events occurring several weeks after treatment. Unfortunately, the researchers did not measure acid concentrations and ester concentration during the same study period, eliminating

the possibility of associating these increases in the acid concentration with hydroloysis of the ester. While these researchers do not speculate as to why these increases occurred, they do conclude that rainfall was the most important factor controlling the persistence of the herbicides in the vegetation. In a search of available literature, the study conducted by Morton et al. (1967) was the only study found that showed an increase in surface-soil herbicide concentration following a rain event.

Another increase in the median surface concentration occurred at 288 DAT, following the surface soils thaw during spring breakup. However, it should be noted that random sampling conducted at the site may have contributed to the observed concentration increase. It is also possible that the increased surface concentrations after spring breakup were caused by a release mechanism similar to the one that caused the concentration increase at day forty-seven, such as the reverse conjugation of the amino acids to free 2,4-D in the roots of susceptible plants (Davidonis et al., 1980) or continued hydrolysis of the ester to the acid form, as speculated from the results presented by Morton et al. (1967).

An additional explanation for the increase in concentration following spring break-up is movement of dissolved phase 2,4-D in soil water that is moving upward from depth toward the downward progressing freezing front as the soil horizon freezes in the fall. Wilson and Cheng (1976) propose a similar transport mechanism in a dry relatively more temperate climate. These researchers discuss the possibility of dissolved herbicide moving upward in soil-water due to capillarity during a dry period. Evidence of soil-water movement to the freezing front has been most recently documented by Iwata and Hirota (2005). If these soils are conducive to this transport mechanism, then 2,4-D mass would accumulate in the frozen upper soil horizon prior to spring thaw. The surface samples collected immediately following spring breakup were collected when the root and below root zone depths were still frozen, which means that any additional 2,4-D in the surface was unable to leach through the soil column before the sample event at day 288. An increase in concentration was not observed in subsurface soils following spring breakup. It is possible that a concentration increase occurred as the thaw front moved through the soil column, but root zone and below root zone samples were collected over a week after the ground thawed, allowing time for any increased 2,4-D to leach through the soil column. If the concentration increase is valid, then the Delta Junction results would confirm the results found by Torstenssen and Stark (1982), who also observed increased concentrations of the herbicide triclopyr in soils following spring breakup in Sweden. Measured increased concentration values following spring break up in comparison to values found prior to winter freeze up will be discussed further in Section 4.3.

As shown by others, the progression of 2,4-D into the subsurface in this study followed the peak concentration in the surface soils (Wilson and Cheng, 1976; Newton et al., 1990; Crespin et al., 2001). The majority of root zone and below root zone samples exhibited small concentrations of 2,4-D one DAT. Rain events immediately following the application may have contributed to the transport of 2,4-D to the subsurface so soon after the application. While the Delta Junction 20 SE weather station did not record any rain on July 6, 2006, the day of the application, a rain event was observed at the site. The small rain event at the Delta Junction study site may reasonably explain the 2,4-D detected in the root and below root zone samples one day following the application. Secondary porosities in surface soils created by root channels, burrowing animals, and insects can create preferential flow paths for infiltrating water. Such preferential flow paths could be the reason a small rain event was able to cause leaching at the Delta Junction site one DAT. In addition, the rain event on July 6, 2006 occurred within three

hours after the application when little herbicide dissipation by plant uptake, photooxidation, and volatilization had occurred.

The root zone and below root zone samples had similar detectable concentrations, especially when compared to the concentrations detected in the surface samples (Table 4.1). As shown in Figure 4.2, the highest median concentrations in the root zone and below root zone samples occurred 27 DAT. The median concentrations in the root zone increased from day one through day 27, at which point they decreased throughout the study period and were no longer detected 362 days following the application. The below root zone samples, which exhibited a higher median concentration than the root zone samples 1 DAT, had decreasing median concentrations through day 11. The below root zone samples saw an increase in median concentration on day 27, after which a steady decrease was observed through the rest of the study period, with no detectable concentrations on day 362 (Figure 4.1).

4.2 Triclopyr Concentration in Continental Right-of-Way Field Site Soil

A summary of triclopyr concentration (triclopyr concentration units are mg/L) versus time data for the three depths are tabulated in Table 4.2 and graphically illustrated in Figure 4.3. As with the 2,4-D results, triclopyr concentration results were analyzed using nonparametric statistics. In addition, non-detectable concentrations were treated as zero as was done in the analysis of the 2,4-D results. Concentrations for each sample point as a function of time and depth are provided in Appendix B. Initially, two plots were to be sampled for the course of the study however, it was determined that one of the plots received only partial triclopyr application and produced erroneous results. Therefore, the results in this section consist of data collected from one plot only and conclusions are to be made on four sample points per sampling date. The herbicide extraction process from the soil resulted in an efficiency of 74% ± 6%, similar to Mulkey (1990). Results shown in Table 4.1, Figure 4.3 and in Appendix B are not corrected for the extraction efficiency.

As with the 2,4-D results, the first notable result is the relatively large spread in the concentration values for the early sample dates; specifically in the results from the surface soils. This spread is most likely represents uneven distribution of the herbicide due to blockage of the spray by vegetation during application. As discussed, these results are typically associated with field studies on unclipped vegetation.

Unlike the concentration trend found in the 2,4-D study, the maximum median concentration of triclopyr was measured in the surface soil one DAT. This result could be an artifact of the sampling procedure, four samples analyzed for triclopyr as opposed to eight for 2,4-D, resulting in a greater chance of randomly selecting a sampling location with a high concentration. Conversely, the results could be due to a more rapid hydrolysis of the triclopyr ester formulation in comparison to the 2,4-D ester formulation. Further, this differing trend may be a result of a more thorough wash-off of the herbicide from the vegetation during the precipitation event less than three hours following application. A decrease in concentration follows until 47 DAT where a slight increase in the median concentration is found as with the 2,4-D study. Counter to the 2,4-D results an increase in the median concentration was not detected in the surface soil after spring break up.

Table 4.2 Triclopyr concentration (mg/kg) summary for the Delta Junction ROW field site. Root zone and below root zone samples were not collected at 288 DAT because those soil layers were still frozen at that time.

Sample Date	DAT	No. of Samples	Median	Low	High	Lower Quantile	Upper Quantile
Surface							
7/7/06	1	4	3.31	0.291	6.256	0.350	6.25
7/11/06	5	4	0.149	ND	1.521	0.073	0.531
7/17/06	11	4	0.236	0.096	0.902	0.159	0.445
8/2/06	27	4	0.172	0.084	0.276	0.088	0.260
8/22/06	47	4	0.782	0.232	1.386	0.449	1.13
10/6/06	92	4	0.126	ND	0.316	0.005	0.263
4/20/07	288	4	0.008	0.002	0.016	0.005	0.011
5/18/07	316	4	0.031	0.011	0.074	0.025	0.043
7/3/07	362	4	ND	ND	ND	ND	ND
Root Zone							
7/7/06	1	4	0.023	ND	0.219	ND	0.090
7/11/06	5	4	0.027	ND	0.168	ND	0.082
7/17/06	11	4	0.040	ND	0.086	ND	0.081
8/2/06	27	4	0.052	0.028	0.066	0.043	0.059
8/22/06	47	4	ND	ND	0.008	ND	0.002
10/6/06	92	4	ND	ND	ND	ND	ND
4/20/07	288	0	NT	NT	NT	NT	NT
5/18/07	316	4	ND	ND	ND	ND	ND
7/3/07	362	4	ND	ND	ND	ND	ND
Below Root Zone							
7/7/06	1	4	ND	ND	ND	ND	ND
7/11/06	5	4	ND	ND	ND	ND	ND
7/17/06	11	4	0.035	ND	0.082	0.011	0.062
8/2/06	27	4	0.040	ND	0.051	0.029	0.045
8/22/06	47	4	ND	ND	0.008	ND	0.002
10/6/06	92	4	0.001	ND	0.004	ND	0.002
4/20/07	288	0	NT	NT	NT	NT	NT
5/18/07	316	4	ND	ND	ND	ND	ND
7/3/07	362	4	ND	ND	ND	ND	ND

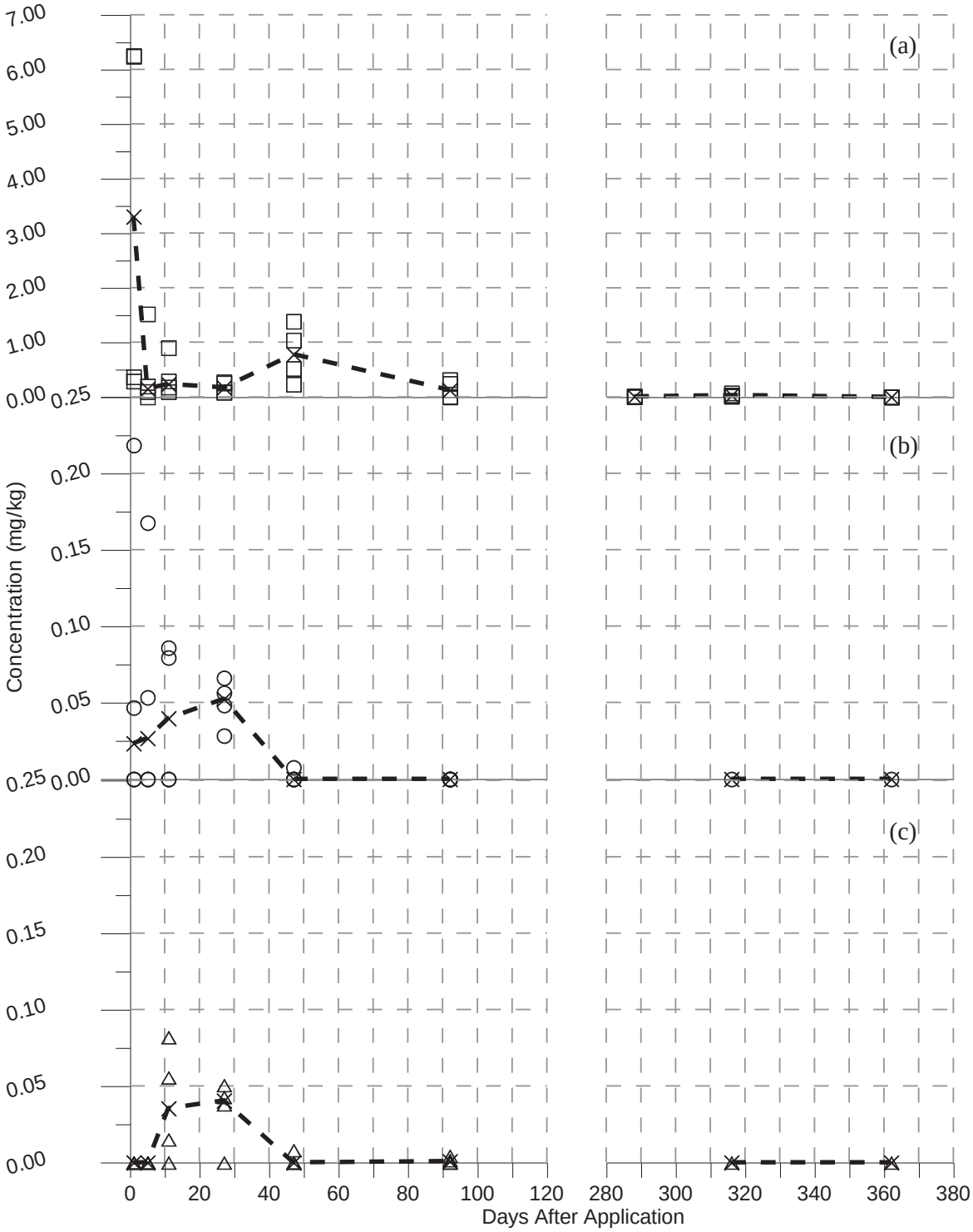


Figure 4.3. Triclopyr concentration measured in surface (a, 0-5 cm), root zone (b, 10-18 cm), and below root zone (c, 30-38 cm) soil at the Delta Junction ROW test section. The trend lines in each plot represent the sample concentration median. Herbicide was applied to the site on July 6, 2006. The soil froze approximately 120 days after application and thawed approximately 286 days after application. The break in the ordinate axis represents this frozen period. Note the concentration scale difference between (a) and both (b) and (c).

Triclopyr was not detected in the subsurface samples taken after spring thaw. Further, triclopyr was not measured in the soils samples obtained from the root zone just prior to freeze-up (92 DAT, October 6), though below root zone samples did have detectable amounts of triclopyr. Microbial degradation of triclopyr in the root zone, which is most likely a more microbially active section of the soil than below the root zone due to the greater amounts of organic material, could have reduced the concentration of triclopyr to values that are not detectable by the analytical procedure used in this study.

Triclopyr concentration measured in the three soil depths is plotted against precipitation in Figure 4.4. As with the 2,4-D result, increase in herbicide concentration is not detected in the subsurface 47 DAT. The subsurface results at 47 DAT are inconsistent with the triclopyr and 2,4-D concentration found in subsurface soils one DAT, which again follows a precipitation event. It is interesting to note that an increase in triclopyr concentration found in surface soils is not detected after the rain events prior to sampling at 27 DAT, which is counter to the 2,4-D results. Again, this result could be due to the fewer number of samples obtained in the triclopyr study as opposed to the 2,4-D study.

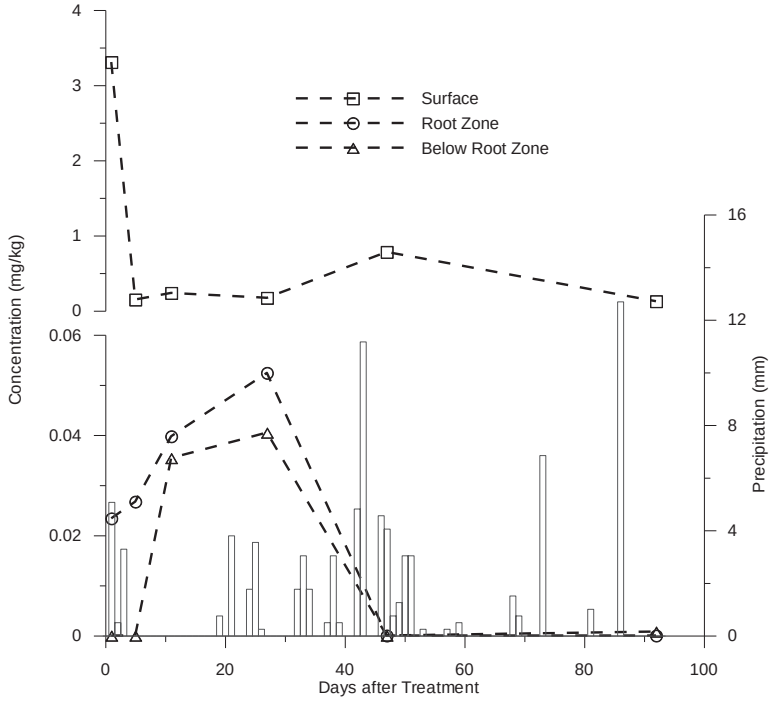


Figure 4.4. Median triclopyr concentrations at the Delta Junction ROW site and daily precipitation amounts measured at the Delta Junction 20 SE meteorological station for the first 92 days after treatment.

4.3 Triclopyr Concentration in Agricultural Field Site Soil

Results from the four different dose amounts are shown in Tables 4.3-4.6 and Figures 4.5-4.8. The trend in concentration over time for each of the application amounts is similar and the medium concentrations at each sampling time is representative of the dilution, in other words

the median concentration at an application amount of 2.2 kg/ha is relatively greatest in comparison to the lower dilutions. Also evident for each dilution is an increase in median concentration in surface soils after spring break-up (283 DAT). This increase is comparably much greater than the increase found in the 2,4-D ROW study discussed previously. The possible reasons for this increase were discussed previously. However, the explanation is complicated by the fact that the vegetation was clipped prior to herbicide application at the agriculture study site.

Additional insight on the increase in concentration at 283 DAT can be found in Ranft (2008) and Ranft et al. (in press). These references report the results of a soil bioassay conducted in consortium with the chemical extraction method of the collected soils from the agricultural field site described in this report. A soil bioassay utilizes plants as bioindicators of herbicide residue in the soil by measuring the toxicity of the herbicide residues present in the soil to the plant; a response known as phytotoxicity. In Ranft's (2008) study, mustard was planted in soils collected from the study site at each sampling date. After one week in a growth chamber, the biomass of the mustard growing in the triclopyr treated soils was analyzed and compared against a control consisting of mustard planted in soil not treated with triclopyr. Comparison of the bioassay results to the results obtained from chemical extraction indicate that the two measurement methods give equivalent results. Yet, a comparison of the chemical extraction results to the bioassay results found in the soil collected at 283 DAT differ. While the concentration results from chemical extraction show similar triclopyr concentrations to those measured the first week after treatment, the phytotoxicity of the residues in the soil measured by bioassay result in a only a slight decrease in biomass compared to the control. In fact, the results of the bioassay at 283 DAT were no different than the bioassay results at 35 DAT when the median measured concentration in the soil was 0.016 mg/kg (Ranft et al., in press).

A possible explanation for this result may be found in a study presented in Lewer and Owen (1990). These researchers determined that the triclopyr susceptible plant chickweed (*Stellaria media L.*) did not metabolize triclopyr as rapidly as more tolerant plants (barley and wheat). They also determined that the major metabolite in the susceptible plant was triclopyr aspartate, which can be hydrolyzed to the phytotoxic triclopyr acid. It is possible that at spring thaw triclopyr and triclopyr aspartate could have been released from triclopyr susceptible and other vegetation hat had been killed the previous autumn or during the first hard freeze in mid-September (about 55 DAT). In a study conducted by Jotcham et al. (1989) triclopyr was found to be still present in soil two months following application, yet was found to be no longer toxic to lentils used as a bioassay plant. This study further indicates that the triclopyr measured in the soil at 283 DAT could have been a metabolite that was hydrolyzed to triclopyr acid during the chemical extraction process.

Relatively low concentrations of triclopyr in the surface soils were still detectable 365 DAT, which was the last sampling event for this study. At 283 DAT, triclopyr was still detectable in the subsurface soil, though at 365 DAT triclopyr was not longer detectable at these depths. This result is counter to the triclopyr ROW study. In the ROW study, triclopyr was no longer detected in the subsurface soils after 92 DAT, which was prior to winter freeze-up.

