The soil adsorption, mobility, degradation, and residual properties of AC 222,293
by Gary Milton Fellows

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Agronomy
Montana State University

Abstract:
AC 222,293 (m-Toluic acid, 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-, methyl ester and p-Toluic acid, 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-, methyl ester) was applied preplant incorporated at rates of 0.1, 0.2, 0.4, 0.8, and 1.4 kg/ha to field plots at Havre, Bozeman, and Kalispell, Montana in the spring of 1985.

Twelve crops were planted into the plots in 1985 and eleven in 1986. Lentils, yellow mustard, oats, rape, and sugar beet were injured by soil residues of AC 222,293. Crop injury varied by site. Soil pH was the most highly correlated soil factor with crop injury. Injury increased as the soil pH decreased.

The soil mobility of AC 222,293 was measured by soil thin-layer chromatography. AC 222,293 had an average Rf value of 0.53 in eight soils. The herbicide moved as a dispersed band through the soil. Soil adsorption of AC 222,293 is low, with an average Freundlich K value of 1.79 on nine soils. Adsorption of AC 222,293 was positively correlated with soil organic matter.

The degradation of AC 222,293 under controlled conditions varied by soil type. Degradation was greater in soil treated with 2 ppm than 1 ppm AC 222,293. Degradation was greater when the treated soil was stored at 18.5 C than at 4.5 C. Microbial degradation is suggested as a major factor in the degradation of AC 222,293.

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APPROVAL

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Gary Milton Fellows

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready fo submission to the College of Graduate Studies.

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Date Feb. 9. 1987

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TABLE OF CONTENTS

TABLE OF CONTENTS-Continued

LIST OF TABLES

LIST OF TABLES-Continued

LIST OF TABLES-Continued

LIST OF TABLES-Continued

LIST OF TABLES-Continued

LIST OF FIGURES

ABSTRACT

AC 222,293 (m-Toluic acid, 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-, methyl ester and p-Toluic acid, 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-, methyl ester) was applied preplant incorporated at rates of 0.1, 0.2, 0.4, 0.8, and 1.4 kg/ha to field plots at Havre, Bozeman, and Kalispell, Montana in the spring of 1985. Twelve crops were planted into the plots in 1985 and eleven in 1986. Lentils, yellow mustard, oats, rape, and sugar beet were injured by soil residues of AC 222,293. Crop injury varied by site. Soil pH was the most highly correlated soil factor with crop injury. Injury increased as the soil pH decreased.

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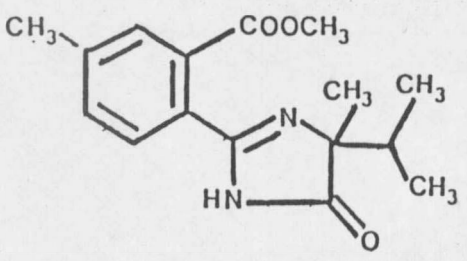
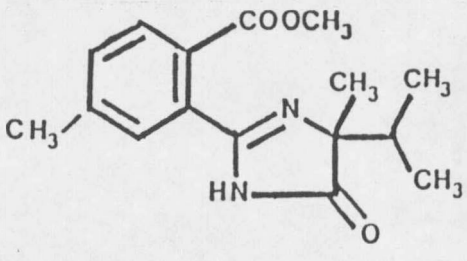
CHAPTER 1

LITERATURE REVIEW

AC 222,293 [m-Toluic acid, 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-, methyl ester and p-Toluic acid, 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-, methyl ester] is a selective postemergence herbicide marketed under the trade name Assert. AC 222,293 provides control of wild oat (*Avena fatua* L.), blackgrass (*Alopecurus mysuroides* Huds.), wild buckwheat (*Polygonum convolvulus* L.) and Brassica species. Additionally, AC 222,293 has shown excellent crop tolerance for wheat (*Triticum aestivum* L.) and barley (*Hordeum vulgare* L.).



m-isomer



p-isomer

Figure 1. Structure of AC 222,293 isomers.

AC 222,293 is an equal mixture of two positional isomers, meta(m) and para(p), which differ only in the location of the methyl moiety on the benzene ring (Figure

1)(91). The herbicidal activity of the two isomers is different. The meta-isomer is more active on wild oat and blackgrass but is weak on mustards. The para-isomer controls mustards but is less effective on wild oat and blackgrass.

AC 222,293 belongs to the imidazolinone family of herbicides. The structure common to the imidazolinone family consists of a five-membered ring containing the two nitrogen atoms and a carbonyl group (91).

Imidazolinone herbicides are uncompetitive inhibitors of acetohydroxyacid synthase (AHAS)(84,85). AHAS is the first common enzyme in the biosynthetic pathway of the three branched chain aliphatic amino acids; valine, leucine, and isoleucine (93). Imidazolinones rapidly inhibit AHAS three hours after application causing a reduction in the levels of valine, leucine, and isoleucine which disrupts protein synthesis, inhibits meristematic growth, and causes eventual death of mature tissue (4,85). The phytotoxic effect caused by imidazolinones can be reversed or prevented by exogenous applications of valine, leucine, and isoleucine (85).

AC 222,293 is taken up through both the foliage and root system of emerged plants. AC 222,293 is readily absorbed into the leaves of tolerant and susceptable plants. Seventy five and ninety percent of the applied AC 222,293 was absorbed into the leaf of wild oat and wheat plants respectively, within three days after application (86). Shaner et al. (86) reported that root uptake of AC 222,293 is

important for herbicidal activity of the compound, and herbicidal activity and crop safety varied for different soil types. As soil organic matter content increased, the rate of AC 222,293 needed for control of wild oat increased. Alternatively, Pillmoor and Caseley (76) found that under a controlled environment foliar application was as effective as a combined foliar and soil application. Soil application alone was less effective.

Radiotracer studies showed that AC 222,293 is xylem and phloem mobile. Shaner et al (86) studied the translocation of foliar and root absorbed AC 222,293 and found that 51% of the root absorbed herbicide was translocated to the first leaf, 40% to the second leaf, with 9% remaining in the root three days after application. When applied to the first leaf, 0.3% was translocated to the root, 2.7% to the second leaf, and 97% remained in the treated leaf. The distribution of AC 222,293 in wheat plants was not significantly different from wild oat plants.

The acid form of AC 222,293 is the herbicidally active form (86). The acid form is more active on wild oat than the ester form and exhibits no selectivity for wheat or barley. Wheat and barley are not affected by 4.0 kg/ha of the ester form but are injured by 0.1 kg/ha of the acid form of AC 222,293. It appears that selectivity is regulated by the concentration of free acid present in the plant. Stidham (91) reported that 39% of the AC 222,293 extracted from wild oat

plants was in the acid or alcohol acid form with the remainder being parent ester, an alcohol ester, or a conjugated metabolite. When extracted from wheat plants only 3.1% of the AC 222,293 was in an acid or alcohol acid form. Wheat plants are unable to metabolize significant amounts of the ester form of the herbicide into its active form and instead convert it into inactive glucosides. The proposed pathway for AC 222,293 metabolism is presented in Figure 2.

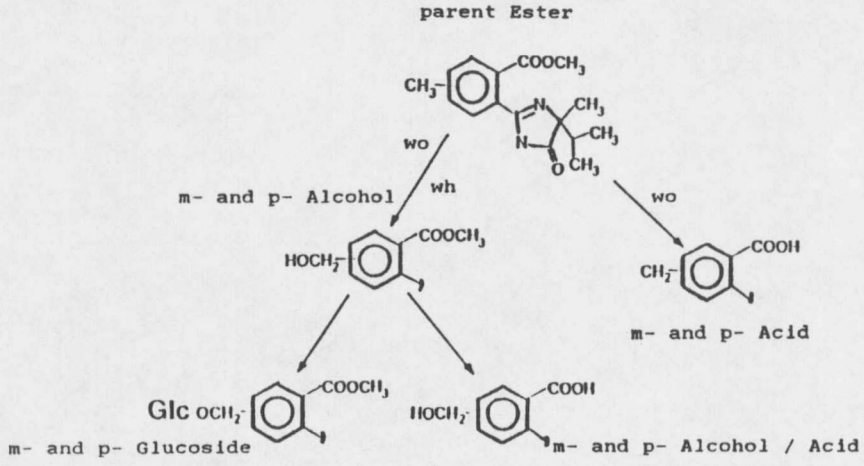


Figure 2. Metabolic fate of AC 222,293 in wheat and wild oat. (wh=wheat, wo=wild oat) (91).

AC 222,293 is most effective when applied when the wild oat plants are in the 1 to 4 leaf stage (4). Pillmoor and Caseley (76) showed that the susceptibility of wild oat declined when the application was delayed until the 5 leaf stage. The lower uptake of AC 222,293 into older plants was due to reduced entry of the herbicide into the younger leaves. The metabolism of the herbicide by wild oat plants

was affected by leaf age. There was less metabolism of the parent molecule, and less of the acid form was recovered as the leaf aged.

Visual symptoms of AC 222,293 are first expressed as a purple discoloration or chlorosis of the youngest leaves. These areas later becomes necrotic. Environmental factors significantly influence the rate of herbicidal activity the rate of activity increases under high temperatures and favorable moisture conditions (4).

Bioassays

Bioassays use a biological response of a living organism to determine the presence or concentration of a chemical in the substrate. Typical herbicide bioassays involve planting a sensitive plant species in herbicide treated soil. The plant response is then compared to similar plants grown in untreated soil or in soil containing a known concentration of the herbicide.

Chemical assays are routinely used to measure herbicide concentrations in soil. While chemical analyses are usually precise they are normally specific for a single chemical and do not measure phytotoxic metabolites. They often require a lengthy extraction and expensive equipment. Bioassays are usually much less expensive and do not require extraction of the substance from soil. Bioassays measure the effect of phytotoxic breakdown products in addition to the parent compound.

Field Bioassays.

Field bioassays or "plant-back" experiments utilize potentially sensitive crops which are planted under field conditions at various intervals after herbicide application (5). Relative growth or yield of the test crops are compared to the performance of controls as an indication of the presence or absence of the herbicide. Burkhart (10) measured the response of 12 crops originally treated with 5 rates of chlorsulfuron (2-chloro-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]-carbonyl]benzenesulfonamide) at 5 locations in Montana. The twelve crops were separated into five classes based on their tolerance to chlorsulfuron residues. This data was used to develop a model for prediction of chlorsulfuron disappearance.

Greenhouse and Laboratory Bioassays.

Greenhouse and laboratory bioassays have been used to evaluate the effect of various enviromental and soil factors under controlled conditions. Adoption of uniform conditions and procedures allow the bioassay to be repeated at different locations and times with similar results. Santelman et al (82) conducted a cooperative study on the accuracy and reproducibility of bioassays at several locations. Oats (*Avena sativa* L.) were used as a bioassay crop for prometryne (N,N',-bis(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine) detection. Assay results varied initially and ranged from 147% below to 234%

above the actual amount present in the soil. When uniform procedures and environmental conditions were adapted at the four sites the results ranged from 37% below to 0% above the prometryne applied.

Measurement of plant physical characteristics such as plant height, fresh weight, dry weight, color, and growth rate are the most common comparisons used in laboratory bioassays. Santelman et al (82) measured the reduction in plant height, fresh weight, and dry weight of oats from prometryne residues and found that they all gave similar results. Injury to barnyardgrass (*Echinochloa crus-galli* L. Beauv.) treated with four thiocarbamate herbicides was more severe than the reduction in plant weight indicated (58). In that study plant height was a better indicator of herbicide injury than plant weight. Visual ratings have been used effectively to measure herbicide injury from amitrole (1H-1,2,4-triazol-3-amine) (22) and picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid) (83). Visual ratings permit an evaluator to incorporate all relevant criteria. When visual ratings are used it is important to clearly define the two extremes of the rating scale.