A comparison of the median concentrations found in the soil at the agricultural study site versus precipitation events is shown in Figure 4.9 through 4.12. An interesting comparison between the ROW study sites (both triclopyr and 2,4-D) and the agricultural study site can be made. In both the ROW studies increase in herbicide were found in the surface soils following the rain event that occurred 43 DAT. Due to a different treatment date on the agricultural field, this precipitation event occurred 33 DAT. The sampling event following the precipitation only

showed an increase in concentration on the plot that received a dose of 1.1 kg/ha. The other study plots did not show increases in herbicide concentration as was found in the ROW study. The reason for this difference is not known.

Table 4.3 Triclopyr concentration (mg/kg) summary for the Delta Junction Agricultural field site. Mass aerial application equal to 2.2 kg/ha

Sample Date	DAT	No. of Samples	Median	Low	High	Lower Quantile	Upper Quantile
Surface							
7/18/06	1	8	0.516	0.225	1.09	0.304	0.691
7/19/06	3	4	0.991	0.492	3.08	0.589	1.79
7/23/06	7	8	0.560	0.122	1.65	0.331	0.653
8/6/06	21	4	0.163	0.078	0.198	0.116	0.198
8/20/06	35	8	0.016	ND	0.072	0.008	0.058
4/25/07	283	8	0.622	0.174	1.72	0.403	0.992
7/16/07	365	8	0.023	ND	0.096	0.012	0.036
Root Zone							
7/19/06	3	4	0.064	ND	0.078	0.038	0.078
7/23/06	7	8	0.096	0.046	0.199	0.075	0.113
8/6/06	21	4	0.067	0.037	0.075	0.055	0.074
8/20/06	35	8	0.015	0.002	0.671	0.012	0.038
4/25/07	283	8	0.041	0.023	0.088	0.029	0.083
7/16/07	365	8	ND	ND	ND	ND	ND
Below Root Zone							
7/23/06	7	8	0.055	ND	0.095	0.029	0.076
8/6/06	21	4	0.057	0.047	1.129	0.048	0.332
8/20/06	35	8	0.025	ND	0.234	0.015	0.047
4/25/07	283	8	0.023	0.015	0.548	0.019	0.226
7/16/07	365	8	ND	ND	ND	ND	ND

Table 4.4 Triclopyr concentration (mg/kg) summary for the Delta Junction Agricultural field site. Mass aerial application equal to 1.1 kg/ha

Sample Date	DAT	No. of Samples	Median	Low	High	Lower Quantile	Upper Quantile
Surface							
7/18/06	1	8	0.384	0.250	0.996	0.283	0.555
7/19/06	3	4	0.217	0.080	0.326	0.103	0.324
7/23/06	7	8	0.257	0.160	0.411	0.232	0.308
8/6/06	21	4	0.062	0.050	0.194	0.056	0.098
8/20/06	35	8	0.094	ND	0.226	0.047	0.131
4/25/07	283	8	0.294	0.011	0.681	0.242	0.401
7/16/07	365	8	0.009	ND	0.036	ND	0.011
Root Zone							
7/19/06	3	4	0.044	ND	0.069	0.032	0.052
7/23/06	7	8	0.070	0.021	0.096	0.059	0.077
8/6/06	21	4	0.018	ND	0.639	ND	0.187
8/20/06	35	8	0.011	0.006	0.020	0.007	0.017
4/25/07	283	8	0.020	0.012	0.159	0.016	0.022
7/16/07	365	8	ND	ND	ND	ND	ND
Below Root Zone							
7/23/06	7	8	0.058	ND	0.112	0.041	0.097
8/6/06	21	4	0.296	0.025	0.573	0.049	0.544
8/20/06	35	8	0.011	ND	0.053	0.003	0.012
4/25/07	283	8	0.017	0.010	0.024	0.013	0.021
7/16/07	365	8	ND	ND	ND	ND	ND

Table 4.5 Triclopyr concentration (mg/kg) summary for the Delta Junction Agricultural field site. Mass aerial application equal to 0.55 kg/ha

Sample Date	DAT	No. of Samples	Median	Low	High	Lower Quantile	Upper Quantile
Surface							
7/18/06	1	8	0.147	0.043	0.306	0.105	0.223
7/19/06	3	4	0.191	0.065	0.320	0.126	0.258
7/23/06	7	8	0.176	0.030	1.162	0.133	0.228
8/6/06	21	4	0.066	0.056	0.106	0.063	0.077
8/20/06	35	8	0.061	0.016	0.179	0.041	0.074
4/25/07	283	8	0.099	0.057	0.181	0.090	0.114
7/16/07	365	8	0.002	ND	0.021	ND	0.008
Root Zone							
7/19/06	3	4	0.086	0.067	0.093	0.081	0.089
7/23/06	7	8	0.065	0.035	0.091	0.063	0.074
8/6/06	21	4	0.198	0.056	0.416	0.065	0.349
8/20/06	35	8	0.006	ND	0.051	ND	0.020
4/25/07	283	8	0.012	0.011	0.026	0.012	0.015
7/16/07	365	8	ND	ND	ND	ND	ND
Below Root Zone							
7/23/06	7	8	0.041	0.029	0.070	0.036	0.062
8/6/06	21	4	0.048	0.039	0.367	0.046	0.128
8/20/06	35	8	0.012	ND	0.015	0.009	0.013
4/25/07	283	8	0.014	ND	0.016	0.010	0.016
7/16/07	365	8	ND	ND	ND	ND	ND

Table 4.6 Triclopyr concentration (mg/kg) summary for the Delta Junction Agricultural field site. Mass aerial application equal to 0.275 kg/ha

Sample Date	DAT	No. of Samples	Median	Low	High	Lower Quantile	Upper Quantile
Surface							
7/18/06	1	8	0.078	0.038	0.110	0.039	0.092
7/19/06	3	4	0.150	ND	0.184	0.108	0.164
7/23/06	7	8	0.130	0.018	0.807	0.097	0.218
8/6/06	21	4	0.078	0.050	0.102	0.056	0.098
8/20/06	35	8	0.039	0.013	0.082	0.022	0.045
4/25/07	283	8	0.047	0.026	0.079	0.033	0.057
7/16/07	365	8	ND	ND	0.011	ND	0.001
Root Zone							
7/19/06	3	4	0.026	ND	0.057	ND	0.053
7/23/06	7	8	0.067	0.033	0.877	0.054	0.085
8/6/06	21	4	0.079	0.072	0.190	0.075	0.110
8/20/06	35	8	0.007	ND	0.019	0.005	0.009
4/25/07	283	8	0.012	ND	0.026	0.011	0.013
7/16/07	365	8	ND	ND	ND	ND	ND
Below Root Zone							
7/23/06	7	8	0.028	ND	0.821	ND	0.051
8/6/06	21	4	0.056	0.041	0.170	0.043	0.093
8/20/06	35	8	0.002	ND	0.015	ND	0.008
4/25/07	283	8	0.010	ND	0.018	0.009	0.012
7/16/07	365	8	ND	ND	ND	ND	ND

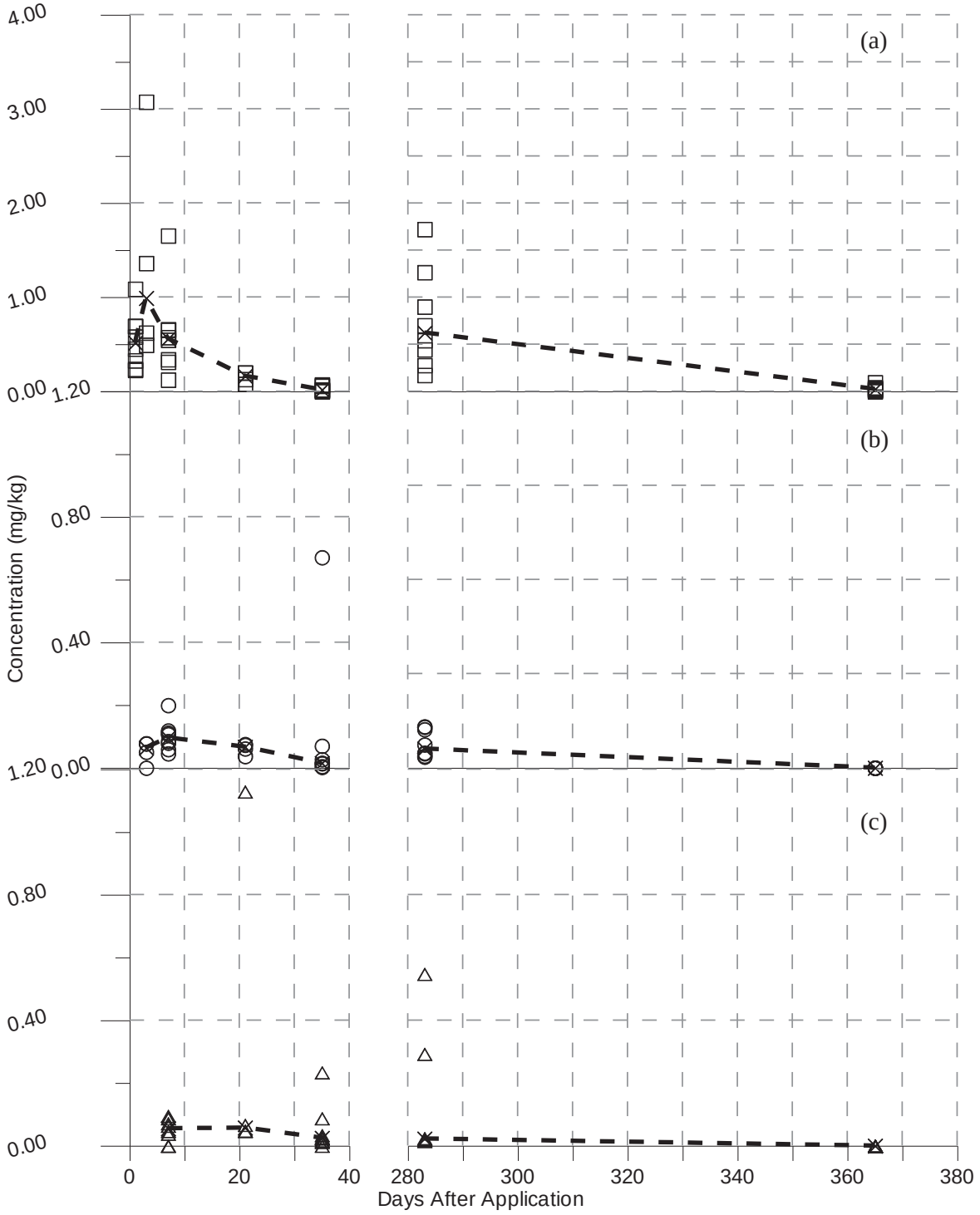


Figure 4.5. Triclopyr concentration measured in surface (a, 0-5 cm), root zone (b, 5-15 cm), and below root zone (c, 15-30 cm) soil at the Delta Junction agricultural test section for an application rate of 2.2 kg/ha. The trend line in each plot represents the sample concentration median. Herbicide was applied to the site on July 17, 2006. The soil froze approximately 110 days after application and thawed approximately 276 days after application. The break in the ordinate axis represents the period from approximately the last sampling prior to freeze up and the first sampling after thaw. Note the concentration scale difference between (a) and both (b) and (c).

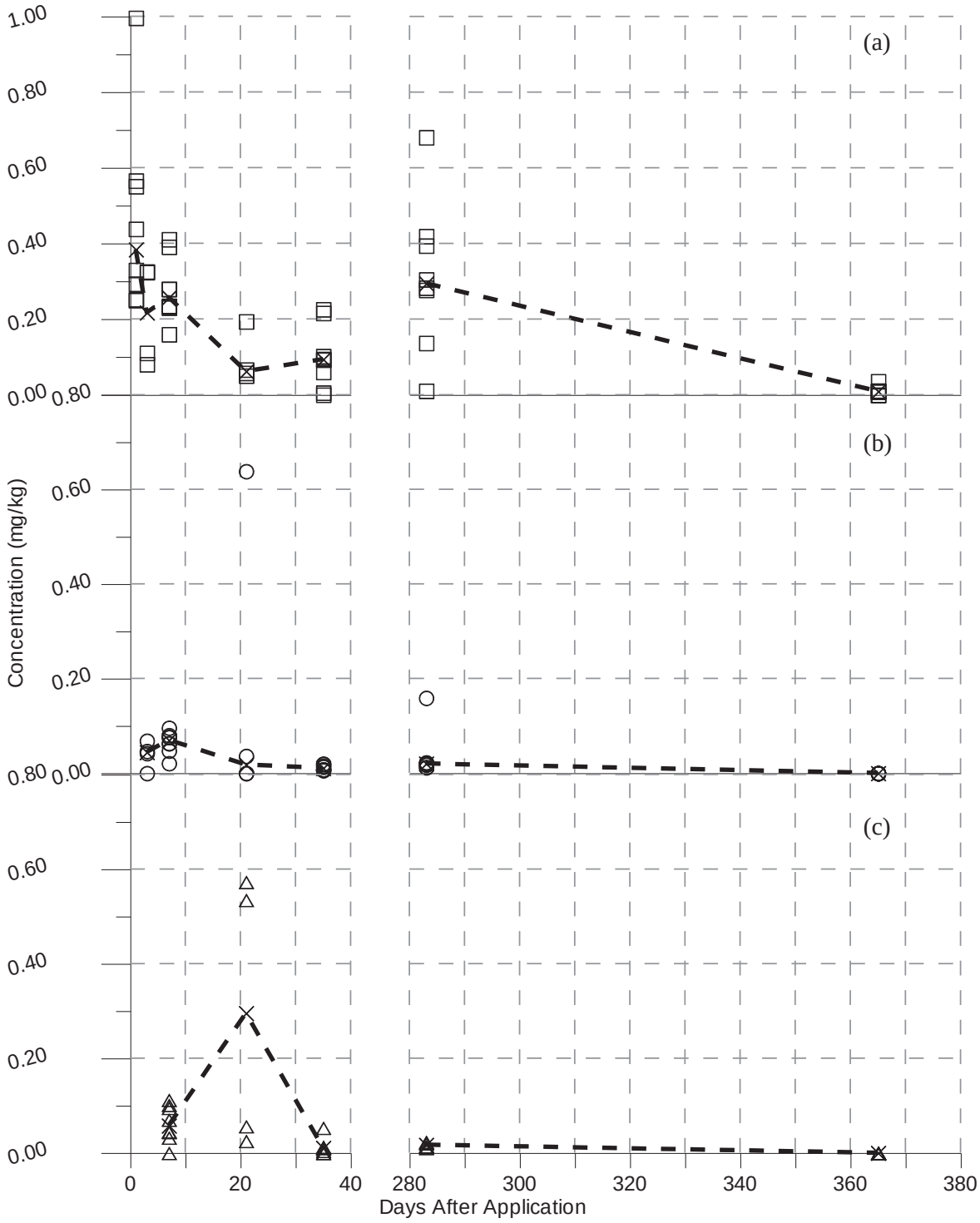


Figure 4.6. Triclopyr concentration measured in surface (a, 0-5 cm), root zone (b, 5-15 cm), and below root zone (c, 15-30 cm) soil at the Delta Junction agricultural test section for an application rate of 1.1 kg/ha. The trend line in each plot represents the sample concentration median. Herbicide was applied to the site on July 17, 2006. The soil froze approximately 110 days after application and thawed approximately 276 days after application. The break in the ordinate axis represents the period from approximately the last sampling prior to freeze up and the first sampling after thaw. Note the concentration scale difference between (a) and both (b) and (c).

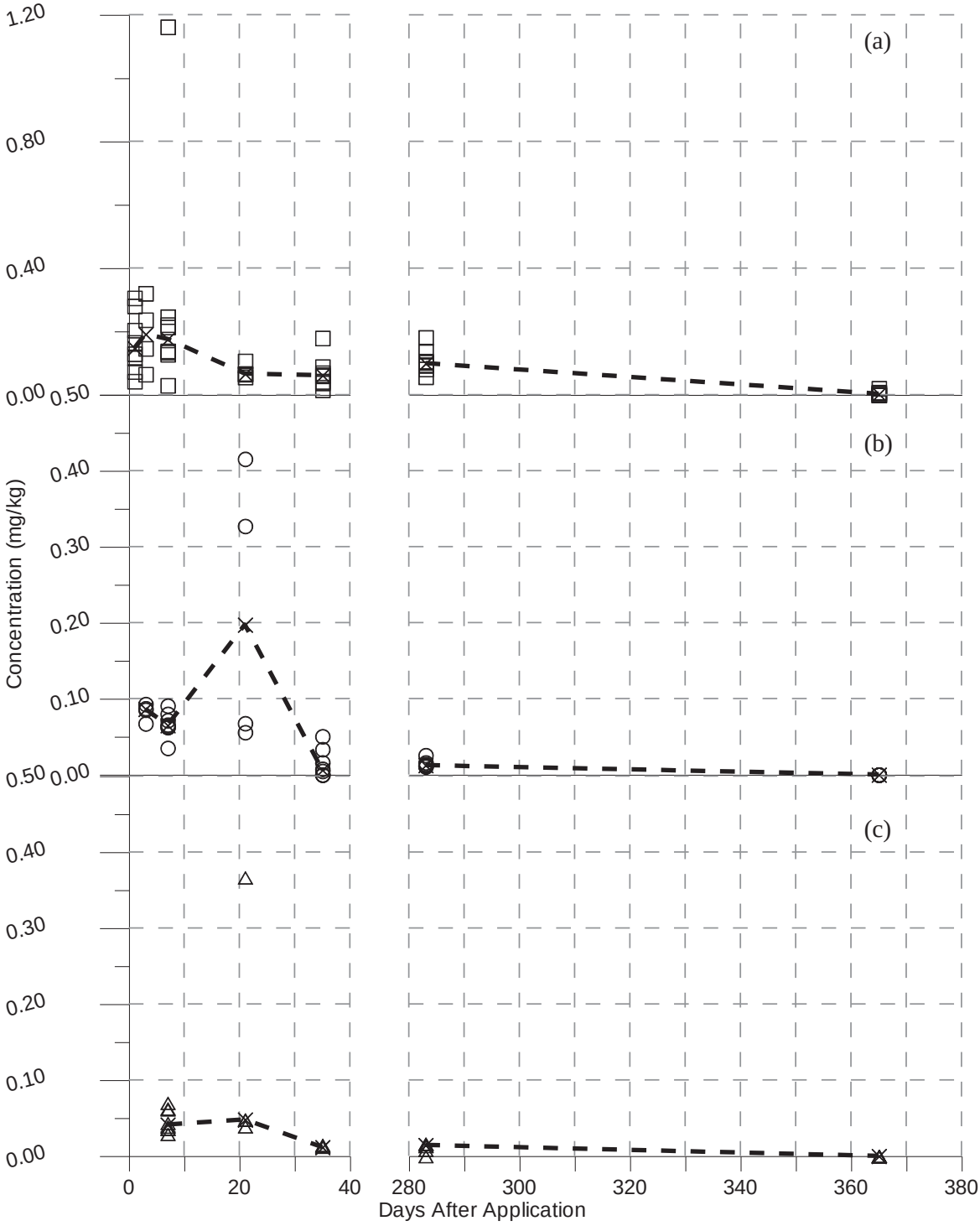


Figure 4.7. Triclopyr concentration measured in surface (a, 0-5 cm), root zone (b, 5-15 cm), and below root zone (c, 15-30 cm) soil at the Delta Junction agricultural test section for an application rate of 0.55 kg/ha. The trend line in each plot represents the sample concentration median. Herbicide was applied to the site on July 17, 2006. The soil froze approximately 110 days after application and thawed approximately 276 days after application. The break in the ordinate axis represents the period from approximately the last sampling prior to freeze up and the first sampling after thaw. Note the concentration scale difference between (a) and both (b) and (c).