Inhibition of germination, and radicle or shoot elongation have also been used as a measurement of plant response. Gronwald (30) studied the effect of haloxyfop (2-[4-[{3-chloro-5-(trifluoromethyl)-2-pyridinyl}oxy]phenoxy] propanoic acid) and haloxyfop-methyl on corn (*Zea mays* L.)

radicle elongation. Corn root elongation was completely inhibited within 24 hours after exposure to 10^{-6} M of either compound. Parker (74) placed sorghum (*Sorghum bicolor* L. Moench) seeds in plastic petri dishes and covered them with treated soil. The soil was moistened and the dishes covered and placed in a tilted position which forced the roots to grow down along the transparent cover. Nondestructive measurements of daily root growth were taken to evaluate the effect of several herbicides. In this test the system was sealed which permitted use of the technique for volatile compounds such as pebulate (S-propyl butylethylcarbamothiate) (52) and easily leached compounds like diphenamid (N,N-dimethyl-2,2-diphenylacetamide) (54). Parker (74) developed a split petri dish technique to assay the difference in sensitivity to root versus shoot uptake of several herbicides. Two square petri dishes were placed together and filled with sand moistened with water or herbicide solution. Pregerminated seeds were placed into one dish with the radicle extending into the next. The dishes were covered and growth was measured. With this system either the plant root or shoot could be exposed to the herbicide.

Certain physiological and morphological events can be used as a bioassay response. Went (101) used oat coleoptile curvature to measure the presence of auxins. Eshel (24) measured the reduction in photosynthetic activity caused by

pyrazon (5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone) in leaf disks. Santelmann et al (82) used water consumption of oat plants as a bioassay for prometryne. Measurement of water consumption was a more sensitive assay than plant weight or height since the decline in water consumption by plants in prometryne-treated soil occurred several days before the appearance of injury symptoms.

Several specialized bioassay techniques have been developed for determining the presence of various herbicides. Algae has been used as a bioassay for several herbicides which inhibit photosynthesis and respiration. The response of algae to herbicides has been studied by measuring chlorophyll concentration with a spectrophotometer (60), O^2 evolution (60), algae growth turbidimetrically (2), and measurement or visual estimation of the growth inhibition on plated media (48,97). Truelove et al (98) developed a method for detecting photosynthetic inhibitors based on the observation that leaf disks floating on a liquid medium sank if photosynthesis was inhibited. This technique was sensitive to prometryne concentrations of 0.002 to 0.02 ppm and required only two to six hours for completion.

Factors Influencing Bioassays.

The presence of plants can effect herbicide persistance in the soil. Talbert and Fletchall (94) observed significantly more weed growth where the corn rows were

located the previous year in fields treated with simazine (5-chloro-N,N-diethyl-1,3,5-triazine-2,4-diamine).They concluded that the weed growth was a result of nonuniform disappearance of simazine caused by absorption and metabolism of the herbicide by corn. Similar observations were reported after atrazine (6-chloro-N-ethyl-N-(1-methylethyl)-1,3,5-triazine-2,4-diamine) or propazine (6-chloro-N,N-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine) had been applied to sorghum (103).

Soil factors normally play a major role in both the period of herbicide persistence, and plant response to a given herbicide concentration. Peterson and Arnold (75) positively correlated the persistance of chlorsulfuron to soil pH. Similarly, Burkhart (10) showed that crop injury from chlorsulfuron carryover was inversely related to soil pH and precipitation. Organic matter and clay content can alter the availablity of a herbicide by increasing the adsorptive sites of the soil. Mapplebeck and Waywell (63) found a high negative correlation between linuron (N-(3,4-dichlorophenyl)-N-methoxy-N-methylurea) activity and organic matter. This correlation has also been demonstrated for simazine, atrazine, chloramben (3-amino-2,5-dichlorobenzoic acid), fluometuron (N,N-dimethyl-N-[3-(trifluromethyl) phenyl]urea), propachlor (2-chloro-N-(1-methylethyl)-N-phenylacetamide), trifluralin (2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl) benzenamine), and dinitramine (N3,N3-

diethyl-2,4-dinitro-6-(trifluoromethyl)-1,3-benzenediamine) (31,43,72).

Soil moisture can effect the herbicide availability which influences plant response to herbicide residues. Water can compete for adsorption sites, causing more herbicide to be in the soil solution and available for plant uptake (6). Walker (100) reported that phytotoxicity of several herbicides increased as soil water content.

Soil moisture can also effect the degradation of a herbicide. Stickler et al (90) found the toxicity of atrazine and EPTC (S-ethyl dipropyl carbamothioate) to giant foxtail (*Setaria faberi* Herrm.) increased with increasing soil moisture. Alternatively, the phytotoxicity of trifluralin decreased linearly as soil moisture increased. This was attributed to increased trifluralin degradation under wetter conditions.

The location of the herbicide in the soil profile can effect plant response to herbicide residues. A narrow concentrated band of herbicide can be more phytotoxic than an equal amount of herbicide distributed uniformly through a greater soil volume (71). Okafor et al (73) found that the maximum phytotoxic effect of dinitramine to french bean (*Phaseolus vulgaris* L.) seedlings occurred when the seeds were sown into a zone where the herbicide had been incorporated. The herbicidal activity of dinitramine was inversely related to incorporation depth because of the

dilution effect from deeper incorporation.

Soil nutrient levels can influence herbicide toxicity. Stolp and Penner (92) found that high phosphate levels increased the toxicity of atrazine to soybeans (*Glycine max* L. Merr.) because of increased respiration. Adams (1) reported an interaction between soil phosphorus levels and simazine phytotoxicity. He concluded that simazine reduced the amount of P required to cause salt injury. McReynolds and Tweedy (65) found that the form of nitrogen fertilizer used influenced herbicide injury. Nitrate increased simazine uptake by corn and soybean, and increased simazine toxicity to soybean more than the ammonium form of nitrogen.

Plant populations can effect the efficacy of a herbicide. Burrill and Appleby (14) found that italian ryegrass (*Lolium multiflorum* Lam.) control with diuron (N-(3,4-dichlorophenyl)-N,N-dimethylurea) decreased as plant density increased. Hoffman and Lavy (50) obtained similar results using atrazine with soybeans. They found that less atrazine was absorbed by each plant at high densities than at low densities. They could adjust the herbicide sensitivity of the plant by varying the bioassay plant density.

Temperature can influence the herbicide availability in soil, herbicide uptake and translocation, and numerous other physiological processes in plants. Dao and Lavy (21) showed that the availability of atrazine in soil was temperature

dependent. They reported more adsorption of atrazine at 30 than at 5 C. Mulder and Nalewaja (70) studied temperature effects on several herbicides. Diclofop methyl ester (2-[4-(2,4-dicholorophenoxy)phenoxy]propanoic acid) was more toxic to wild oat shoots at 24 C than at 10 or 17 C. Likewise, atrazine was more toxic to barley, and alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide) was more injurious to oats at 17 C than at 10 C. Temperatures within the range of 10 to 24 C did not effect the efficacy of trifluralin or chloramben.

Crop cultivars can also exhibit differences in their response to herbicides. Varying degrees of sensitivity to metribuzin (4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one) among crop cultivars have been reported in soybean (8), potato (*Solanum tuberosum* L.) (29), wheat (71), and tomato (*Lycopersicon lycopersicum* L. Karsten) (89). Differences in tolerance to atrazine have been shown among cultivars in cucumbers (*Cucumis sativus* L.) (102).

Herbicide Degradation

Herbicide persistance is a major concern since extended persistance may lead to residue problems for succeeding crops. Alternatively, if a herbicide degrades too rapidly its effectiveness and usefulness for weed control is limited.

Degradation is the process by which a herbicide is

structurally transformed to nonphytotoxic end products. Degradation can occur by chemical, biochemical, or photochemical processes. Disappearance of a herbicide can also occur by leaching, mass flow, and volatilization.

Kinetic analysis of herbicide degradation can be used to predict the rate of disappearance and the residual life of a herbicide in the soil environment. Kinetic studies quantitatively show the rate of degradation as a function of time and concentration. First-order, second-order, one-half-order, and zero-order rate laws are used to describe the rate of herbicide degradation (Table 1).

Table 1. Equations for kinetic rate laws.

Type of kinetics	Equation[1]
Zero-order	$C_0 - C = kt$
Half-order	$2(C_0 - C) = kt$
First-order	$\text{Log}(C_0/C) = kt$
Second-order	$\frac{1}{C} - \frac{1}{C_0} = kt$

[1] Where t = Time, C_0 = initial concentration, C = concentration at time t, k = rate constant (37)

In first-order kinetics the rate of loss is directly proportional to the herbicide concentration and the percent loss is independant of concentration (37). Second-order kinetics occur when the rate of loss is proportional to the square of the concentration (34). One-half-order kinetics

occur when the rate of loss is proportional to the square root of the concentration. Zero-order kinetics occur when the rate of decomposition is independent of the concentration of the herbicide. The degradation curve of the four rate laws for a chemical with a half life of one year and a relative initial concentration of one is shown (Figure 3).

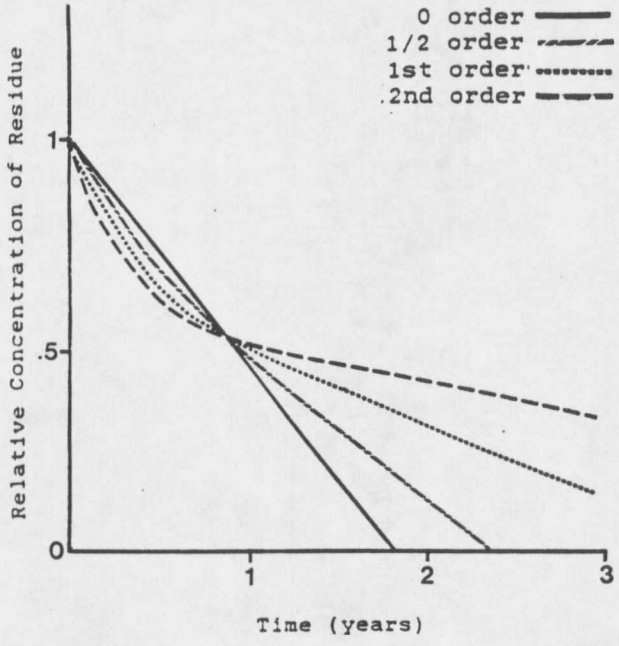


Figure 3. Decay curve for different rate laws for a chemical with a half-life of 1 year and an initial concentration of 1. (34)

The degradation of some compounds begins with an initial lag-period during which little or no change in concentration occurs. Following the lag-phase the degradation rate follows one of the kinetic rate laws. Riepma (80) observed first-order degradation of amitrole following a lag-phase period. He also found that the duration of the lag-phase increased with increasing

concentration. Thirunarayanan et al (96) found that chlorsulfuron displayed first-order degradation with a half-life ranging from 38 to 99 days in four soils. When the half-life was calculated excluding the zero time concentration the half-life for the four soils was increased to 88 to 143 days.

Hamaker and Goring (35) found a similar pattern of breakdown for picloram residues in soil with a rapid initial breakdown followed by a slower rate of breakdown. They proposed the following two compartment model to explain this phenomenon. The pesticide is divided between available and unavailable fractions in the soil. Only the available fraction is subject to degradation. Freshly added chemical is predominantly in the available state so the initial rate of breakdown is rapid. However, as an equilibrium is established between the available and unavailable form the rate of release to the available state controls the degradation rate. Hance and McKone (41) thought that reduced degradation at higher initial concentrations might be due to a limited number of reaction sites in the soil. It has also been suggested that high rates of herbicides may have a toxic effect on the microorganisms or enzymes involved in breakdown or that the microorganisms are adapting or increasing during the lag-period (55).

Temperature effects the rate of herbicide degradation. Since all chemical and biological reactions are influenced

by temperature, increased temperatures increase the rate of breakdown. This was found to be true for oryzalin (4-(dipropylamino)-3,5-dinitrobenzenesulfonamide) and isopropalin (4-(1-methylethyl)-2,6-dinitro-N,N-dipropylbenzenamine) (28), metribuzin (56), amitrole (23), simazine (26),and several other herbicides. The dependence of many rate constants on temperature can be expressed in terms of the Arrhenius activation energy equation, a measure of the amount of energy molecules must have to react. It is calulated by the following equation:

$$Ae = 2.303\ RT_1T_2/T * \log k_2/k_1$$

where Ae=Arrhenius activation energy, R=gas constant (1.987 cal deg^{-1} $mole^{-1}$), k_1 and k_2 are the rate constants at temperatures in Kelvin T_1 and T_2 respectively and $T = T_1 - T_2$. Zimdahl et al (105) calculated the Arrhenius activation energies of several triazine and uracil herbicides. He then compared the Ae values to the known energy of several bond types and was able to predict the sites of breakdown on the herbicide molecules.