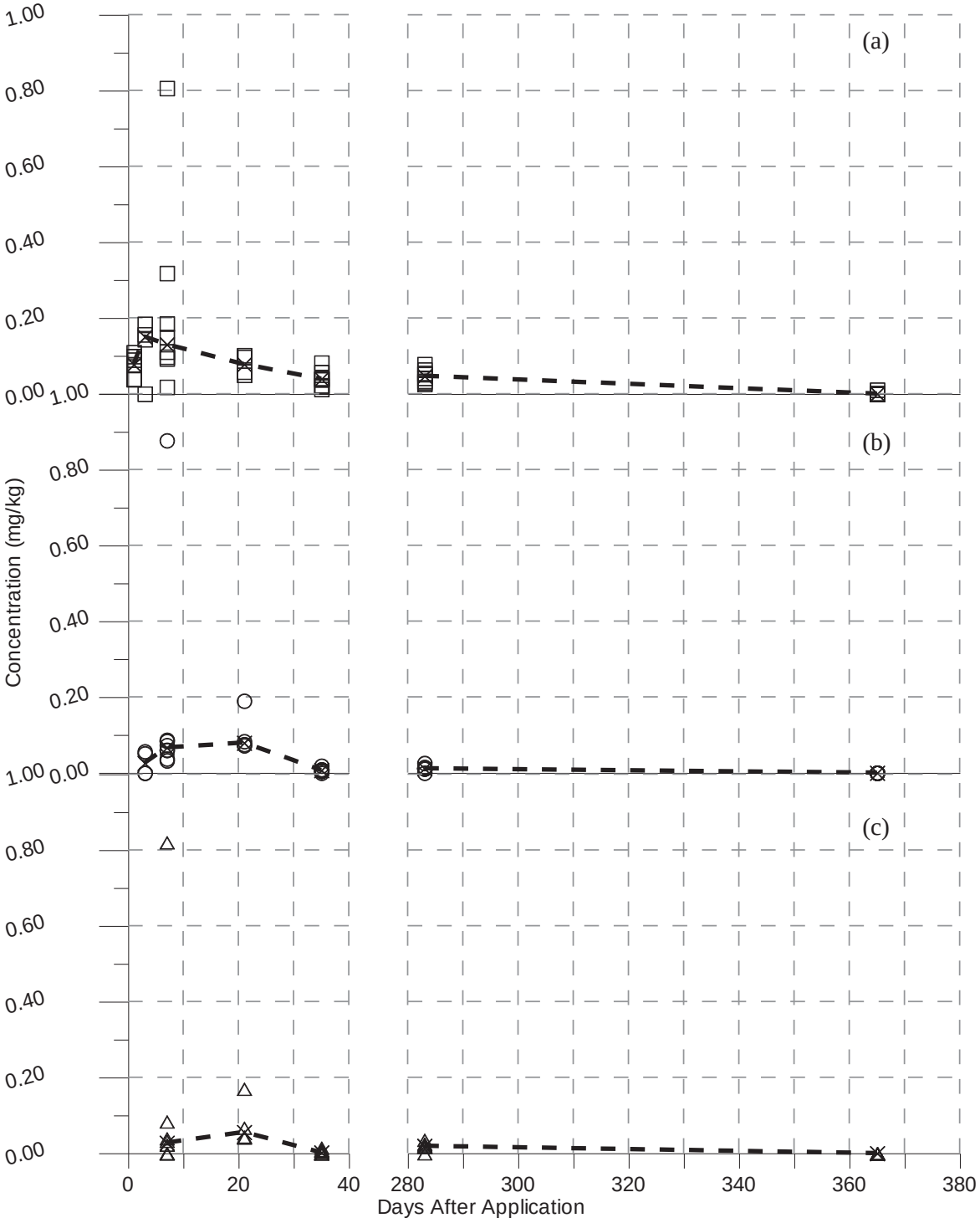


Figure 4.8. Triclopyr concentration measured in surface (a, 0-5 cm), root zone (b, 5-15 cm), and below root zone (c, 15-30 cm) soil at the Delta Junction agricultural test section for an application rate of 0.275 kg/ha. The trend line in each plot represents the sample concentration median. Herbicide was applied to the site on July 17, 2006. The soil froze approximately 110 days after application and thawed approximately 276 days after application. The break in the ordinate axis represents the period from approximately the last sampling prior to freeze up and the first sampling after thaw. Note the concentration scale difference between (a) and both (b) and (c).

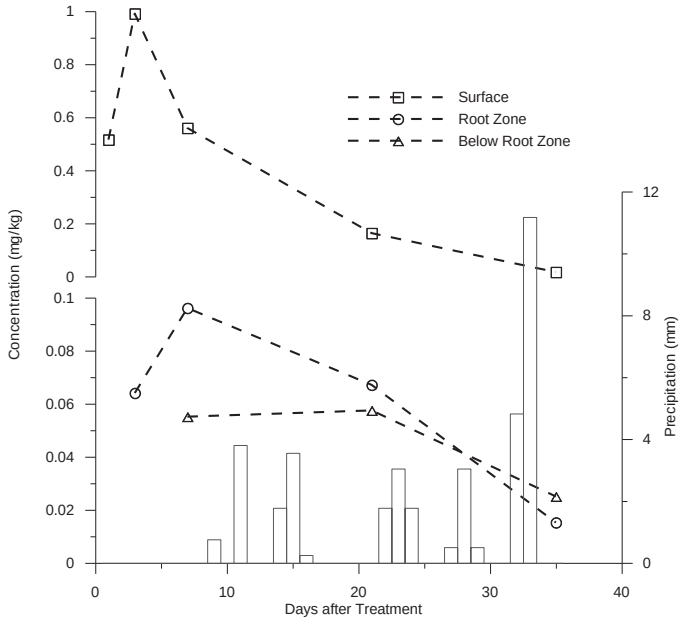


Figure 4.9. Median triclopyr concentrations at the Delta Junction agricultural site for the 2.2 kg/ha application and daily precipitation amounts measured at the Delta Junction 20 SE meteorological station for the first 35 days after treatment.

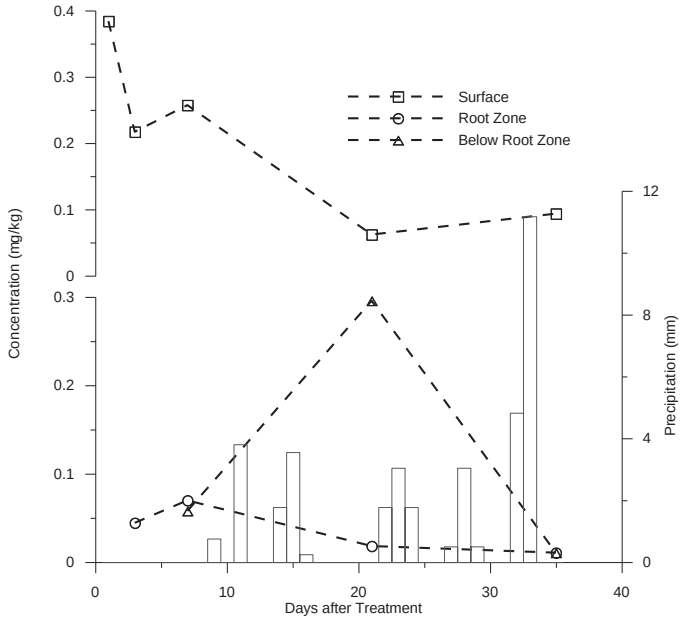


Figure 4.10. Median triclopyr concentrations at the Delta Junction agricultural site for the 1.1 kg/ha application and daily precipitation amounts.

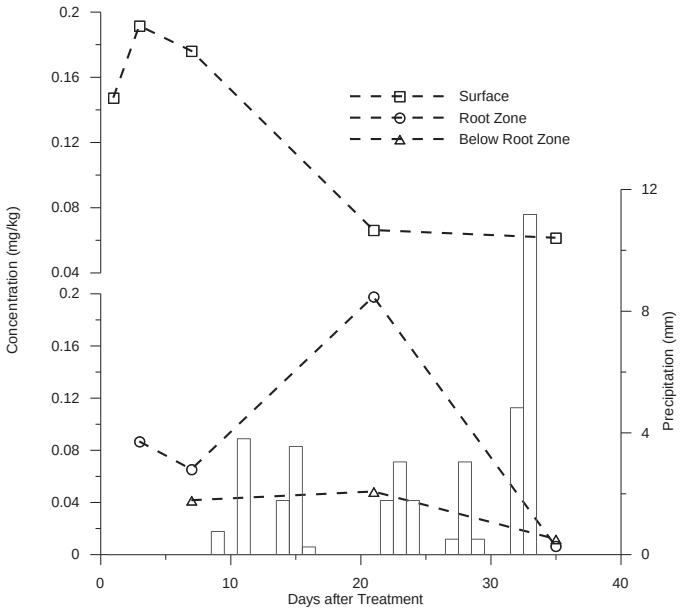


Figure 4.11. Median triclopyr concentrations at the Delta Junction agricultural site for the 0.55 kg/ha application and daily precipitation amounts.

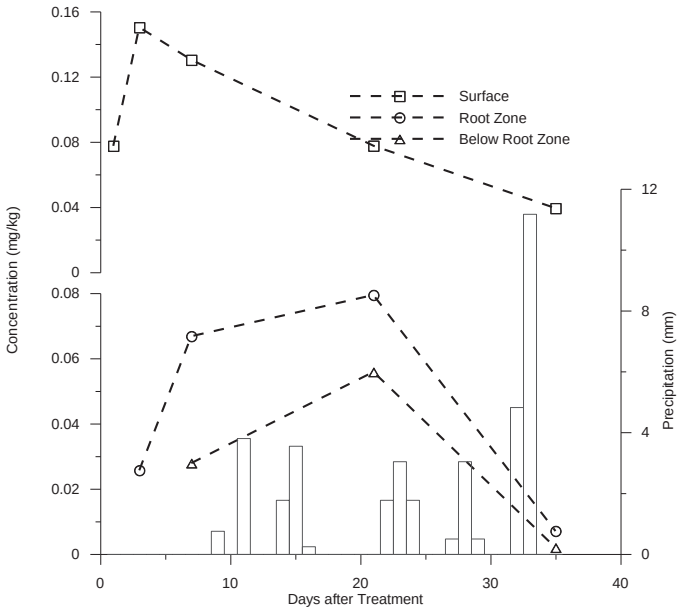


Figure 4.12. Median triclopyr concentrations at the Delta Junction agricultural site for the 0.275 kg/ha application and daily precipitation amounts.

5.0 Results from the Coastal Study Sites

The results consist of data collected and analyzed for triclopyr and 2,4-D from the Valdez, Alaska, area Richardson Highway right-of-way sites over the course of two field seasons. The data from the 2,4-D study will be presented first followed by the data from the triclopyr ROW study.

5.1 2,4-D Concentration in Coastal Right-of-Way Field Site Soil

Surface and subsurface concentration of 2,4-D from the study site near Valdez, Alaska, are shown in Table 5.1 and Figure 5.1. Concentration values can be found in Appendix C. As in the continental study, concentrations in both the table and figure are given in units of microgram 2,4-D per kilogram soil. The trend in the herbicide concentrations found in the surface soil at this site prior to spring break-up is somewhat similar to that found in the continental study, albeit the median concentrations are a bit lower. Following spring breakup, a relatively large increase in surface soil concentrations was measured. If herbicide can be released from dead vegetation as previously discussed, than this mechanism is possibly responsible for the increase in concentration.

Table 5.1 2.4-D concentration (μg/kg) summary for the Valdez field site

Sample Date	DAT	No. of Samples	Median	Low	High	Lower Quantile	Upper Quantile
Surface							
7/16/07	0.5	2	5.93	ND	11.9	2.96	8.89
7/17/07	1	4	19.0	ND	21.8	12.4	21.5
7/23/07	7	3	7.83	ND	8.76	3.91	8.29
8/8/07	23	4	7.69	ND	15.9	ND	15.5
9/13/07	59	3	8.44	ND	34.2	6.12	21.3
5/19/08	308	4	62.0	29.9	271	45.3	122
7/18/08	368	4	ND	ND	42.1	ND	10.5
Root Zone							
7/17/07	1	4	3.31	ND	37.1	ND	14.2
7/23/07	7	4	ND	ND	8.72	ND	2.18
8/8/07	23	4	3.25	ND	23.2	ND	10.7
9/13/07	59	3	ND	ND	2.58	ND	1.29
5/19/08	308	4	ND	ND	55.2	ND	13.8
7/18/08	368	4	ND	ND	0.00	ND	ND
Below Root Zone							
7/17/07	1	3	6.49	ND	12.9	3.24	9.71
7/23/07	7	3	ND	ND	0.00	ND	ND
8/8/07	23	3	ND	ND	5.08	ND	2.54
9/13/07	59	3	ND	ND	0.00	ND	ND
5/19/08	308	4	ND	ND	0.00	ND	ND
7/18/08	368	4	ND	ND	0.00	ND	ND

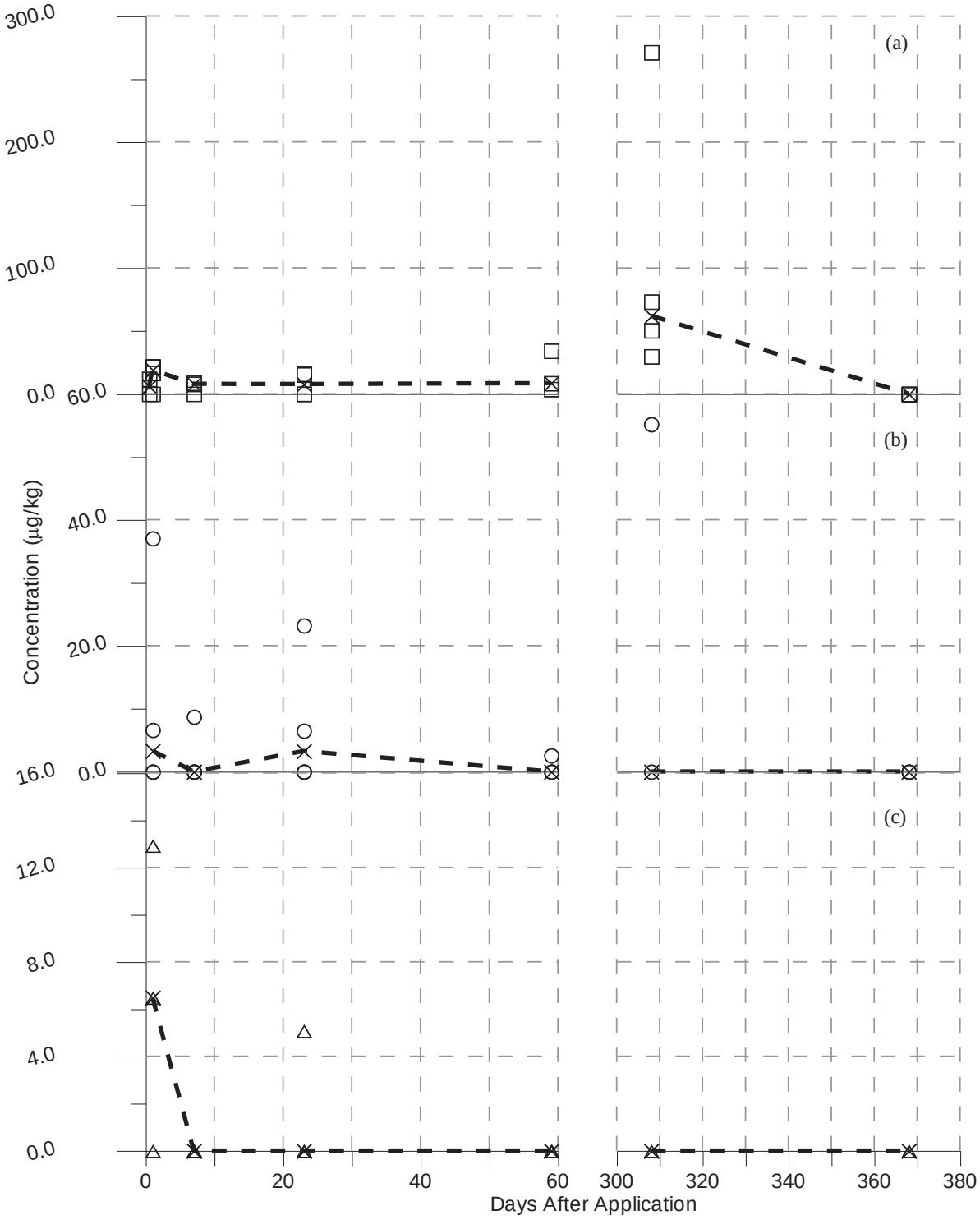


Figure 5.1. 2,4-D concentration measured in surface (a, 0-7.5 cm), root zone (b, 10-30 cm), and below root zone (c, 36-60 cm) soil at the Valdez site. The trend line in each plot represents the median sample concentration. Herbicide was applied to the site on July 6, 2006. Note the concentration scale difference between (a) and both (b) and (c).

The influence of interception of the herbicide by vegetation is illustrated by comparing the relatively low concentration values in the surface soils measured at the Valdez study shortly after application to those measured in the Delta Junction study plot surface soils measured in the same time period. Concentrations in the surface soil at both study sites converge to similar values later in the study period prior to winter freeze up. Following spring breakup, a comparable larger increase in concentration is measured in the surface soil at the Valdez study site in comparison to the Delta Junction study site.