Water acts as a solvent, a transport agent, and a reaction medium for both biological and non-biological processes. Herbicide degradation rates generally increase with increased soil moisture. For example the half-life for dinitramine was found to be 4.3 weeks at 22% moisture and 38.1 weeks at 2.2% moisture in a clay loam soil (77). Increased biological activity at higher moisture levels is

considered to be one reason for the increased rate of breakdown of herbicides in moist soils (55). Hollist and Foy (51) however, suggested that increased soil moisture content blocked absorptive sites for trifluralin, thereby increasing the amount available for degradation in soil solution.

While soil type exerts a major influence on herbicide persistence, it is difficult to isolate individual soil factors for study. For example, higher soil organic matter usually means increased adsorption of the herbicide which results in a slower rate of breakdown. At the same time higher organic matter is often correlated with increased soil microorganism populations which results in an increased rate of degradation. The influence of soil organic matter, pH, cation exchange capacity (CEC), and other factors combine to influence the breakdown rate of herbicides.

Herbicide adsorption plays an important role in herbicide degradation. The adsorption of a herbicide to soil particles can act to protect the herbicide from breakdown by reducing the amount in solution (55). Conversely, adsorptive sites may catalyse non-biological reactions resulting in adsorbed herbicides being degraded more rapidly (11).

Adsorption

The soil adsorption of a herbicide affects its mobility, biological activity, and persistence. Adsorption is the attraction of a herbicide molecule to the soil particles or fractions. Positive adsorption occurs when

there is attraction between the herbicide and soil resulting in the concentration of the herbicide being higher at the interface than in the soil solution. Negative adsorption occurs when the adsorbate concentration is greater in the bulk solution than at the interface.

Several equations have been used to describe adsorption isotherms. The Freundlich equation is the most commonly used and is expressed as follows:

$$x/m = K\ (C)^{1/n}$$

where x/m = amount of herbicide adsorbed/g of the adsorbant, C = equilibrium solution concentration, K is an equilibrium constant, and 1/n is an exponent constant which approximates 1 in value. When the equation is expressed in its logarithmic form, a linear relationship is obtained. The constant 1/n is indicative of the degree of linearity between solution concentration and adsorption. The equilibrium constant K is a measure of the degree or strength of adsorption. K values for herbicides can vary over a wide range. Paraquat (1,1'-dimethyl-4,4'-bipyridinium ion), a tightly adsorbed herbicide has a K value of 5400 (20). Grover (32) reported K values of 0.09 to 0.75 for picloram, indicating very low adsorption.

The Freundlich equation is limited in its use in describing the adsorption of herbicides to soil. The most noticeable flaw is that as the equilibrium concentration is increased there is assumed to be no limit to the surface

area of the adsorbant. This is a false assumption since any adsorbant will have limited surface area which limits adsorption. Therefore, adsorption isotherms must be measured over a range of concentrations which are relevant to field use rates and no extrapolation of the isotherms above the range of the experimental concentrations tested should be made.

The Langmuir equation is less frequently used to describe herbicide adsorption. The Langmuir equation was developed to describe the adsorption of gases onto solids, and is written in terms of concentration as:

$$x/m = \frac{K_1 K_2 C}{1 + K_2 C}$$

where K_1 and K_2 are constants for the system.

This equation also has some inherent problems which limit its usefulness. One of the primary assumptions on which the Langmuir equation is based is that the energy of adsorption is constant for all surfaces. However, since soil is a heterogenous mixture it is unconceivable that the energy of adsorption would be constant for all portions of the soil surface.

The distribution adsorption constant, K_d, based on simple proportionality, has also been used to describe herbicide adsorption. K_d values are derived from the following equation:

$$K_d = (x/m)/C$$

K_d values are an indication of the degree of adsorption by soil. Thirunarayanan et al (96) reported K_d values of 0.055 to 0.140 for chlorsulfuron when measured on four soils at two temperatures. Thus, 5.5 to 14% of the herbicide was adsorbed to the soil. The concentration of the adsorbed material can also be expressed per unit of organic matter according to this equation:

$$K_{oc} = \frac{x/m \text{ (ug/g of organic carbon)}}{C}$$

Since adsorption is positively correlated with soil organic carbon content, K_{oc} is more constant among soils than K_d (36).

Soil adsorption of a herbicide is influenced by the chemical properties of the herbicide, the physical and chemical properties of the soil, and the experimental conditions under which the adsorption is studied. The most important factor affecting adsorption is the chemical composition of the herbicide. The molecular structure of the molecule dictates the type and characteristics of the charge interactions which occur between the soil and the herbicide. Paraquat, which is positively charged, is held tightly to the soil by ionic binding with clays (20). Linuron, a noncharged molecule is bound to clays by ligand exchange (40). Hydrogen bonding is responsible for the adsorption of EPTC to montmorillonite clay (69).

The solubility of the herbicide may also have an effect

on the adsorption of the herbicide. The degree of adsorption of four substituted-urea herbicides (fenuron (1,1-dimethyl-3-phenylurea mono(trichloroacetate)), monuron (3-(p-chlorophenyl)-1,1-dimethylurea mono(trichloacetate)), diuron (N'-(3,4-dichlorophenyl)-N,N-dimethylurea) , and neburon) was inversely related to the order of their solubility (104). Leopold et al (61) also found an inverse correlation between the solubility and the adsorption of the phenoxy acid herbicides. Alternatively, Harris and Warren (42) found no correlation between members of different families and their respective solubilities. It appears that the relationship between solubility and adsorption is valid only within a family of herbicides (6).

The soil components most important to adsorption are the mineral and organic fractions. Organic matter has the highest cation exchange capacity of all the soil constituents and a large surface area, from 500 to 800 square meters per gram (6). These properties give organic matter a large potential for adsorption. Kozak and Weber (95) used regression analysis to correlate the Freundlich K values of five phenylurea herbicides with several soil characteristics of eight soils. Soil organic matter was most highly correlated with adsorption with r values of 0.84 to 0.94. Herbicide adsorption can vary greatly due to the nature of the organic matter in the soil. Damanakis et al (20) studied the adsorption of paraquat on different soil

constituents and reported a wide range of Freundlich K values. Pure cellulose powder had a K value of 64, humic acids had a K value of 42,000, and 6 peat soils had K values ranging from 3100 to 7000. Another difficulty in characterizing the role of organic matter in adsorption is that its properties are not constant and vary as a result of soil chemical and biological processes. Morita (68) studied the Freundlich K value of linuron on a peat soil in its original and in a humified state and found that the K values increased from 24 to 297 respectively.

Clays are the most important soil mineral affecting adsorption because of their abundance and surface properties (15). The anionic nature of the surface of clays results in strong adsorbance of positively charged molecules like paraquat (20). Conversely, picloram which is anionic in nature shows very little adsorption to clay particles (32,7).

The ionic composition of the clay surface is affected by the composition of the soil solution. The presence of cations in the soil solution can alter the adsorption of the herbicide in several ways. Cations can lower adsorption by competing for the adsorption sites with positively charged herbicides as with atrazine (39) and paraquat (44). Cations can improve adsorption by forming coordination bonds as with linuron (40). Cations such as Al^{3+} and Fe^{3+} can improve adsorption by forming hydroxides on the clay surface

resulting in improved adsorption capacity of the mineral (15).

The effect of soil pH on herbicide adsorption depends on the herbicide molecule and its site and mode of binding. Hamaker and Thompson (36) divided herbicides into six classes and determined their response to pH changes in the soil. Changes in pH had a small effect on strongly acidic and polar herbicides. Herbicide molecules that are neutral in charge are not affected by a change in pH. Weakly acidic herbicides such as picloram exist as free acids at lower pH and are more highly adsorbed in this form than in the anionic form which exists at higher soil pH. Weakly basic herbicides such as ametryne are converted to cationic forms under low pH regimes which results in more adsorption than in the free base form. However, as the soil pH is decreased, the increase in H+ concentration competes with cationic herbicides for adsorptive sites and adsorption decreases. Adsorption of strong bases is strong but does decrease at very low pH. The full effect of pH changes in the soil depends on the specific herbicide, the soil characteristics, and the types of binding occuring between them.

Since soil adsorption processes are exothermic, an increase in temperature would be expected to reduce adsorption and favor desorption (6). This is true for picloram (25) and several s-triazine herbicides (95). However, Hayes et al (44) found that adsorption of paraquat

on vermiculite increased as temperature increased. In most other cases changes in temperature caused no detectable changes in the adsorption.

The soil:water ratio used when conducting the adsorption experiments can effect adsorption. Grover and Hance (33) found that the Freundlich K value for atrazine decreased from 2.1 to 0.8 when the soil:water ratio was decreased from 10:1 to 1:4. Likewise, K values for linuron decreased from 12.3 to 2.7. They suggested that the difference in the K values between the two moisture regimes was due to the degree of dispersion of the soil colloids. More surface area of the soil colloids is exposed in the dilute suspensions resulting in more adsorption. A water:soil ratio of 10:1 is the most commonly used ratio in the literature.

CHAPTER 2

THE EFFECT OF AC 222,293 ON ROTATIONAL CROPS IN MONTANA

Introduction

AC 222,293 is a promising new postemergence herbicide for wild oat control in wheat and barley. It also controls a limited number of broadleaf weeds. Richardson et al (79) tested AC 222,293 preemergence on 69 plant species and found several that were sensitive to rates as low as 0.1 kg/ha. Crops that were especially sensitive to AC 222,293 included several members of the Cruciferae and Leguminosae families, and sugar beet (*Beta vulgaris* L.).

AC 222,293 has both soil and foliar activity. Shaner et al demonstrated foliar and soil activity on emerged wild oat plants (87). Pillmoor and Casely reported that soil applications of AC 222,293 were as effective as foliar application for wild oat control (76).

AC 222,293 persists in soil with a half-life ranging from 30 to 276 days (4). Richardson et al (79) found that AC 222,293 reduced sugarbeet fresh weight more than 80% one year after a preemergence application of 0.1 kg/ha. He concluded that the soil persistence of AC 222,293 was similar to the soil persistence of simazine, a moderately-long to long residual herbicide.

The objectives of this experiment were to determine the sensitivity of common rotational crops grown in Montana to AC 222,293 residues in soil, to determine the rate of degradation of AC 222,293 in soil, and to determine which factors influence the degradation rate of AC 222,293.

Materials and Methods

Plantback Study.

Field plots were established at the Post Research Farm in Bozeman on a Bozeman silty clay loam soil (fine-silty, mixed, Frigid Argic Pachic Cryoboroll), the Northern Agricultural Research Center in Havre on a Scobey clay loam soil (fine, montmorillonitic, Ardic Argiboroll), and the Northwestern Agricultural Research Center in Kalispell on a Creston sandy loam soil (coarse-silty, mixed, Udic Haploboroll) in the spring of 1985. Soil characteristics of each location are presented in Table 2. All locations were fallowed the previous cropping season. The plot design at each location was a randomized complete block with four replications. Individual plots were 13.4 m by 3.7 m at Bozeman and Kalispell, and 10.1 m by 5.5 m at Havre.

AC 222,293 was applied at 0, 0.1, 0.2, 0.4, 0.8, and 1.4 kg/ha using a CO^2-pressurized backpack sprayer delivering 94 l/ha at 276 kpa immediately prior to planting at each location in 1985. The herbicide was incorporated twice to a depth of 7.6 cm in one direction which corresponded to the long axis of the plots using a

rototiller at Bozeman, and a field cultivator at Havre and Kalispell for the first incorporation. A spring tooth harrow was used for the second incorporation at all locations. Twelve crops were planted perpendicular to the long axis of the plots as described in Table 3. Crops were randomized by block and location. Weeds were controlled by hand throughout the season.

Table 2. Soil characteristics of each experimental site.

Location	Soil Texture	Soil pH	CEC	Organic matter	sand	silt	clay
Bozeman	silty clay loam	6.0	18.1	1.6	13.2	52.0	34.8
Havre	clay loam	7.7	16.7	1.2	39.2	32.0	28.8
Kalispell	sandy loam	6.9	12.2	3.8	69.2	20.0	10.8

Visual crop injury was assessed eight weeks after planting in 1985. Injury was expressed from 0 to 100% with 0 = no injury and 100 = complete kill. Crop yields were measured in the fall by harvesting 2 meters of row per crop per plot except for potatoes. Potato yield was measured by weighing the tubers from 10 plants per plot. Sugar beet yield was measured by harvesting roots from 2 meters of row per plot.