Mean 2,4-D concentrations in comparison to precipitation events is shown in Figure 5.2. Movement of 2,4-D into the root zone soils is noted after following several rain events (23 DAT), but little 2,4-D is detected in the below root zone following these events.

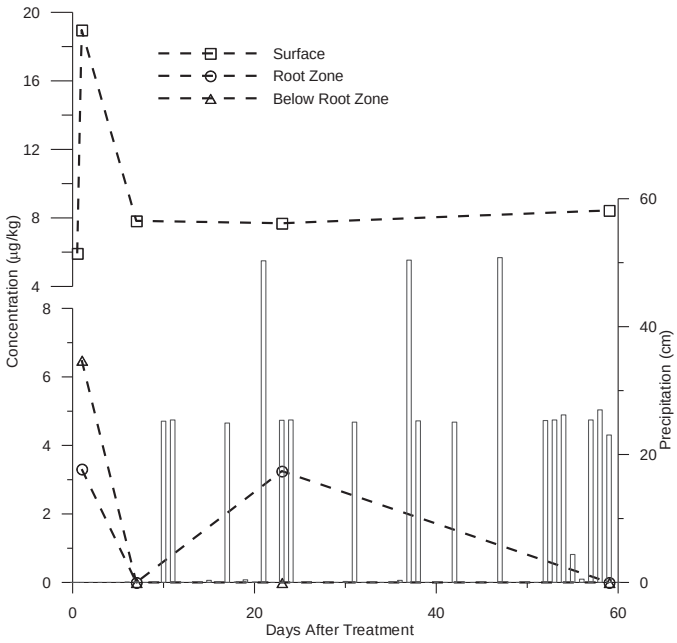


Figure 5.2. Median 2,4-D concentration at the Valdez study site and daily precipitation amounts measured at the WSO weather station for the first 59 days after treatment.

5.2 Triclopyr Concentration in Coastal Right-of-Way Field Site Soil

Comparing the results from the two different plots that were treated with triclopyr in this region indicates that there is a bit of a difference in how the triclopyr distributed throughout the soil horizon after application (Table 5.2, Figure 5.2, Table 5.3, and Figure 5.3). Concentrations at each sample location for each sampling event can be found in Appendix C. Once applied triclopyr was not detected in Plot 42 soil until the sampling event that occurred seven days after treatment, while in Plot 12 the triclopyr was measured in the soil hours after application. Further, in Plot 42 triclopyr was only detected in the subsurface soils during one sampling event, which occurred 59 DAT. Triclopyr was detected in Plot 12 subsurface soils, though only during two sampling events. Most likely, this dissimilarity in detectable concentrations of triclopyr between the two plots is a result of the difference between vegetation densities in each plot. Prior to application, Plot 42 had noticeable more dense vegetation cover in comparison to Plot 12. The reader should also note the frequent occurrence of non-detectable concentrations of triclopyr at both study plots.

Table 5.2 Triclopyr concentration (mg/kg) summary for the Plot 12 Valdez field site

Sample Date	DAT	No. of Samples	Median	Low	High	Lower Quantile	Upper Quantile
Surface							
7/16/07	0.5	4	0.112	ND	0.186	0.077	0.137
7/17/07	1	4	0.062	ND	0.432	0.046	0.156
7/23/07	7	4	0.194	ND	0.478	0.061	0.349
8/8/07	23	4	0.706	0.132	2.00	0.180	1.41
9/13/07	59	4	0.545	0.223	0.705	0.370	0.680
5/19/08	308	4	0.120	0.072	0.298	0.076	0.196
7/18/08	368	4	ND	ND	ND	ND	ND
Root Zone							
7/17/07	1	4	ND	ND	ND	ND	ND
7/23/07	7	4	0.074	0.029	1.08	0.036	0.353
8/8/07	23	4	ND	ND	0.111	ND	0.028
9/13/07	59	4	0.093	ND	0.254	0.048	0.156
5/19/08	308	4	ND	ND	ND	ND	ND
7/18/08	368	4	ND	ND	ND	ND	ND
Below Root Zone							
7/17/07	1	4	ND	ND	0.226	ND	0.056
7/23/07	7	4	0.017	ND	0.177	ND	0.070
8/8/07	23	4	ND	ND	ND	ND	ND
9/13/07	59	4	ND	ND	ND	ND	ND
5/19/08	308	4	ND	ND	ND	ND	ND
7/18/08	368	4	ND	ND	ND	ND	ND

An interesting observation is there was no detectable triclopyr in subsurface soil at either plot after spring break-up as was measured in the 2,4-D study. Given the relatively cold soil temperatures through the winter, biodegradation of each herbicide was most likely not a primary attenuation mechanism during this period. Leaching of the herbicides in the subsurface during snowmelt was probably a comparatively more dominant attenuation mechanism. Leaching of the herbicide will be slowed by sorption onto subsurface organics. Yet, difficulty arises in comparing the sorptive behavior of 2,4-D and triclopyr. As previously discussed, Johnson et al. (1995) found sorption of triclopyr to be slightly greater over 2,4-D in silt loam and silt clay. Conversely, McCall et al. (1988) found triclopyr to exhibit weak adsorptive behavior.

Comparing triclopyr concentration in relation to precipitation events (Figures 5.5 and 5.6) to that for 2,4-D (Figure 5.2) a difference in the concentration found in the surface soil between the two herbicides in relation to the precipitation events. Following the series of precipitation events, which began at 10 DAT, triclopyr concentrations in surface soils increased up to around 23 DAT. In contrast, 2,4-D concentrations fell after peaking one day after treatment. Subsurface concentrations of the two herbicides differ across the study plots as well. A peak in subsurface triclopyr concentrations was detected 7 DAT at Plot 12, which was the plot with comparatively lower vegetation density, while in Plot 42 a peak during this period was not measured. The greater vegetation density on Plot 42 most likely was the controlling factor in this result.

Table 5.3 Triclopyr concentration (mg/kg) summary for the Plot 42 Valdez field site

Sample Date	DAT	No. of Samples	Median	Low	High	Lower Quantile	Upper Quantile
Surface							
7/16/07	0.5	4	ND	ND	ND	ND	ND
7/17/07	1	4	ND	ND	ND	ND	ND
7/23/07	7	4	0.299	0.157	0.574	0.192	0.440
8/8/07	23	4	0.602	0.313	3.59	0.520	1.36
9/13/07	59	4	0.317	0.091	0.768	0.132	0.558
5/19/08	308	4	0.067	0.014	0.616	0.023	0.236
7/18/08	368	4	ND	ND	0.096	ND	0.024
Root Zone							
7/17/07	1	4	ND	ND	ND	ND	ND
7/23/07	7	4	ND	ND	ND	ND	ND
8/8/07	23	4	ND	ND	ND	ND	ND
9/13/07	59	4	0.034	ND	0.119	0.021	0.060
5/19/08	308	4	ND	ND	ND	ND	ND
7/18/08	368	4	ND	ND	ND	ND	ND
Below Root Zone							
7/17/07	1	4	ND	ND	ND	ND	ND
7/23/07	7	4	ND	ND	ND	ND	ND
8/8/07	23	4	ND	ND	ND	ND	ND
9/13/07	59	4	ND	ND	ND	ND	ND
5/19/08	308	4	ND	ND	ND	ND	ND
7/18/08	368	4	ND	ND	ND	ND	ND

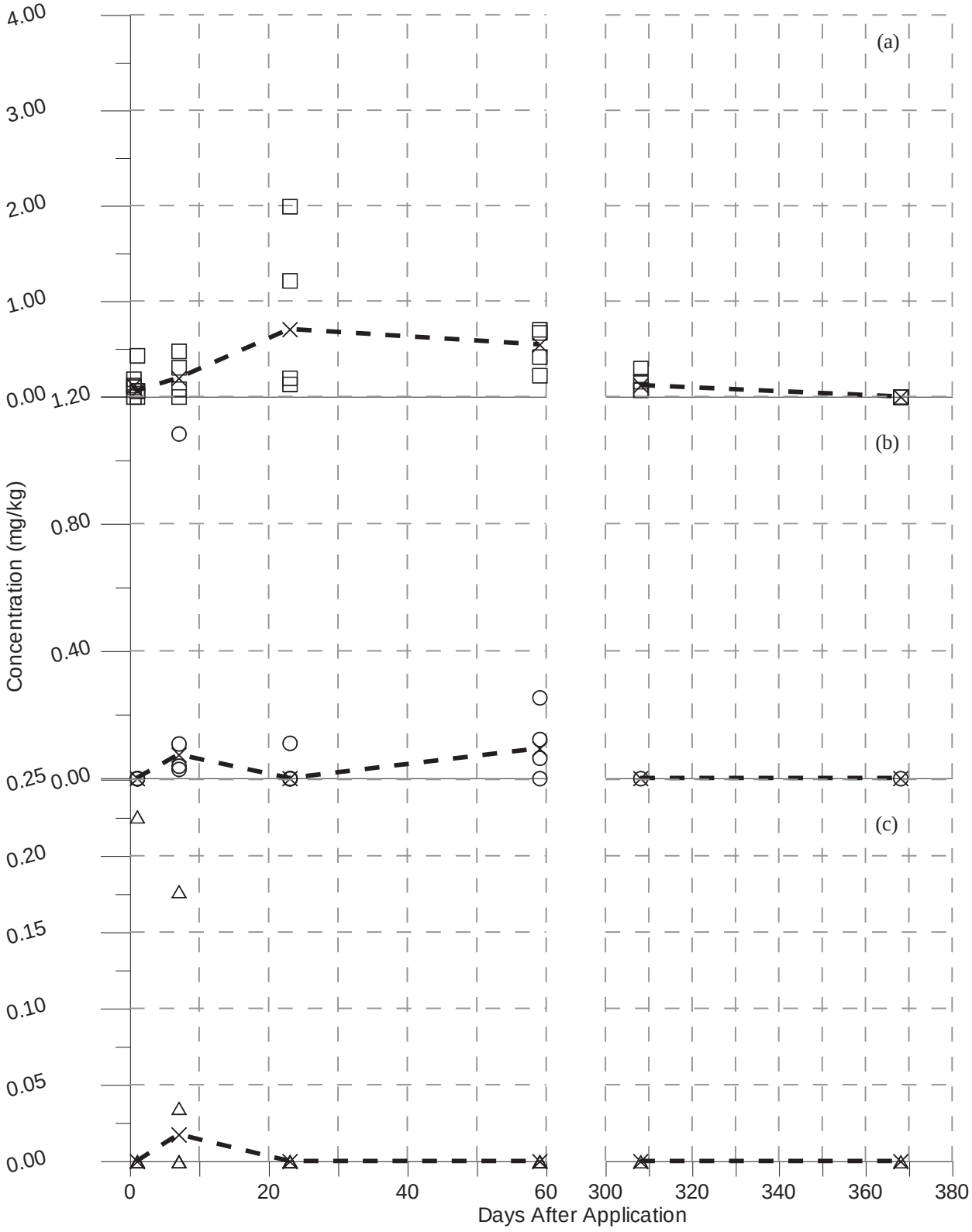


Figure 5.3. Triclopyr concentration measured in surface (a, 0-7.5 cm), root zone (b, 10-30 cm), and below root zone (c, 36-60 cm) soil at the Valdez site – Plot 12. The trend line in each plot represents the median sample concentration. Herbicide was applied to the site on July 6, 2006. Note the concentration scale difference in the three graphs.

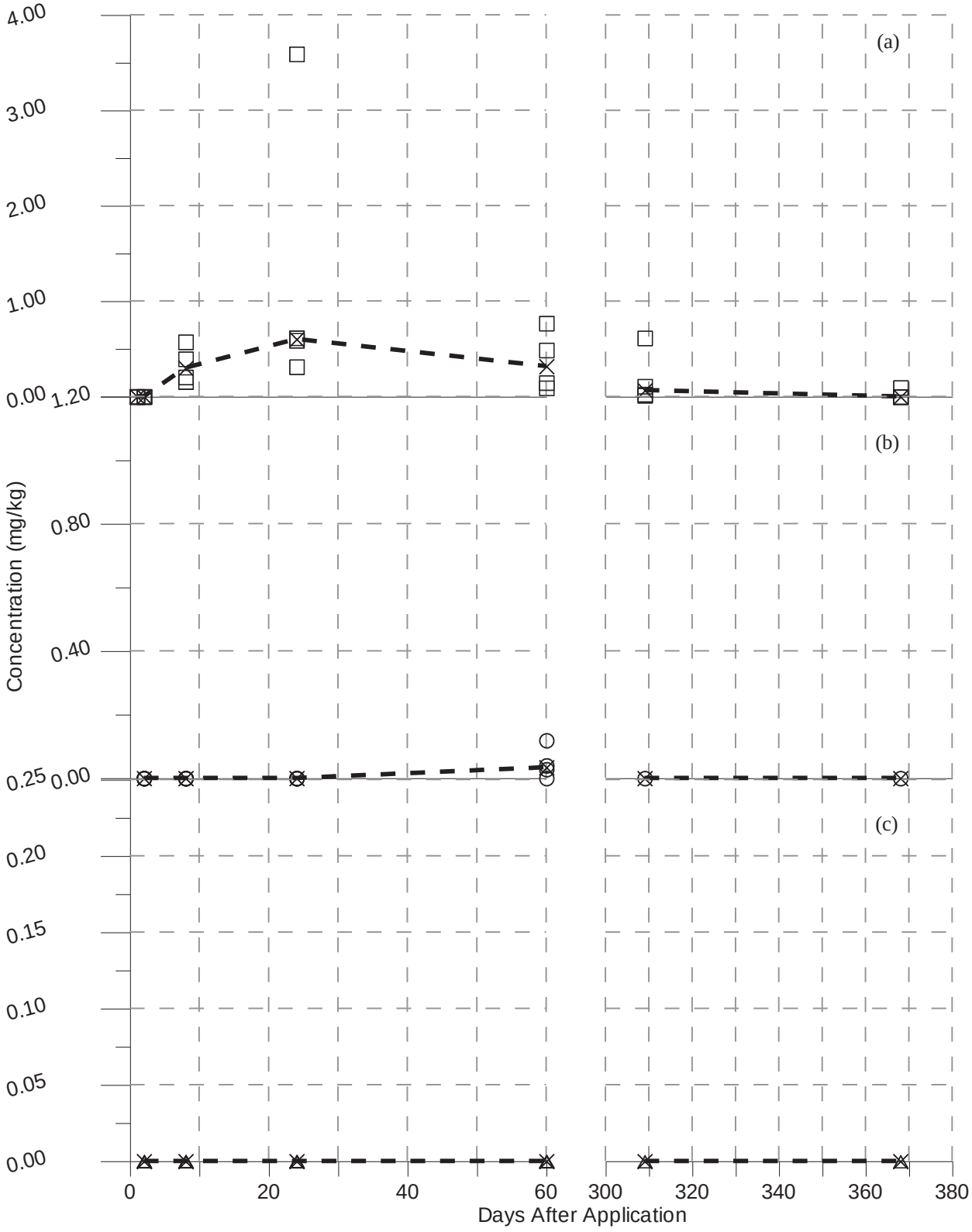


Figure 5.4. Triclopyr concentration measured in surface (a, 0-7.5 cm), root zone (b, 10-30 cm), and below root zone (c, 36-60 cm) soil at the Valdez site – Plot 42. The trend line in each plot represents the median sample concentration. Herbicide was applied to the site on July 6, 2006. Note the concentration scale difference in the three graphs.

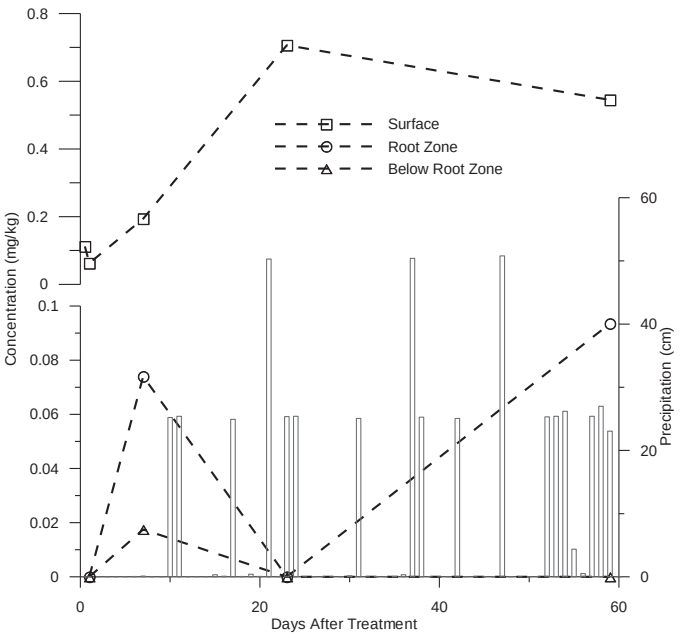


Figure 5.5. Median triclopyr concentration at the Valdez study site Plot 12 and daily precipitation amounts measured at the WSO weather station for the first 59 days after treatment.

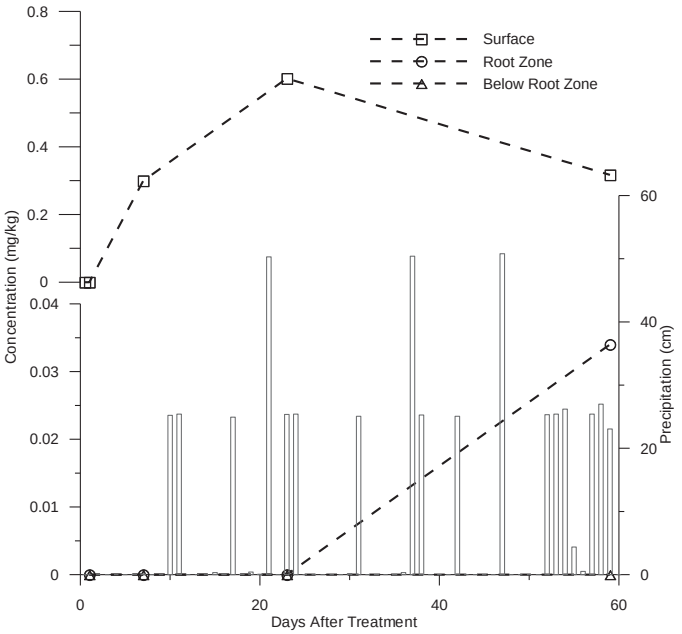


Figure 5.6. Median triclopyr concentration at the Valdez study site Plot 42 and daily precipitation amounts measured at the WSO weather station for the first 59 days after treatment.