Following harvest in 1985 the plots were fertilized with 78 kg/ha of nitrogen as nitrate (34-0-0), 45 kg/ha of phosphorus as diammonium phosphate (18-64-0), and 45 kg/ha

of potassium as potash (0-0-60). The plots were cultivated with an offset disc followed by a field cultivator to incorporate the fertilizer and prepare a seed bed. Four rows of winter wheat were planted in each plot. The remaining 10 crops were planted as described above in the spring, 1986 (Table 3). Eight weeks after planting visual crop injury ratings were taken as described above. Grain yields were determined by harvesting seed from 2 meters of row per crop per plot. Above ground biomass was taken from 2 meters of row for alfalfa yield. Potato tubers were harvested from ten plants per plot and sugar beet roots were harvested from 2 meters of row. Grain from the winter wheat plots were harvested from the entire plot with a small plot combine. Harvest data for each year was expressed as a percentage of the yield of the control plots. Raw yield data is found in Appendix A.

Potato Injury.

Potato tubers were harvested and planted in the greenhouse to determine if the injury observed in the field in 1985 would effect subsequent growth from tubers. Tubers were taken from the plots in 1985 and stored under cool dry conditions for three months to overcome dormancy. Round tuber pieces approximately 2 cm in diameter were removed from the potatoes and placed in a grid pattern 4 cm apart on the soil surface of 30 by 40 by 10 cm deep metal flats containing 6 cm of greenhouse soil mix comprised of 3 parts

Bozeman silt loam: 1 part sand. The tuber pieces were covered with 2 cm of soil mix, watered daily, and grown in a greenhouse at 24 C without supplemental lighting. Thirty days after planting the above ground biomass was harvested and dry weights determined.

Table 3. Crops planted in 1985 and 1986 in soil treated with AC 222,293 preplant incorporated in 1985.

Crop	Row Width	Rows
1985		
	cm	No.
Alfalfa (*Medicago sativa* L.'Apollo II')	30	3
Corn (*Zea mays* L.'Greenway G-X 33')	60	2
Faba bean (*Vicia faba* L.'Acuperle')	30	3
Flax (*Linum usitatissimum* L.'Culbert')	30	3
Garbanzo bean (*Cicer arietinum* L.'UC-5')	30	3
Lentils (*Lens culinaris* Medik.'Chilean')	30	3
Lettuce (*Lactuca sativa* L.'Black-seeded simpson')	30	2
Pinto beans (*Phaseolus vulgaris* L.'UI 111')	30	3
Potatoes (*Solanum tuberosum* L.'Russet burbank')	60	2
Safflower (*Carthamus tinctorius* L.'S-108')	30	3
Sugar beet (*Beta vulgaris* L.'Betaseed 1433')	60	2
Sunflower (*Helianthus annuus* L.'IS984')	60	2
1986		
Alfalfa ('Apollo II')	30	4
Faba bean (Acuperle')	30	3
Flax ('Culbert')	30	3
Garbanzo bean ('UC-5')	30	3
Lentils ('Chilean')	30	3
Oats (*Avena sativa* L.'Otana')	30	3
Potatoes ('Russet burbank')	60	4
Rape (*Brassica napus* L.'Tower')	30	3
Sugar beet ('Betaseed')	60	2
Yellow mustard (*Brassica alba* L. 'unknown variety')	30	3
Winter wheat (*Triticum aestivum* L.'Norstar')	30	6

Results and Discussion

Crop Tolerance.

Tolerance of crops to AC 222,293 residues in soil varied significantly (Table 4). Lentils and sugar beet were the most sensitive with 23 and 46% injury, respectively, in plots treated with the lowest rate tested. Lettuce, safflower, and sunflower were not injured at any rate of AC 222,293 in 1985, and were not planted in 1986. Although corn and pinto beans were slightly injured at the higher rates tested, they suffered no yield reduction and were not planted in 1986.

Table 4. Average visual crop injury of 12 crops rated eight weeks after planting in 1985 in soil treated with AC 222,293 applied preplant incorporated at three locations in Montana.

	Crop injury[1]					
	AC 222,293 rate (kg/ha)					
Crop	-0-	0.1	0.2	0.4	0.8	1.4
	%					
Alfalfa	0 a	11 ab	9 ab	12 ab	23 b	25 b
Corn	0 a	0 a	0 a	0 a	0 ab	1 b
Faba beans	0 a	6 a	9 ab	22 b	38 c	35 c
Flax	0 a	2 a	4 a	11 ab	21 b	15 ab
Garbanzo bean	0 a	2 ab	4 ab	10 bc	18 c	18 c
Lentils	0 a	23 b	33 bc	49 c	70 d	72 d
Lettuce	0 a	0 a	0 a	0 a	0 a	1 a
Pinto beans	0 a	0 a	1 a	2 a	6 b	6 b
Potatoes	0 a	2 a	4 a	20 b	40 c	54 d
Safflower	0 a	0 a	0 a	0 a	0 a	0 a
Sugar beets	0 a	46 b	54 bc	61 bc	72 bc	80 c
Sunflower	0 a	0 a	0 a	0 a	0 a	0 a

[1] Numbers in a row followed by the same letter are not significantly different at the 5% level using the LSD test.

The sensitivity of sugar beet, and the tolerance of lettuce, corn, and pinto bean to AC 222,293 was also determined by Richardson et al (79) in greenhouse experiments where AC 222,293 was applied preemergence. Richardson also observed a lack of herbicidal activity on members of the Composite family. The tolerance of sunflower and safflower to the higher rates of AC 222,293 used in this study confirms the lack of activity on composites.

Table 5. Dry weight of above ground biomass of potatoes grown from tuber pieces taken from plants grown in soil containing AC 222,293.

Original field rate of AC 222,293	Dry weight per plant of above ground biomass[1]
kg/ha	mg
-0-	317 a
0.1	280 a
0.2	295 a
0.4	261 a
0.8	280 a
1.4	275 a

[1] Average of two experiments. Numbers followed by the same letters are not significantly different at the 5% level using the LSD test.