6.0 Results from Herbicide Effectiveness Assessment

At the Delta Junction site, shrub cover was 30 to 40% in all areas before treatment application (Figure 6.1). After treatment application, shrub cover was reduced in herbicide treatments to 5 to 10%. In the following year, shrub cover in the herbicide treatments did not increase. Mowing on control plots with no herbicide application did not reduce shrub cover by the end of the first year and then in the following year shrub cover increased. In the control plots, as expected, shrub cover continued to increase. For shrub control both herbicides (triclopyr and 2,4-D) and both application methods (broadcast and wet blade) were equally effective. Non-woody cover declined the year of treatment application in the triclopyr treatments, this decline was mostly due to a decrease in fireweed and grass cover as shown in Figure 6.1. The following year non-woody cover had increased to amounts greater than both the mow control and control plots. Non-woody vegetation in the mow and mow control plots increased from the pre-treatment to the autumn 2007 measurement due to normal growth in the growing season, however the cover of the non-woody vegetation in the mowed control lagged behind the control treatment as the mower did cut down some of the that vegetation type.

Because of the AKDOT&PF mowing at the Valdez site, all shrub cover declined in all treatments from about 50% cover to less than 10% (Figure 6.1). Any treatment effects on the shrubs were lost. Similarly, the mowing masked the effects of the treatments on the non-woody vegetation as shown in Figure 6.1. It is possible that the wet blade treatments (with both triclopyr and 2,4-D) resulted in non-woody covers that matched the previous year and all other treatments, plus the mowing reduced non-woody cover.

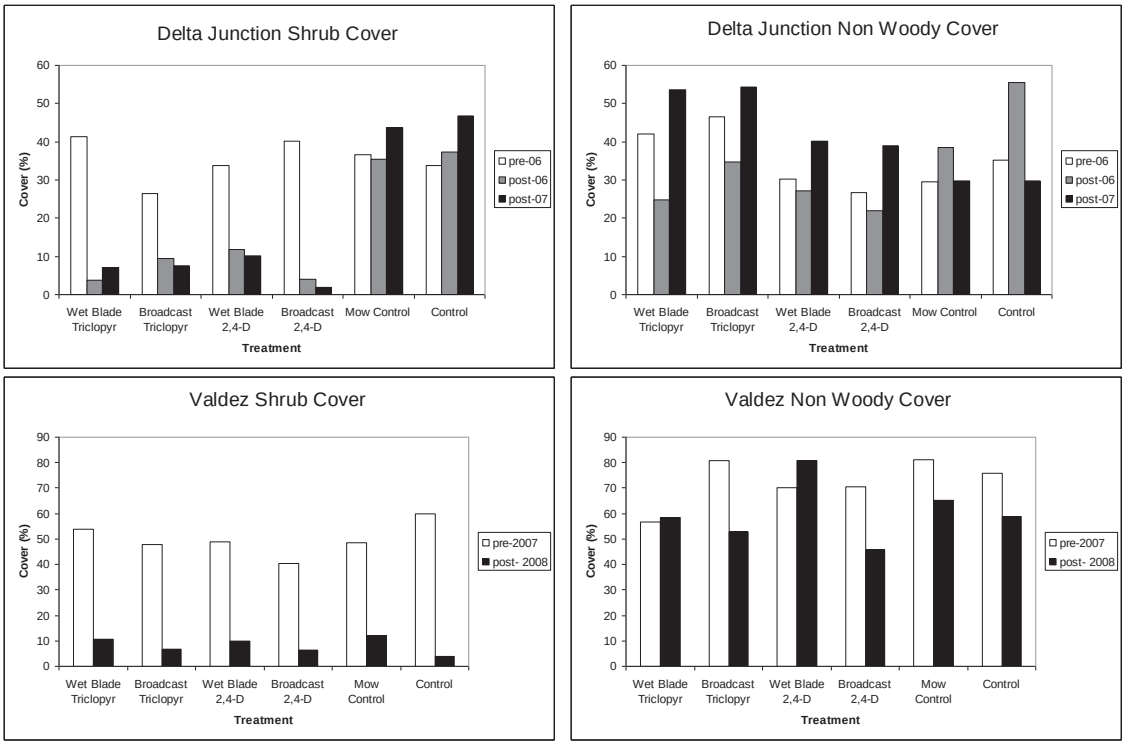


Figure 6.1. Comparison of shrub and non-woody cover before and after herbicide application at both study sites.

7.0 Discussion

Two selective herbicides were tested in this study to determine their effectiveness in reducing the woody vegetation along highway rights-of-way in Alaska and their rate of attenuation under subarctic conditions. The overall effectiveness of the herbicides and the attenuation rate of 2,4-D and triclopyr at the two study locations will be discussed. Attenuation of 2,4-D and triclopyr in Alaska's subarctic environment will be assessed by first comparing the overall results obtained from this study to similar studies conducted by others. The concentration and estimated mass of each herbicide measured in the soil at each study site will then be evaluated and compared. Finally, the rate of attenuation will be modeled using first-order kinetics.

In Delta Junction, use of the wet blade mower or a broadcast application of triclopyr or 2,4-D are useful for reducing the amount of woody vegetation and increasing the amount of non-woody vegetation a year later along the road ROW. This increase in non-woody vegetation may result in a slowing of the growth rate and reestablishment of the woody vegetation. Future measurements at this site will provide evidence for this suppression. In Valdez, the second mowing of all plots has masked the results of this study. Follow up measurements may provide data that could be used to determine whether the herbicide applications will have long-term impacts on recovery of the vegetation, but at this point, no management recommendations can be made.

To assess the attenuation of each herbicide it is worthwhile to compare the overall results found in this study to similar studies. Generally, making this comparison, concentration values for both herbicides found in this study are similar to values measured by others. Review of literature results in three published studies on triclopyr and 2,4-D that were conducted in subarctic conditions; two studies on triclopyr and one study on 2,4-D (Newton et al., 2008; Mulkey, 1990; Torstensson and Stark, 1982). These studies were previously discussed in Section 2.3.6. In a study conducted near Fairbanks, Alaska, Newton et al. (2008) measured triclopyr concentrations in surface soil near Fairbanks, Alaska similar in magnitude to those found in this study at both the Delta Junction ROW and agriculture site. In addition, Newton et al. (2008) conducted a similar study located at Windy Bay, Alaska (on the southern tip of the Kenai Peninsula). Triclopyr concentrations reported from this site were comparable in magnitude with those found at the Valdez study site; though it appears that triclopyr was still detectable up to 456 days after treatment. Triclopyr was applied at a dose of 2.2 kg a.i./ha in both studies. The reader should note that an assumption has to be made that the triclopyr values reported by these authors are for triclopyr acid and not triclopyr ester, as they do not specify the form of the herbicide they are reporting in their publication.

Concentrations of triclopyr measured by Mulkey (1990) applied to railroad ballast in Alaska are once again comparable in magnitude to those found in this current study. Mulkey found residual triclopyr in the surface soil at six out of seven study sites one year after application. These results are consistent with concentrations measured in surface soil at the Delta Junction and Valdez study plots. Counter to results presented here for Delta Junction and Valdez, Mulkey (1990) found detectable amounts of triclopyr in the subsurface at all seven of his study sites.

Comparing results found in this current study to those found by Torstensson and Stark (1982) for 2,4-D and triclopyr attenuation in Northern Sweden is a bit more challenging in that these authors present their concentration results in units of herbicide mass per sample (μg/sample) as opposed to herbicide mass per mass of soil. Nevertheless a comparison of the

persistence of triclopyr and 2,4-D can still be made. These researchers investigated the attenuation of both herbicides in multiple locations throughout Sweden; four of these locations were located in Northern Sweden. 2,4-D was applied at a dose of 2.0 kg a.i./ha and triclopyr was applied at a dose of 2.2 kg a.i./ha. At their labeled sites 5 through 8, 2,4-D was still detectable at 75, 302, 313, and 378 days, respectively. Subsequent sampling events at each site resulted in concentration values below the detectable limit. Exact location of each study site and climatic conditions were not provided for this study, however the persistence values are comparable to the 2,4-D results found at both the Delta Junction and Valdez study sites; though the study in Delta Junction was not carried out to the point where non-detectable concentrations of 2,4-D were measured. Further, these researchers found triclopyr was more persistent than 2,4-D. Triclopyr was detectable up to approximately 750 days after application in two of the four study sites. This result is most likely contrary to the results found in Delta Junction and Valdez, though in both locations measurements were stopped after approximately one year limiting the possibility of making a definitive comparison.

Results found in this study are comparable to those found in more-temperate locations as well. Newton et al. (1990) reports comparable triclopyr concentration values measured in surface and subsurface soils from a study located in Southwest Oregon. Two doses of triclopyr were used in their study: 3.3 kg a.i./ha and 1.65 kg a.i./ha. These researchers measured triclopyr concentrations in surface and subsurface soils at the same order of magnitude that was found in the Delta Junction ROW and agriculture site. These same authors also report values of 2,4-D applied at a dose of 2.2 kg a.i./ha that are an order of magnitude greater 37 days following application (concentrations values for early time were not reported in their study) than those found in the Delta Junction ROW study during approximately the same time after application. Though, at 325 days following application concentrations of 2,4-D measured by Newton et al. (1990) in the surface and subsurface were comparable to those found in Delta Junction at 316 DAT. Wilson and Cheng (1976) applied 2,4-D to winter wheat and fallowed soil in Eastern Washington at a dose of 1.1 kg/ha. Concentrations reported by these authors for the top 24 cm of soil are comparably greater than those measured in the Delta Junction study soon after application (up to eight days after application). However, later in the study the concentrations values are similar to the results found at the Delta Junction study site. Owing to the comparable results found in this study to those found by others it appears that the attenuation of the herbicides in the Delta Junction and Valdez study sites are following a predictable pattern.

Referring to Figures 4.1, 4.3, 5.1, 5.2 and 5.3, the concentration values for 2,4-D found in the soil at the Delta Junction site and the Valdez study site are comparably lower than the measured triclopyr concentrations found at both Delta Junction study sites (ROW and agriculture) and the Valdez site. The reader should note however that the concentrations of both herbicides at both study sites are low, specifically in the subsurface soils where the greatest concentrations measured were approximately 1.1 mg/kg (triclopyr measured at the Valdez Plot 12 study site and the Delta Junction agriculture site) and the rest of the measurements were less than approximately 0.55 mg/kg.

Theoretically, at a herbicide dose of 2.2 kg/ha and a soil density of 2000 kg/m^3 the concentration measured in the top 5 cm would be approximately 2.2 mg/kg. Comparing this theoretical value to the maximum measured value for 2,4-D at either the Delta Junction or Valdez site surface soils the measured concentrations are lower than the theoretical by an order of magnitude (Figures 4.1 and 5.1). Most likely the difference in values between the theoretical

and the average concentrations is a result of photooxidation, plant uptake directly after application and metabolism in the plant and by soil microorganisms at later time.

Conversely, the value of the theoretical maximum concentration and the actual measured concentration for triclopyr measured in the surface soil at either site is comparable (2.2 mg/kg versus 6.25 mg/kg, Figure 4.3, 4.5, 5.2 and 5.3). Though, the majority of concentrations values measured are more than one order of magnitude less than the theoretical value. Differing volatilization rates of the herbicides is most likely not a factor since triclopyr acid is comparably more volatile than 2,4-D. Therefore, the differing results between the two herbicides suggests that the plant uptake of 2,4-D and possibly photooxidation may be a more dominant factor in the early attenuation of 2,4-D in comparison to triclopyr.

An interesting result is the overall maximum measured 2,4-D concentration was measured following spring break-up at the Valdez study site – 308 days following treatment. This result suggests that though vegetation is a dominant factor in 2,4-D attenuation, the vegetation may be releasing a small fraction of the acid form of the herbicide long after application as previously discussed.

Referring to Figures 4.1 and 4.3, at around 27 DAT in both the Delta Junction ROW studies the maximum median concentration was measured in the subsurface soils. Following sampling events resulted in comparable lower concentrations. Similar results were found at the agricultural site, where downward migration of triclopyr peaked at around 7 DAT (Figures 4.5 to 4.8). Hence, it appears from these results that small amounts of the herbicide may be leaching down into the soil column; though the amount the maximum depth the herbicide migrated to and the amount leached cannot be determined from this study.

Estimating the total amount of mass measured in the soil for each sampling event is another method of comparing the overall relatively low amount of 2,4-D detected in the soil compared to triclopyr in this study. Total mass can be estimated by taking a simple integration of the concentration with depth. A linear relationship between the concentrations at each measured depth is assumed for this calculation. The same density as was used to determine the theoretical maximum concentration is assumed. Results for the two herbicides at the Delta Junction ROW site are shown in Figures 7.1 and 7.2. Results for triclopyr at the Delta Junction agricultural site (2.2 kg a.i./ha dose) is shown in Figure 7.3.

As illustrated in Figure 7.1, less than approximately 10% of the original mass of 2,4-D applied to the study plots in Delta Junction is detected in the soil during the sampling events. This result can be attributed to a high rate of volatilization, photooxidation, and plant uptake of the herbicide shortly after application. At later time, microbial degradation most likely contributes to the low amount of mass measured in the soil. Though, the amount of mass detected in the soil is somewhat steady at around 2% of the original mass applied possibly indicating that the rate of microbial degradation may be somewhat slow. Though not measured, a relatively slow microbial degradation rate is expected in the subsurface soil given the overall relatively cold subsurface soil temperatures (Figure 3.3). In comparison, the percentage of the original triclopyr mass applied to the soil is high as shown in both the ROW study and the study on agricultural land. As previously discussed, plant uptake and photooxidation of 2,4-D seem to be more dominant attenuation mechanism in comparison to triclopyr. Comparable results are found in the Valdez results shown in Figures 7.4 to 7.6.

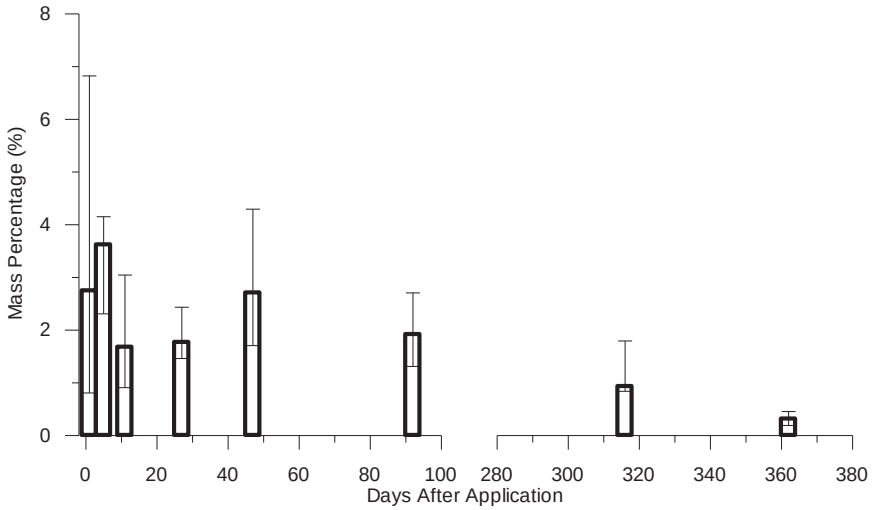


Figure 7.1. Percent 2,4-D mass measured at Delta Junction site. Bars represent the ratio of the median value of mass measured in the soil to the total mass applied. Error bars indicate the upper (75%) and lower (25%) quartile of the measured mass datum set.

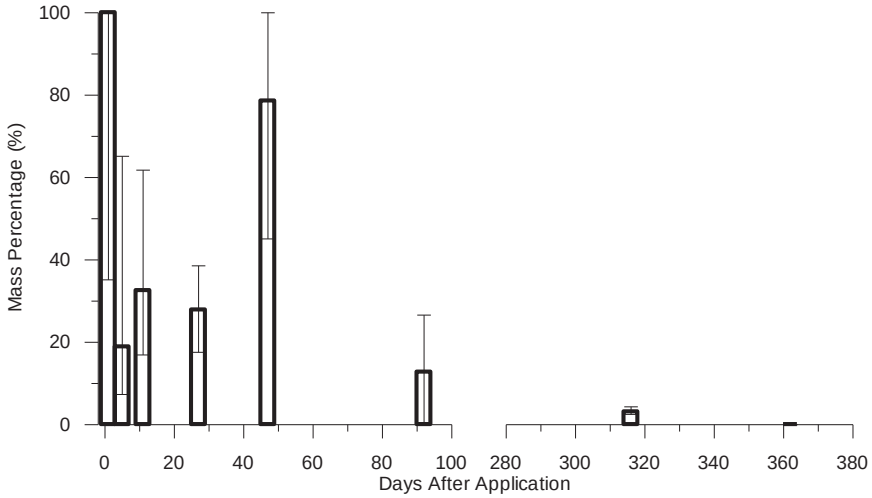


Figure 7.2. Percent triclopyr measured at the Delta Junction ROW site. Bars represent the ratio of the median value of mass measured in the soil to the total mass applied. Error bars indicate the upper (75%) and lower (25%) quartile of the measured mass datum set.

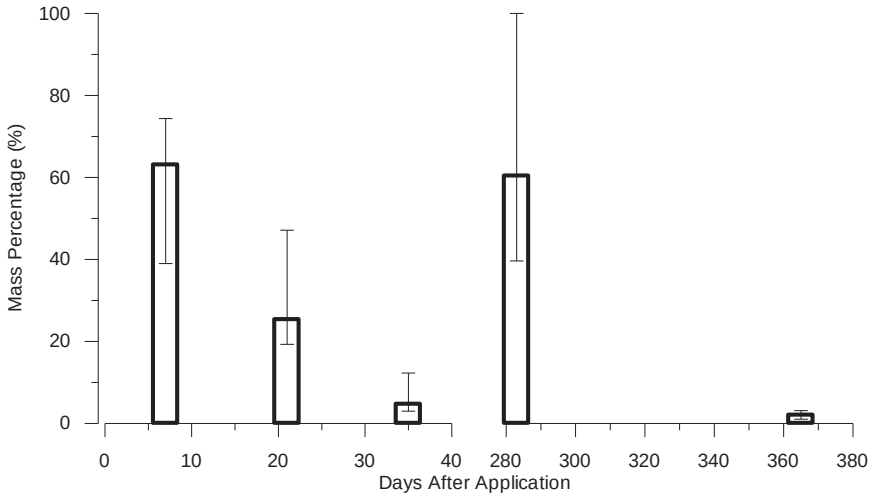


Figure 7.3. Percent triclopyr measured at the Delta Junction agriculture site (dose equal to 2.2 kg/ha). Bars represent the ratio of the median value of mass measured in the soil to the total mass applied. Error bars indicate the upper (75%) and lower (25%) quartile of the measured mass datum set.

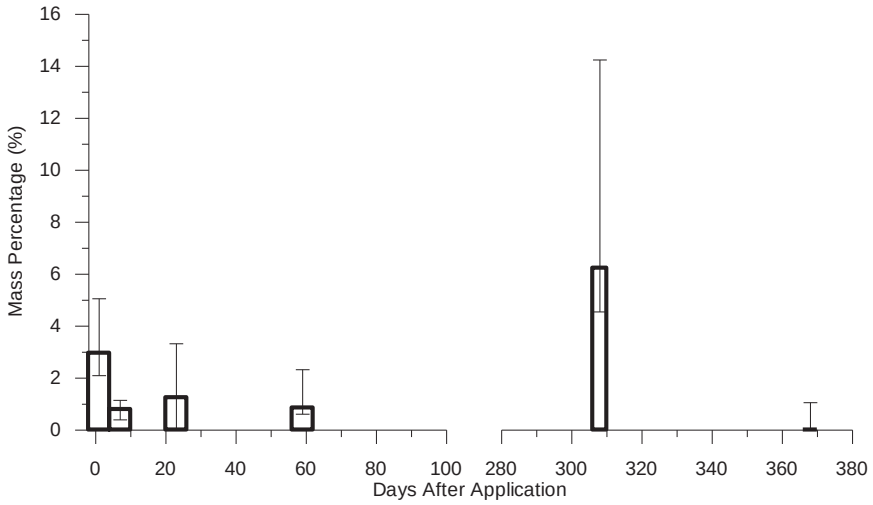


Figure 7.4. Percent 2,4-D measured at the Valdez study site. Bars represent the ratio of the median value of mass measured in the soil to the total mass applied. Error bars indicate the upper (75%) and lower (25%) quartile of the measured mass datum set.

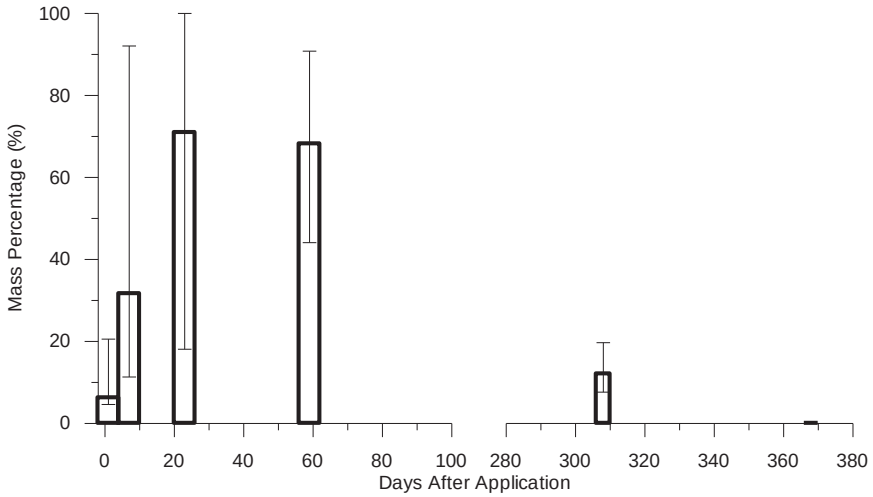


Figure 7.5. Percent triclopyr measured at the Valdez study site (plot 12). Bars represent the ratio of the median value of mass measured in the soil to the total mass applied. Error bars indicate the upper (75%) and lower (25%) quartile of the measured mass datum set.

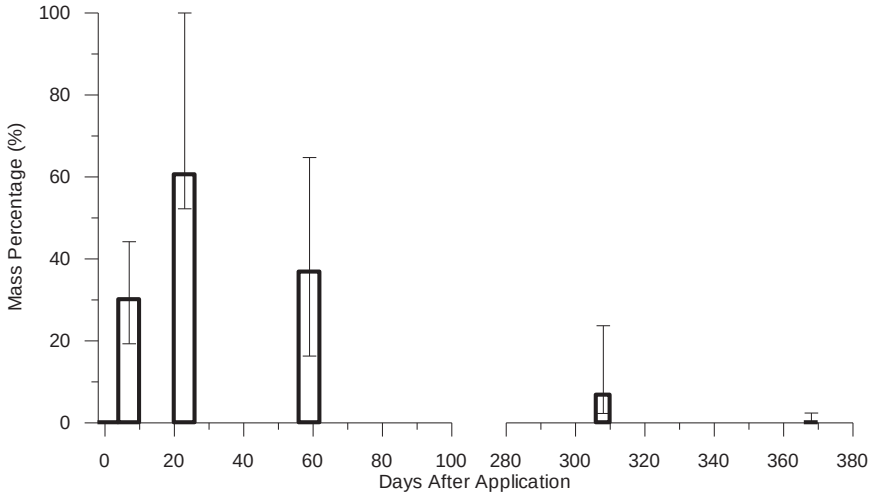


Figure 7.6. Percent triclopyr measured at the Valdez study site (plot 42). Bars represent the ratio of the median value of mass measured in the soil to the total mass applied. Error bars indicate the upper (75%) and lower (25%) quartile of the measured mass datum set.

Often the attenuation rate of herbicides in surface soils is represented by making the assumption that herbicides degrade according to first-order decay kinetics. Making this assumption, a half-life of the herbicide, or the time it takes for half of an initial mass of herbicide to attenuate, in the surface soil can be estimated. This analysis is only applicable to the results from the Delta Junction study sites (ROW and agricultural) and not the Valdez site due to the poor fit of the first-order decay model to the results from the Valdez study site. Fitting the measured median 2,4-D concentrations for the nine sampling events taken during the entire 362 day testing period at the Delta Junction ROW site to the first-order decay model results in a half-life of approximately 278 days. The fit of the first decay model in relation to the data is shown in

Figure 7.7. A relatively poor correlation coefficient of 0.24 results from a fit of the model to the data.

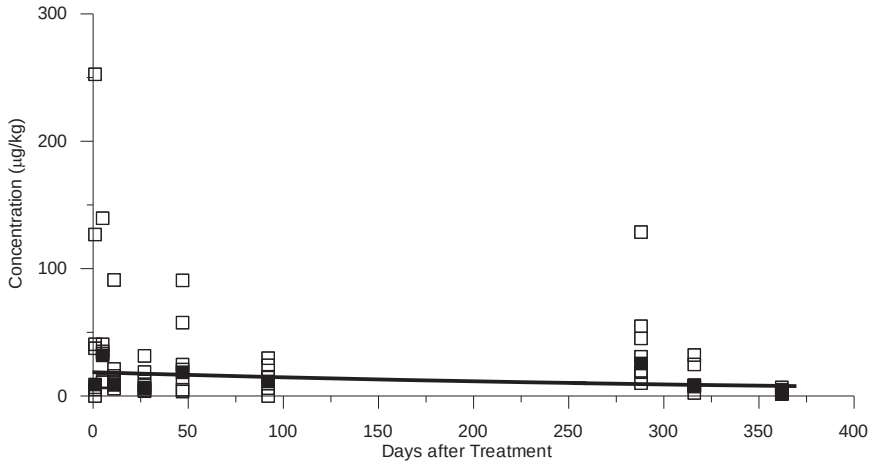


Figure 7.7. First order decay model fit (solid line) to the median 2,4-D concentration in surface soils at the continental ROW field site for the entire study period. Concentration values at each sample location are represented with open markers. Median concentration value is represented with solid markers. The resulting calculated half-life is 278.4 days. The correlation coefficient (R^2) is 0.24.

This calculated half-life is appreciably greater than the measured 2,4-D half-life reported by others and discussed in Section 2.3.6 of this report. These other studies found half-lives ranging from a short as 1.7 days to as long as 27.5 days (Wilson et al., 1997). Wilson et al. (1997) applied 2,4-D to several sites that may be considered to be cold (locations with defined winter season when the vegetation is dormant), though the authors did not define the climatic conditions of each of their study sites. These sites include North Dakota, Colorado, and Nebraska. Each of these sites was either pastureland or cropped in wheat or corn. For these sites, Wilson et al. (1997) calculated half-life values for 2,4-D (applied as an ester) ranging from 2.2 days (Colorado, wheat applied at a dose of 1.4 kg a.i./ha applied twice once in May and again in July) to 5.3 days (North Dakota, wheat applied at a dose of 1.4 kg a.i./ha twice once in June and again in August); much shorter than the value measured in this current study.

Torstensson and Stark (1982) report concentrations of 2,4-D found in surface soils at eight different sites in Sweden. Four of these sites are located in northern Sweden according to the authors; though the authors do not provide the latitude of these sites. 2,4-D was applied at a dose of 2.0 kg/ha. Assuming these sites are located in cold climates, estimates of 2,4-D half-life can be made using the data in Torstensson and Stark (1982) and compared to results from this current study. For this comparison, an assumption has to also be made that the unit “sample” (µg/sample), which is most likely either a volume or mass measurement, is comparable across all the sampling events. Their results are shown in Table 7.1.

Table 7.1. 2,4-D Half-life values estimated from concentrations measured in surface soils by Torstensson and Stark (1982) at four study sites in northern Sweden

Site	Approximate Number of Days Concentration was Detectable	Half-life (days)	Correlation Coefficient
5	75	23	0.65
6	302	51	0.99
7	313	114	0.78
8	378	211	0.61

Though the authors did not provide exact locations of their study sites, the trend in their persistence results suggests that site 5 and 6 may have been relatively warmer and or wetter climates than sites 7 and 8; however, other conditions may have led to this trend in Torstensson and Stark's results. Half-life values calculated from sites 7 and 8 and comparable to the results from the Delta Junction ROW site, indicating that the persistence of 2,4-D in subarctic environments is longer in comparison to more southerly latitudes. Torstensson and Stark (1982) arrive at the same conclusion.

Referring to Figure 4.1, the lack of attenuation during the time the soil is frozen is evident. In accordance, half-life estimations can be calculated by considering only the periods the soil is thawed, or what can be considered the growing season. Considering the median 2,4-D concentrations during the first 92 DAT, a half-life of approximately 32 days results. After thaw, the three sampling events that occurred on 288, 316, and 362 DAT results in a half-life of approximately 24 days. The fit of the first-order decay model to this bimodal trend in the data is shown in Figure 7.8.

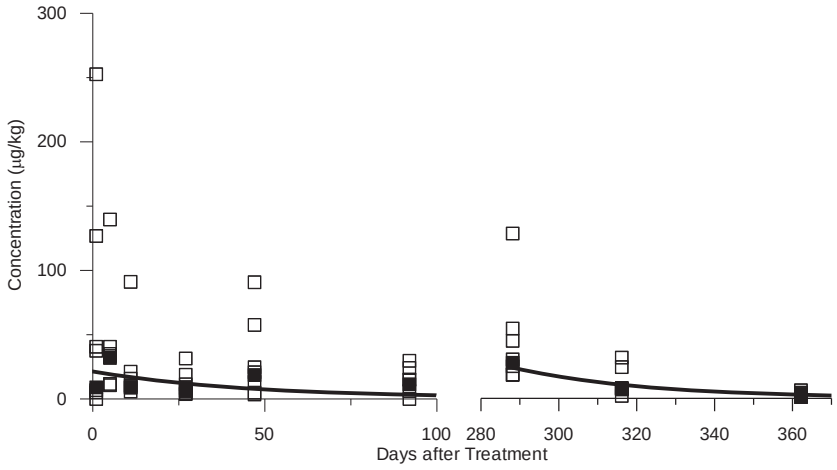


Figure 7.8. First-order decay model fit to median 2,4-D concentration values measured prior to winter freeze-up and following spring thaw. Concentration values at each sample location are represented with open markers. Median concentration value is represented with solid markers. The resulting half-life of 2,4-D prior to freeze up is 31.7 days with a correlation coefficient of 0.79. The half-life of 2,4-D following spring thaw is 23.9 days with a correlation coefficient of 0.96.

The resulting half-lives during the period the soil is thawed are comparable to half-lives reported by others and discussed in Section 2.3.6. These other studies found half-lives ranging from a short as 1.7 days to as long as 27.5 days (Wilson, 1997). Though, the reader should note that the data used to calculate the half-lives determined by others spans a testing period up to the

point where non-detectable concentration of 2,4-D were found. Whereas the concentration values used to make these calculations are only over relatively small period over the entire time span of the test. Hence, the half-life calculated here is representative of the growing season only.

Similar half-life calculations can be made for triclopyr in the surface soils at both the right-of-way site in Delta Junction and the agricultural testing site. These results are shown in Figures 7.9 and 7.10.

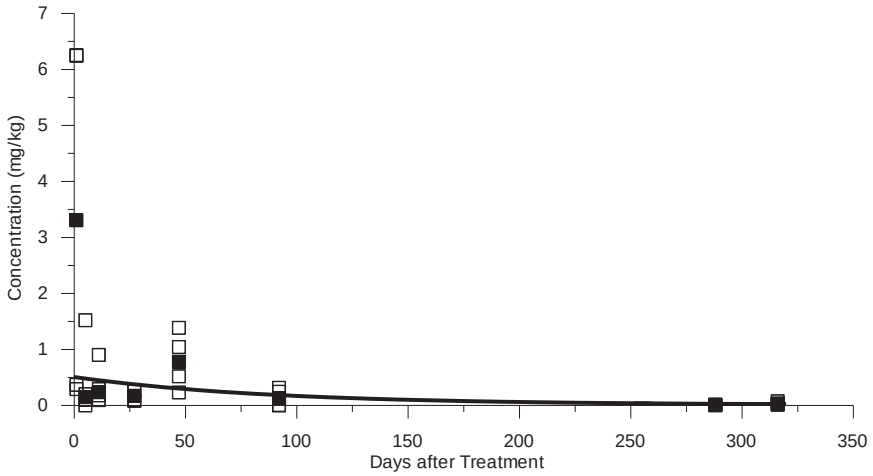


Figure 7.9. First order decay model (solid line) fit to the median triclopyr concentration in surface soils at the continental ROW field site for the study period. Concentration values at each sample location are represented with open markers. Median concentration value is represented with solid markers. The resulting calculated half-life is 60.8 days. The correlation coefficient (R^2) is 0.644.

Triclopyr half-life values calculated from both the ROW site and the agricultural site at a dose of 2.2 kg a.i./ha are not comparable – 60.8 days versus 186.5 days, respectively. Moreover, the half-life values for the period prior to freeze-up again are not comparable. The estimated half-life value for triclopyr calculated for the first 92 days of the ROW study is approximately 49 days. Estimated triclopyr half-life resulting from the agricultural study is approximately 6 days, comparably much shorter than the ROW study. Hence, for the overall study the half-life of the triclopyr applied to the agricultural site, where the vegetation was clipped prior to application, is comparably longer than in the ROW site where the vegetation was left undisturbed. However, when just comparing the estimated half-life values for the period prior to winter freeze-up, the triclopyr applied to the agricultural site had a much shorter half-life than the triclopyr applied to the ROW site. The reason for this result is unclear at this time.

As with the 2,4-D study, the half-life values estimated from the triclopyr ROW and agriculture study at the Delta Junction site can be compared to estimated half-life values calculated from results reported in Torstensson and Stark (1982). These results are shown in Table 7.2.

Table 7.2. Triclopyr half-life values estimated from concentrations measured in surface soils by Torstensson and Stark (1982) at four study sites in northern Sweden

Site	Approximate Number of Days Concentration was Detectable	Half-life (days)	Correlation Coefficient
5	378	103	0.88
6	378	cannot determine	na
7	756	482	0.65
8	754	417	0.18

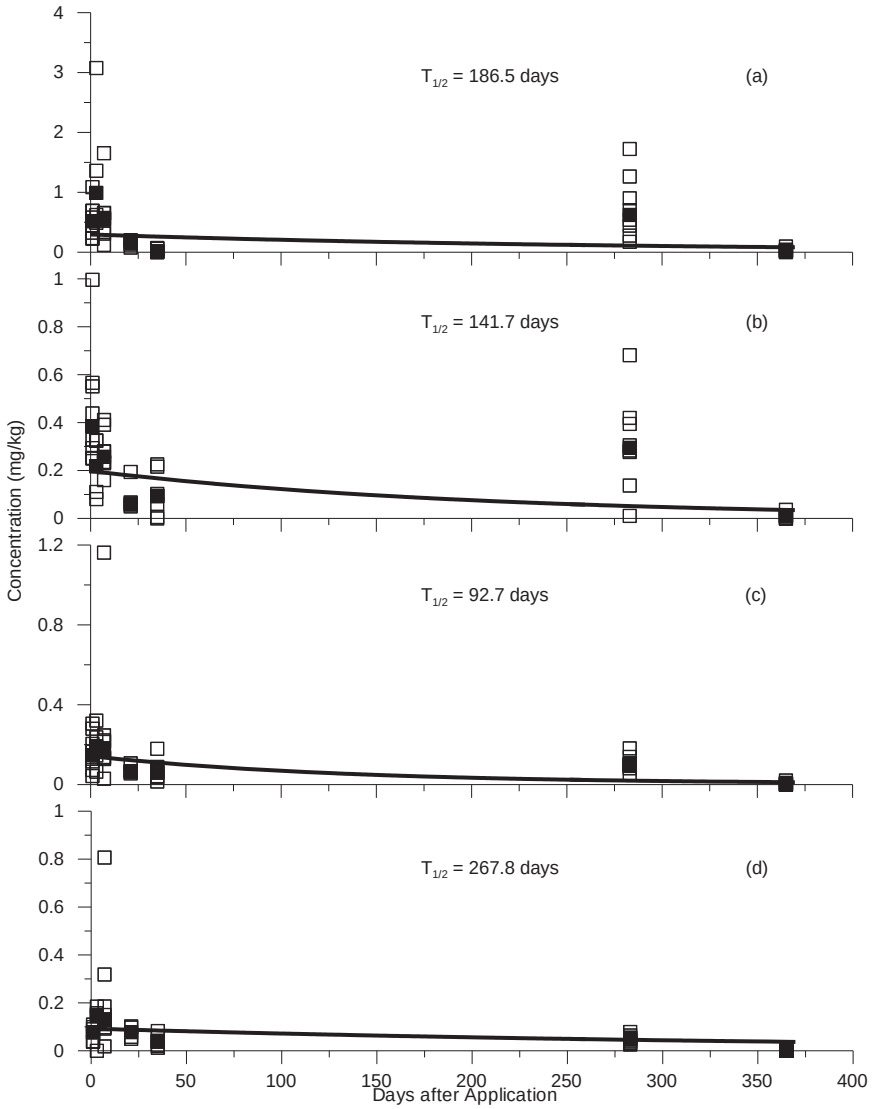


Figure 7.10. Each line in the above graphs represents the best fit of the first order decay model to the median triclopyr concentration values in surface soils at each sample time for each of the different application rates: (a) 2.2 kg/ha, (b) 1.1 kg/ha, (c) 0.55 kg/ha), (d) 0.275 kg/ha at the agricultural field site. The open markers represent the actual sample concentration values and the solid markers represent the median concentration values for each sample period. Half-life ($T_{1/2}$) determined from concentration values measured for the study period is shown for each application rate. The correlation coefficient (R^2) for each application is as follows: 0.117 (2.2 kg/ha), 0.332 (1.1 kg/ha), 0.583 (0.55 kg/ha), 0.290 (0.275 kg/ha).

The half-life value estimated from Torstensson and Stark's (1982) study at their Site 5 is somewhat comparable to the results found at the ROW site, but less comparable to the results from the agriculture site. Half-life values estimated for Sites 7 and 8 (Table 7.2) are comparatively much greater than both the ROW site and the agriculture site. A summary of the half-life results are provided in Table 7.3.

Table 7.3. Herbicide half-life for the Delta Junction study plots.

Herbicide	Location	Time Span Used in Calculation (DAT)	Half-life (days)	Correlation Coefficient
2,4-D	ROW	362	278.4	0.24
2,4-D	ROW	92	31.7	0.79
Triclopyr	ROW	316	60.8	0.64
Triclopyr	ROW	92	49.3	0.15
Triclopyr	Agriculture (2.2 kg/ha)	365	186.5	0.12
Triclopyr	Agriculture (2.2 kg/ha)	35	6.3	0.93
Triclopyr	Agriculture (1.1 kg/ha)	365	141.7	0.33
Triclopyr	Agriculture (1.1 kg/ha)	35	16.0	0.69
Triclopyr	Agriculture (0.55 kg/ha)	365	92.7	0.58
Triclopyr	Agriculture (0.55 kg/ha)	35	19.8	0.84
Triclopyr	Agriculture (0.275 kg/ha)	283	267.8	0.29
Triclopyr	Agriculture (0.275 kg/ha)	35	23.0	0.67

A comparison of the attenuation characteristics of both herbicides can be made at this point. The total mass of 2,4-D measured in the soil at both the Delta Junction site and the Valdez site are appreciably less than the total triclopyr mass measured in the soil (maximum median value of approximately 4% for 2,4-D versus a maximum median value of 100% for triclopyr). From this result it appears that comparably less 2,4-D mass is present in the soil; hence less mass is available to migrate towards water sources (aquifers and surface water). Both herbicides were effective in reducing the woody species at the two study sites. Comparing the half-life results obtained from the ROW study for both herbicides, triclopyr appears to attenuate at a relatively more rapid rate than 2,4-D. Yet, comparing the ROW studies to the agricultural study, 2,4-D and triclopyr seem to have similar half-lives. A relatively higher concentration of herbicides was measured following spring thaw at the 2,4-D ROW study site and the agricultural site, resulting in comparable longer overall half-lives in comparison to the triclopyr ROW site.

8.0 Conclusions

Herbicides have been used by many other state agencies outside of Alaska to control vegetation along rights-of-way. Control of vegetation along highway rights-of-way is necessary for safety, as tall woody vegetation reduces driver's line-of-sight, reduces the possibility of vehicle encounters with animals on the roadway, and is necessary for maintaining a safe driving surface. While herbicides are used in Alaska on private land, the State of Alaska should consider how different herbicides attenuate in the unique environments within Alaska prior to usage on State land. The objective of this study was to examine the migration and dissipation as well as effectiveness of two different phenoxy herbicides in two different subarctic environments: continental (Delta Junction, Alaska) and coastal (Valdez, Alaska). The herbicides tested in this study were 3,5,6-trichloro-2-pyridinyl oxy acetic acid (triclopyr) and 2,4-dichlorophenoxyacetic acid (2,4-D). Both herbicides are selective to broadleaf plant species, such as willow and alder, and ineffective on grasses.

Triclopyr and 2,4-D were found to be effective at reducing the density of woody species at the Delta Junction study site. Further, the amount of non-woody vegetation increased in the study, which may result in slowing of the growth rate and reestablishment of the woody vegetation. This result is important. The slowing or lack of reestablishment of woody vegetation for a period of time implies that less herbicide will be required to reduce the density of woody vegetation over time. Unfortunately, an unscheduled mowing masked the results at the Valdez study site; hence, no conclusions on the effectiveness of the herbicides at this study site can be drawn.

Results from this study indicate that the selective herbicides tested in this study attenuate at the same rate during the growing season as found in more-temperate regions. The overall persistence is longer, however, due to the relatively long period the soil temperatures are below zero Celsius. At both study sites, the mass of 2,4-D measured at any one time in the soil is much less than the mass of triclopyr measured in the soil at the same time. The difference in mass was found to be as much as a factor of approximately 30. However, the overall persistence of 2,4-D appears to be longer than that for triclopyr.

9.0 Recommendations

This study provided key information on the attenuation and effectiveness of two selective, systemic postemergence-type herbicides in subarctic climates. Owing to the persistence past the one-year study time at each site, further long-term studies on herbicide longevity and vegetation grow-back rate is required. These studies should take place on a section of highway right-of-way that is clearly marked and protected from mowing after application, since mowing of the study sites will destroy the study. If the State decides to pursue herbicide application to highway rights-of-way prior to further longevity testing, reapplication should be no sooner than two years after initial application. In addition, soil sampling and analysis for presence of the applied herbicide should be conducted prior to reapplication of herbicide until long-term longevity studies are conducted and a comprehensive herbicide application plan for each climatic zone in the State can be developed.

10.0 References

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Appendix A

Extraction, Esterification, and Standard Preparation Procedure

Extraction

1. Weigh five grams of thoroughly mixed soil on a balance capable of three decimal place accuracy and record weight.

2. Place soil into a 250 mL Erlenmeyer flask and add 15 mL deionized (DI) water, 2 mL 33% potassium hydroxide solution and 25 μL 100 mg/L DCAA. Place flask on mechanical shaker for five minutes.

3. Remove flask from shaker and transfer to a 50 mL centrifuge tube. Rinse flask with DI water using rinsate to bring centrifuge volume up to 50 mL. Centrifuge at 3500 RPM for 3 minutes.

4. Remove from centrifuge and pour liquid back into Erlenmeyer flask. A soil plug will remain at the base of the centrifuge tube. Add 15 mL of DI water to the centrifuge tube and shake to break up soil plug and suspend soil particles. Centrifuge at 3500 RPM for three minutes. Pour liquid into Erlenmeyer flask and discard soil. Keep the centrifuge tube for step 5.

5. Add 20 mL ether to the Erlenmeyer flask and shake for two minutes venting occasionally. Empty the emulsion into two 50 mL centrifuge tubes. To separate the ether and water phases, centrifuge at 3500 RPM for two minutes.

6. Remove tubes from centrifuge and discard the ether phase using a pipette. Transfer the water phase back into the Erlenmeyer flask.

7. Add 4 mL 12 M sulfuric acid and 20 mL ether to the Erlenmeyer flask. Shake for two minutes venting occasionally. Empty the emulsion into two 50 mL centrifuge tubes. Centrifuge at 3500 RPM for two minutes to achieve separation.

8. Remove tubes from the centrifuge and pipette ether phase into a clean 40 mL volatile organic analysis (VOA) vile.

9. Transfer the water phase back into the Erlenmeyer flask and add 10 mL ether. Shake for two minutes venting occasionally and empty the emulsion into the two centrifuge tubes. Centrifuge at 3500 RPM for two minutes. Pipette ether phase into the VOA vial from previous step.

10. Repeat step 9 such that a final volume of approximately 35-40 mL of ether is obtained in the VOA vile. Then, discard water phase.

11. Add 5 g anhydrous sodium sulfate to the VOA vile and place in a dark fume hood for at least one hour.

12. Transfer the ether phase from the VOA vile to a Turbo Vap tube. Rinse the sodium sulfate with 5 mL of ether and add rinsate to Turbo Vap tube. Repeat with 5 mL ether. Discard sodium sulfate.

13. Place Turbo Vap tube in Turbo Vap evaporator and adjust ether phase to 1 mL with nitrogen gas. Pipette ether into a 16 mm glass test tube. Rinse Turbo Vap tube with 1 mL ether and pipette rinsate into the 16 mm test tube. Repeat 1 mL rinse so that 3 mL ether is obtained in the 16 mm test tube.

14. Allow ether to go to dryness in the 16 mm test tube. Sample is now ready for esterification.

Esterification

1. Add 0.5 mL of 10-15% W/V boron trifluoride in methanol to the 16 mm test tube. Place test tube with Teflon lined cap into a block heater for one hour at 808 C.

2. After one hour take sample out of block heater and let cool to room temperature.

3. Pipette 10 mL of 10% W/V sodium chloride solution into the 16 mm test tube. Cap and shake test tube. Transfer contents to a 125 mL separatory funnel. Rinse test tube again with 10 mL of sodium chloride and transfer to separatory funnel.

4. Pipette 15 mL hexane into the separatory funnel and cap. Shake funnel for two minutes. Decant the sodium chloride solution into a clean container and the hexane into a VOA vile.

5. Transfer sodium chloride solution back into separatory funnel and repeat step 4 with 10 mL hexane such that a total of 25 mL hexane is obtained in the VOA vile. Discard sodium chloride solution.

6. Add 8-10 g anhydrous sodium sulfate to the VOA vile and place in a dark hood for at least one hour.

7. Transfer hexane from the VOA vile to a Turbo Vap tube. Rinse the sodium sulfate with 5 mL hexane and add rinsate to Turbo Vap tube. Repeat with 5 mL hexane. Discard sodium sulfate.

8. Use Turbo Vap evaporator to adjust hexane to 1 mL with nitrogen gas. Pipette hexane into a GCMS vial.

9. Rinse Turbo Vap tube with 0.75 mL hexane and pipette into the GCMS vial. Sample is ready for GCMS analysis.

Note: All operations performed in the extraction and esterification procedure were carried out with approved personal protective equipment and engineering controls.

Standard Preparation Procedure

1. Obtain 1 mL each of 100 mg/L triclopyr, TCP and DCAA standards.

2. In a 250 mL Erlenmeyer flask combine 15 mL DI water, each 1 mL standard from step 1 and 4 mL 12 M sulfuric acid. Cap and shake solution for 2 minutes.

3. Add 20 mL ether to the Erlenmeyer flask and shake for two minutes venting occasionally. Empty the emulsion into a 50 mL centrifuge tube. Centrifuge at 3500 RPM for two minutes to achieve separation.

4. Remove tube from the centrifuge and pipette ether phase into a clean 40 mL VOA vile. Transfer the water phase back into the Erlenmeyer flask.

5. Repeat steps 3 and 4 twice, adding 10 mL ether each time such that a total of 40 mL ether is obtained in the VOA vial. Discard water phase.

6. Add 5 g anhydrous sodium sulfate to the VOA vile and place in a dark fume hood for at least one hour.

7. Transfer the ether phase from the VOA vile to a Turbo Vap tube. Rinse the sodium sulfate with 5 mL of ether and add rinsate to Turbo Vap tube. Repeat rinse with 5 mL ether. Discard sodium sulfate.

8. Place Turbo Vap tube in Turbo Vap evaporator and adjust ether phase to 1 mL with nitrogen gas. Pipette ether into a 16 mm glass test tube. Rinse Turbo Vap tube with 1 mL ether and pipette rinsate into the 16 mm test tube. Repeat 1 mL rinse so that 3 mL ether is obtained in the 16 mm test tube. Allow ether to go to dryness.

9. Add 0.5 mL of 10-15% W/V boron trifluoride in methanol to the 16 mm test tube. Place test tube with Teflon lined cap into a block heater for one hour at 808 C.

10. After one hour take sample out of block heater and let cool to room temperature.

11. Pipette 10 mL of 10% W/V sodium chloride solution into the 16 mm test tube. Cap and shake test tube. Transfer contents to a 125 mL separatory funnel. Rinse test tube again with 10 mL of sodium chloride and transfer to separatory funnel.

12. Pipette 15 mL hexane into the separatory funnel and cap. Shake funnel for two minutes. Decant the sodium chloride solution into a clean container and the hexane into a VOA vile.

13. Transfer sodium chloride solution back into separatory funnel and repeat step 4 with 10 mL hexane such that a total of 25 mL hexane is obtained in the VOA vile. Discard sodium chloride solution.

14. Add 8-10 g anhydrous sodium sulfate to the VOA vile and place in a dark hood for at least one hour.

15. Transfer hexane from the VOA vile to a Turbo Vap tube. Rinse the sodium sulfate with 5 mL hexane and add rinsate to Turbo Vap tube. Repeat with 5 mL hexane. Discard sodium sulfate.

16. Use Turbo Vap evaporator to adjust hexane to 25 mL with nitrogen gas. Transfer hexane into a VOA vial. 4 mg/L tryclopyr, TCP and DCAA standard solution is complete.

Appendix B

Herbicide Concentration Values from the Delta Junction Right-of-Way and Agricultural Study Sites

Table B.1: 2,4-D Concentrations Delta Junction ROW Site 0-7.5 cm depth

Date	Days After Treatment	Concentration (μg/kg) at each Location (sample – site)								Median (μg/kg)
		1-24	1-34	2-24	2-34	3-24	3-34	4-24	4-34	
7/7/06	1 (12 hr)	252	37.5	8.96	127	5.22	40.7	ND	6.90	23.2
7/11/06	5	40.6	35.0	33.4	11.7	10.7	139	31.9	NT	33.4
7/17/06	11	91.1	8.85	10.4	21.3	5.83	9.26	15.8	NT	10.4
8/2/06	27	6.58	31.5	3.75	18.9	8.37	5.83	4.17	11.4	7.48
8/22/06	47	24.7	13.3	4.91	90.8	20.8	57.6	3.51	18.6	19.7
10/6/06	92	24.1	11.4	14.9	15.1	29.7	6.23	NT	NT	15.0
4/20/06	288	126	10.1	54.8	45.2	18.7	30.8	18.9	25.5	28.1
5/18/07	316	7.44	24.7	8.52	NT	32.2	8.22	2.36	7.93	8.22
7/3/07	362	4.93	4.16	3.08	6.76	1.63	2.20	1.53	NT	3.08

Note: ND denotes non detectable concentration in soil; NT denotes no sample taken. Units for these concentration values are micrograms per kilogram.

Table B.2: 2,4-D Concentrations Delta Junction ROW Site 10-30 cm depth

Date	Days After Treatment	Concentration (μg/kg) at each Location (sample – site)								Median (μg/kg)
		1-24	1-34	2-24	2-34	3-24	3-34	4-24	4-34	
7/7/06	1 (12 hr)	9.19	0.816	ND	5.32	0.660	1.05	0.932	1.32	0.991
7/11/06	5	NT	1.24	0.692	NT	1.82	ND	1.73	11.5	1.48
7/17/06	11	ND	5.99	ND	NT	5.62	6.82	5.91	3.12	4.37
8/2/06	27	6.07	5.12	5.17	10.4	4.64	NT	4.64	4.12	5.12
8/22/06	47	4.04	2.76	2.70	2.81	3.23	7.90	3.68	6.31	3.46
10/6/06	92	2.63	1.64	2.58	ND	2.47	ND	NT	NT	2.05
5/18/07	316	NT	0.460	0.550	0.370	0.730	NT	0.610	NT	0.550
7/3/07	362	ND	ND	ND	ND	ND	ND	ND	ND	ND

Note: ND denotes non detectable concentration in soil; NT denotes no sample taken. Units for these concentration values are micrograms per kilogram.

Table B.3: 2,4-D Concentrations Delta Junction ROW Site 36-60 cm depth

Date	Days After Treatment	Concentration (μg/kg) at each Location (sample – site)								Median (μg/kg)
		1-24	1-34	2-24	2-34	3-24	3-34	4-24	4-34	
7/7/06	1 (12 hr)	0.504	2.90	ND	2.57	3.63	1.65	2.74	0.475	2.109
7/11/06	5	0.920	1.24	1.17	NT	ND	ND	ND	0.545	0.545
7/17/06	11	ND	4.43	ND	NT	ND	ND	4.67	3.12	ND
8/2/06	27	3.94	3.27	2.91	1.22	3.12	3.32	2.63	3.34	3.197
8/22/06	47	5.17	2.72	2.14	1.63	1.90	2.56	NT	4.80	2.561
10/6/06	92	1.45	0.865	1.70	ND	1.63	ND	NT	NT	1.158
5/18/07	316	ND	0.317	0.497	ND	0.386	ND	0.470	ND	0.158
7/3/07	362	ND	ND	ND	ND	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken. Units for these concentration values are micrograms per kilogram.

Table B.4: Delta Junction triclopyr ROW site 32 – 0-5 cm depth

Date	Days After Treatment	Location 1 Concentration (mg/kg)	Location 2 Concentration (mg/kg)	Location 3 Concentration (mg/kg)	Location 4 Concentration (mg/kg)	Median (mg/kg)
7/7/06	1	6.244	6.256	0.291	0.369	3.306
7/11/06	5	ND	0.098	0.201	1.521	0.149
7/17/06	11	0.902	0.180	0.096	0.293	0.236
8/2/06	27	0.254	0.089	0.084	0.276	0.172
8/22/06	47	1.043	0.521	0.232	1.386	0.782
10/6/06	92	0.246	0.316	0.007	ND	0.126
4/20/07	288	0.009	0.002	0.006	0.016	0.008
5/18/07	316	0.074	0.029	0.032	0.011	0.031
7/3/07	362	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table B.5: Delta Junction triclopyr ROW area site 32 – 10-18 cm depth

Date	Days After Treatment	Location 1 Concentration (mg/kg)	Location 2 Concentration (mg/kg)	Location 3 Concentration (mg/kg)	Location 4 Concentration (mg/kg)	Median (mg/kg)
7/7/06	1	ND	0.047	0.219	ND	0.023
7/11/06	5	ND	0.053	ND	0.168	0.027
7/17/06	11	ND	ND	0.086	0.080	0.040
8/2/06	27	0.056	0.028	0.048	0.066	0.052
8/22/06	47	ND	ND	0.008	ND	ND
10/6/06	92	ND	ND	ND	ND	ND
4/20/07	288	NT*	NT	NT	NT	NT
5/18/07	316	ND	ND	ND	ND	ND
7/3/07	362	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table B.6: Delta Junction triclopyr ROW area site 32 – 30-38 cm depth

Date	Days After Treatment	Location 1 Concentration (mg/kg)	Location 2 Concentration (mg/kg)	Location 3 Concentration (mg/kg)	Location 4 Concentration (mg/kg)	Median (mg/kg)
7/7/06	1	ND	ND	ND	ND	ND
7/11/06	5	ND	ND	ND	ND	ND
7/17/06	11	ND	0.015	0.082	0.056	0.035
8/2/06	27	ND	0.051	0.043	0.038	0.040
8/22/06	47	ND	0.008	ND	ND	ND
10/6/06	92	ND	0.004	0.002	ND	0.001
4/20/07	288	NT*	NT	NT	NT	NT
5/18/07	316	ND	ND	ND	ND	ND
7/3/07	362	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table B.7: Delta Junction Agricultural Site 2.2 kg/ha – 0-5 cm depth

Date	Days After Treatment	Concentration (mg/kg) at each Location (sample – site)								Median (mg/kg)
		1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2	
7/18/06	1 (12hr)	1.087	0.236	0.326	0.580	0.225	0.694	0.451	0.690	0.515
7/19/06	3	1.360	NT	0.492	NT	NT	3.075	NT	0.621	0.991
7/23/06	7	1.654	0.122	0.652	0.657	0.338	0.545	0.574	0.310	0.560
8/6/06	21	NT	0.198	NT	0.129	0.198	NT	0.077	NT	0.163
8/20/06	35	0.017	ND	0.062	0.057	ND	0.072	0.016	0.011	0.016
4/25/06	283	0.900	1.723	0.445	0.277	0.543	1.265	0.174	0.702	0.622
7/16/06	365	0.009	0.095	0.025	ND	0.022	0.042	0.012	0.033	0.023

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table B.8: Delta Junction Agricultural Site 2.2 kg/ha – 5-15 cm depth

Date	Days After Treatment	Concentration (mg/kg) at each Location (sample – site)								Median (mg/kg)
		1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2	
7/18/06	1 (12hr)	NT	NT	NT	NT	NT	NT	NT	NT	-
7/19/06	3	0.078	NT	ND	NT	NT	0.077	NT	0.051	0.064
7/23/06	7	0.080	0.107	0.112	0.199	0.059	0.085	0.046	0.119	0.096
8/6/06	21	NT	0.061	NT	0.073	0.075	NT	0.037	NT	0.067
8/20/06	35	0.014	0.671	0.070	0.015	0.016	0.027	0.002	0.005	0.015
4/25/06	283	0.082	0.087	0.025	0.023	0.031	0.049	0.032	0.088	0.041
7/16/06	365	ND	ND	ND	ND	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table B.9: Delta Junction Agricultural Site 2.2 kg/ha – 15-30 cm depth

Date	Days After Treatment	Concentration (mg/kg) at each Location (sample – site)								Median (mg/kg)
		1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2	
7/18/06	1 (12hr)	NT	NT	NT	NT	NT	NT	NT	NT	-
7/19/06	3	NT	NT	NT	NT	NT	NT	NT	NT	-
7/23/06	7	0.064	ND	0.095	0.038	0.088	0.047	0.072	ND	0.055
8/6/06	21	NT	0.047	NT	0.048	0.067	NT	1.129	NT	0.057
8/20/06	35	0.012	0.023	ND	0.034	0.088	0.027	0.015	0.234	0.025
4/25/06	283	NT	0.021	NT	0.018	0.015	0.024	0.548	0.293	0.023
7/16/06	365	ND	ND	ND	ND	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table B.10: Delta Junction Agricultural Site 1.1 kg/ha – 0-5 cm depth

Date	Days After Treatment	Concentration (mg/kg) at each Location (sample – site)								Median (mg/kg)
		1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2	
7/18/06	1 (12hr)	0.996	0.438	0.293	0.252	0.566	0.330	0.551	0.250	0.384
7/19/06	3	0.326	NT	0.080	NT	NT	0.324	NT	0.110	0.217
7/23/06	7	0.235	0.280	0.160	0.233	0.411	0.279	0.391	0.230	0.257
8/6/06	21	0.058	NT	NT	0.066	0.194	NT	0.050	NT	0.062
8/20/06	35	0.102	0.226	0.216	0.006	0.095	0.093	0.060	ND	0.094
4/25/06	283	0.137	0.394	0.283	0.420	0.305	0.681	0.011	0.277	0.294
7/16/06	365	ND	0.010	0.010	ND	0.011	0.036	ND	0.008	0.009

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table B.11: Delta Junction Agricultural Site 1.1 kg/ha – 5-15 cm depth

Date	Days After Treatment	Concentration (mg/kg) at each Location (sample – site)								Median (mg/kg)
		1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2	
7/18/06	1 (12hr)	NT	NT	NT	NT	NT	NT	NT	NT	-
7/19/06	3	0.042	NT	ND	NT	NT	0.069	NT	0.047	0.044
7/23/06	7	0.076	0.063	0.063	0.048	0.076	0.096	0.080	0.021	0.070
8/6/06	21	NT	ND	NT	0.639	ND	NT	0.036	NT	0.018
8/20/06	35	0.020	0.007	0.006	0.008	0.007	0.013	0.020	0.016	0.011
4/25/06	283	0.013	0.018	0.023	0.159	0.012	0.022	0.019	0.021	0.020
7/16/06	365	ND	ND	ND	ND	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table B.12: Delta Junction Agricultural Site 1.1 kg/ha – 15-30 cm depth

Date	Days After Treatment	Concentration (mg/kg) at each Location (sample – site)								Median (mg/kg)
		1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2	
7/18/06	1 (12hr)	NT	NT	NT	NT	NT	NT	NT	NT	-
7/19/06	3	NT	NT	NT	NT	NT	NT	NT	NT	-
7/23/06	7	ND	0.033	0.102	0.095	0.044	0.045	0.070	0.112	0.058
8/6/06	21	NT	0.573	NT	0.025	0.535	NT	0.056	NT	0.296
8/20/06	35	ND	0.011	0.004	0.010	ND	0.011	0.053	0.013	0.011
4/25/06	283	0.012	0.021	0.010	0.024	NT	0.020	NT	0.014	0.017
7/16/06	365	ND	ND	ND	ND	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table B.13: Delta Junction Agricultural Site 0.55 kg/ha – 0-5 cm depth

Date	Days After Treatment	Concentration (mg/kg) at each Location (sample – site)								Median (mg/kg)
		1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2	
7/18/06	1 (12hr)	0.165	0.116	0.306	0.280	0.204	0.043	0.129	0.073	0.147
7/19/06	3	0.146	NT	0.320	NT	NT	0.065	NT	0.237	0.191
7/23/06	7	1.162	0.221	0.214	0.128	0.246	0.134	0.030	0.138	0.176
8/6/06	21	NT	0.065	NT	0.067	0.056	NT	0.106	NT	0.066
8/20/06	35	0.037	0.069	0.042	0.016	0.063	0.179	0.089	0.060	0.061
4/25/06	283	0.057	0.093	0.082	0.103	0.181	0.138	0.106	0.095	0.099
7/16/06	365	ND	ND	ND	0.005	0.021	0.008	ND	0.007	0.002

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table B.14: Delta Junction Agricultural Site 0.55 kg/ha – 5-15 cm depth

Date	Days After Treatment	Concentration (mg/kg) at each Location (sample – site)								Median (mg/kg)
		1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2	
7/18/06	1 (12hr)	NT	NT	NT	NT	NT	NT	NT	NT	-
7/19/06	3	0.086	NT	0.087	NT	NT	0.093	NT	0.067	0.086
7/23/06	7	0.064	0.035	0.063	0.072	0.062	0.091	0.066	0.080	0.065
8/6/06	21	NT	0.327	0.068	NT	0.416	NT	0.056	NT	0.198
8/20/06	35	0.005	0.034	ND	0.016	ND	0.051	0.008	ND	0.006
4/25/06	283	0.016	0.012	0.011	0.012	0.011	0.026	0.014	0.013	0.012
7/16/06	365	ND	ND	ND	ND	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table B.15: Delta Junction Agricultural Site 0.55 kg/ha – 15-30 cm depth

Date	Days After Treatment	Concentration (mg/kg) at each Location (sample – site)								Median (mg/kg)
		1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2	
7/18/06	1 (12hr)	NT	NT	NT	NT	NT	NT	NT	NT	-
7/19/06	3	NT	NT	NT	NT	NT	NT	NT	NT	-
7/23/06	7	0.039	0.036	0.070	0.029	0.063	0.044	0.062	0.036	0.041
8/6/06	21	NT	0.039	NT	0.367	0.048	NT	0.048	NT	0.048
8/20/06	35	0.015	0.013	0.012	0.010	0.004	0.011	0.014	0.013	0.012
4/25/06	283	ND	0.008	0.013	0.016	NT	0.016	NT	0.016	0.014
7/16/06	365	ND	ND	ND	ND	ND	ND	ND	ND	0.000

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table B.16: Delta Junction Agricultural Site 0.275 kg/ha – 0-5 cm depth

Date	Days After Treatment	Concentration (mg/kg) at each Location (sample – site)								Median (mg/kg)
		1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2	
7/18/06	1 (12hr)	0.039	0.090	0.038	0.039	0.077	0.099	0.110	0.078	0.078
7/19/06	3	0.144	NT	0.157	NT	NT	ND	NT	0.184	0.150
7/23/06	7	0.185	0.018	0.807	0.093	0.111	0.150	0.318	0.098	0.130
8/6/06	21	NT	0.050	NT	0.058	0.097	NT	0.102	NT	0.078
8/20/06	35	0.022	0.041	0.041	0.038	0.020	0.057	0.013	0.082	0.039
4/25/06	283	0.042	0.052	0.026	0.034	0.031	0.079	0.064	0.055	0.047
7/16/06	365	ND	ND	ND	ND	0.011	ND	ND	0.002	0.000

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table B.17: Delta Junction Agricultural Site 0.275 kg/ha – 5-15 cm depth

Date	Days After Treatment	Concentration (mg/kg) at each Location (sample – site)								Median (mg/kg)
		1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2	
7/18/06	1 (12hr)	NT	NT	NT	NT	NT	NT	NT	NT	-
7/19/06	3	0.056	NT	ND	NT	NT	ND	NT	0.051	0.026
7/23/06	7	0.061	0.060	0.877	0.073	0.084	0.087	0.037	0.033	0.067
8/6/06	21	NT	0.072	NT	0.076	0.190	NT	0.083	NT	0.079
8/20/06	35	0.005	0.009	0.004	0.019	0.006	0.008	0.009	ND	0.007
4/25/06	283	0.012	0.012	ND	0.011	0.026	0.012	0.015	0.011	0.012
7/16/06	365	ND	ND	ND	ND	ND	ND	ND	ND	0.000

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table B.18: Delta Junction Agricultural Site 0.275 kg/ha – 15-30 cm depth

Date	Days After Treatment	Concentration (mg/kg) at each Location (sample – site)								Median (mg/kg)
		1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2	
7/18/06	1 (12hr)	NT	NT	NT	NT	NT	NT	NT	NT	-
7/19/06	3	NT	NT	NT	NT	NT	NT	NT	NT	-
7/23/06	7	ND	ND	ND	0.033	0.084	0.023	0.821	0.040	0.028
8/6/06	21	NT	0.170	NT	0.041	0.068	NT	0.044	NT	0.056
8/20/06	35	ND	0.009	ND	0.015	ND	ND	0.004	0.008	0.002
4/25/06	283	NT	0.018	0.008	0.013	ND	0.009	NT	0.011	0.10
7/16/06	365	ND	ND	ND	ND	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Appendix C

Herbicide Concentration Values from the Valdez Study Site

Table C.1: 2,4-D Concentrations Valdez 0-5 cm depth

Date	Days After Treatment	Location 1 Concentration (μg/kg)	Location 2 Concentration (μg/kg)	Location 3 Concentration (μg/kg)	Location 4 Concentration (μg/kg)	Median (μg/kg)
7/16/07	0.5	11.86	ND	NT	NT	5.93
7/17/07	1	21.79	21.39	16.55	ND	18.97
7/23/07	7	8.76	7.83	ND	NT	7.83
8/8/07	23	15.89	15.38	ND	ND	7.69
9/13/07	59	34.19	8.44	3.80	NT	8.44
5/19/08	308	271.40	73.40	50.50	29.90	61.95
7/18/08	368	0.04	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken. Units for these concentration values are micrograms per kilogram.

Table C.2: 2,4-D Concentrations Valdez 10-15 cm depth

Date	Days After Treatment	Location 1 Concentration (μg/kg)	Location 2 Concentration (μg/kg)	Location 3 Concentration (μg/kg)	Location 4 Concentration (μg/kg)	Median (μg/kg)
7/16/07	0.5	NT	NT	NT	NT	NT
7/17/07	1	37.07	6.62	ND	ND	3.31
7/23/07	7	8.72	ND	ND	ND	ND
8/8/07	23	23.22	6.50	ND	ND	3.25
9/13/07	59	2.58	ND	ND	NT	ND
5/19/08	308	55.20	ND	ND	ND	ND
7/18/08	368	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken. Units for these concentration values are micrograms per kilogram.

Table C.3: 2,4-D Concentrations Valdez 15-30 cm depth

Date	Days After Treatment	Location 1 Concentration (μg/kg)	Location 2 Concentration (μg/kg)	Location 3 Concentration (μg/kg)	Location 4 Concentration (μg/kg)	Median (μg/kg)
7/16/07	0.5	NT	NT	NT	NT	NT
7/17/07	1	12.93	6.49	ND	NT	6.49
7/23/07	7	ND	ND	ND	NT	ND
8/8/07	23	5.08	ND	ND	NT	ND
9/13/07	59	ND	ND	ND	NT	ND
5/19/08	308	ND	ND	ND	ND	ND
7/18/08	368	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken. Units for these concentration values are micrograms per kilogram.

Table C.4: Triclopyr Concentrations Valdez Site 12 0-5 cm depth

Date	Days After Treatment	Location 1 Concentration (mg/kg)	Location 2 Concentration (mg/kg)	Location 3 Concentration (mg/kg)	Location 4 Concentration (mg/kg)	Median
7/16/07	0.5	0.186	0.121	0.103	ND	0.112
7/17/07	1	0.432	0.064	0.061	ND	0.0625
7/23/07	7	0.478	0.306	0.082	ND	0.194
8/8/07	23	1.996	1.217	0.196	0.132	0.7065
9/13/07	59	0.705	0.672	0.418	0.223	0.545
5/19/08	308	0.298	0.162	0.078	0.072	0.12
7/18/08	368	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken. Units for these concentration values are micrograms per kilogram.

Table C.5: Triclopyr Concentrations Valdez Site 12 10-15 cm depth

Date	Days After Treatment	Location 1 Concentration (mg/kg)	Location 2 Concentration (mg/kg)	Location 3 Concentration (mg/kg)	Location 4 Concentration (mg/kg)	Median
7/16/07	0.5	NT	NT	NT	NT	NT
7/17/07	1	ND	ND	ND	ND	ND
7/23/07	7	1.084	0.109	0.039	0.029	0.074
8/8/07	23	0.111	ND	ND	ND	ND
9/13/07	59	0.254	0.123	0.064	ND	0.0935
5/19/08	308	ND	ND	ND	ND	ND
7/18/08	368	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken. Units for these concentration values are micrograms per kilogram.

Table C.6: Triclopyr Concentrations Valdez Site 12 15-30 cm depth

Date	Days After Treatment	Location 1 Concentration (mg/kg)	Location 2 Concentration (mg/kg)	Location 3 Concentration (mg/kg)	Location 4 Concentration (mg/kg)	Median
7/16/07	0.5	NT	NT	NT	NT	NT
7/17/07	1	0.226	ND	ND	ND	ND
7/23/07	7	0.177	0.035	ND	ND	0.0175
8/8/07	23	ND	ND	ND	ND	ND
9/13/07	59	ND	ND	ND	ND	ND
5/19/08	308	ND	ND	ND	ND	ND
7/18/08	368	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken. Units for these concentration values are micrograms per kilogram.

Table C.7: Triclopyr Concentrations Valdez Site 42 0-5 cm depth

Date	Days After Treatment	Location 1 Concentration (mg/kg)	Location 2 Concentration (mg/kg)	Location 3 Concentration (mg/kg)	Location 4 Concentration (mg/kg)	Median
7/16/07	0.5	ND	ND	ND	ND	ND
7/17/07	1	ND	ND	ND	ND	ND
7/23/07	7	0.574	0.395	0.204	0.157	0.2995
8/8/07	23	3.592	0.615	0.589	0.313	0.602
9/13/07	59	0.768	0.488	0.146	0.091	0.317
5/19/08	308	0.616	0.109	0.026	0.014	0.0675
7/18/08	368	0.096	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table C.8: Triclopyr Concentrations Valdez Site 42 10-15 cm depth

Date	Days After Treatment	Location 1 Concentration (mg/kg)	Location 2 Concentration (mg/kg)	Location 3 Concentration (mg/kg)	Location 4 Concentration (mg/kg)	Median
7/16/07	0.5	NT	NT	NT	NT	NT
7/17/07	1	ND	ND	ND	ND	ND
7/23/07	7	ND	ND	ND	ND	ND
8/8/07	23	ND	ND	ND	ND	ND
9/13/07	59	0.119	0.04	0.028	ND	0.034
5/19/08	308	ND	ND	ND	ND	ND
7/18/08	368	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.

Table C.9: Triclopyr Concentrations Valdez Site 42 15-30 cm depth

Date	Days After Treatment	Location 1 Concentration (mg/kg)	Location 2 Concentration (mg/kg)	Location 3 Concentration (mg/kg)	Location 4 Concentration (mg/kg)	Median
7/16/07	0.5	NT	NT	NT	NT	NT
7/17/07	1	ND	ND	ND	ND	ND
7/23/07	7	ND	ND	ND	ND	ND
8/8/07	23	ND	ND	ND	ND	ND
9/13/07	59	ND	ND	ND	ND	ND
5/19/08	308	ND	ND	ND	ND	ND
7/18/08	368	ND	ND	ND	ND	ND

Note: ND denotes non-detectable concentration in soil; NT denotes no sample taken.