Potatoes were visually injured by rates exceeding 0.4 kg/ha, however, plants derived from tuber pieces from affected potatoes were not injured in greenhouse tests (Table 5). Evidently, AC 222,293 was not translocated into the tubers of the affected plants in sufficient quantities for injury or was metabolized by the growing plants. However, the visual injury observed when grown in soil

containing AC 222,293 will limit its use where potatoes are grown.

There was significantly less crop injury from AC 222,293 residues in soil in 1986 than in 1985 (Table 6). All crops tested were injured when grown in soil which received 0.8 and 1.4 kg/ha. Sugar beet were injured by all rates of AC 222,293 applied 14 months previously. These results are in agreement with the findings of Richardson et al (79) who reported that sugar beets were severely injured when planted 52 weeks after the soil was treated with 0.1 kg/ha of AC 222,293 applied either as a surface or a preplant incorporated treatment.

Table 6. Average visual crop injury of 11 crops rated eight weeks after planting in 1986 in soil treated preplant incorporated with AC 222,293 in 1985 at three locations in Montana.

	Crop Injury[1]					
	AC 222,293 Rate (kg/ha)					
Crop	-0-	0.1	0.2	0.4	0.8	1.4
	%					
Alfalfa	0 a	0 a	0 a	0 a	3 b	4 b
Faba beans	0 a	0 a	0 a	3 a	13 b	14 b
Flax	0 a	0 a	0 a	5 ab	8 b	11 b
Garbanzo beans	0 a	0 a	0 a	0 a	3 b	3 b
Lentils	0 a	4 a	8 ab	25 bc	38 c	59 d
Potatoes	0 a	0 a	1 a	5 ab	8 b	9 b
Sugar beets	0 a	18 ab	26 b	42 bc	58 cd	77 d
Yellow mustard	0 a	0 a	2 a	15 ab	30 b	31 b
Oats	0 a	0 a	1 a	12 a	28 b	30 b
Rape	0 a	5 a	15 ab	30 bc	39 bc	54 c
Winter wheat	0 a	0 a	0 a	1 a	4 b	11 c

[1] Numbers in a row followed by the same letter are not significantly different at the 5% level using the LSD test.

The proposed labeled use rate of AC 222,293 at the present time is 0.4 kg/ha. Crops that are affected by that rate or lower should not be planted the year after application. Crops that are especially sensitive include sugar beet, lentils, rape, and yellow mustard. Accurate field records of the rate and location of AC 222,293 applications will have to be kept so that producers can avoid injury to sensitive rotational crops.

Effect of Rate and Location.

Crop injury at each location was measured in 1985. Corn, lettuce, pinto bean, safflower, and sunflower were not injured at any rate at any location. Injury levels for the remaining seven crops (alfalfa, faba bean, flax, garbanzo bean, lentils, potatoes, and sugar beet) were averaged for each rate of application (Table 7).

Crops planted in soil treated with 0.1 kg/ha were not injured at Havre. At Kalispell, the seven crops were not injured at 0.1 and 0.2 kg/ha but were injured at the higher rates. The seven crops were significantly injured at all locations in soil treated with 0.4 kg/ha, the expected labeled use rate for Montana.

Crop injury in 1985 to AC 222,293 applied preplant incorporated varied by location. There was consistently more injury at Bozeman than at Havre or Kalispell at all application rates. However, injury at the highest rate of application was similar at all three locations. Injury

levels at Havre were similar to the injury observed at Kalispell.

Table 7. Average visual injury in 1985 of alfalfa, faba bean, flax, garbanzo bean, lentils, potatoes, and sugar beet from AC 222,293 applied preplant incoporated at three locations in Montana.

Rate of AC 222,293	Crop injury[1]		
	Experimental Location		
	Havre	Bozeman	Kalispell
kg/ha	%		
-0-	0 a	0 a	0 a
0.1	9 ab	24 b	7 a
0.2	12 b	28 bc	10 a
0.4	13 b	44 cd	22 b
0.8	32 c	58 d	31 b
1.4	38 c	45 d	45 c

[1] Numbers in columns followed by the same letter are not significantly different at the 5% level using the LSD test.

Table 8. Average visual injury in 1986 of alfalfa, faba bean, flax, garbanzo bean, lentils, potatoes, and sugar beet from AC 222,293 applied preplant incoporated in 1985 at three locations in Montana.

Rate of AC 222,293	Crop Injury[1]		
	Experimental Location		
	Havre	Bozeman	Kalispell
kg/ha	%		
-0-	0 a	0 a	0 a
0.1	0 a	9 a	0 a
0.2	0 a	15 ab	0 a
0.4	2 ab	29 bc	3 a
0.8	7 b	41 c	9 b
1.4	16 c	36 c	22 c

[1] Numbers in columns followed by the same letter are not significantly different at the 5% level using the LSD test.

Injury in 1986 followed a similar pattern to that observed in 1985(Table 8). Crops at Bozeman were significantly injured at rates of 0.2 kg/ha and higher. Crops at Havre and Kalispell were injured only at the two highest rates tested. There was more injury at Bozeman in 1986 than at Havre and Kalispell.

Table 9. Pearson correlation coefficients (r) of the average visual injury in 1985 and 1986 of alfalfa, faba bean, garbanzo bean, lentils, potatoes, and sugar beet to AC 222,293 applied preplant incorporated in 1985 with selected soil properties of soils at three locations in Montana.

	Pearson Correlation Coefficients (r)[1]					
Factor	1985 Injury	1986 Injury	Precip-itation[2]	% clay	OM	CEC
Soil pH	-.93	-.90	.01	-.27	-.11	-.26
CEC	.60	.66	-.97	<u>.99</u>	-.93	
OM	-.27	-.34	<u>.99</u>	-.93		
% clay	.62	.67	-.97			
Precipitation	-.39	-.45				
1986 injury	<u>.99</u>					

[1] Correlation coefficients that are underlined are significant at the 0.05 level.
[2] Precipitation includes all moisture received from the time of AC 222,293 application until the crops were rated for injury.

The difference in injury at the three locations illustrates the influence of soil type on either the availability or the degradation rate of the herbicide. When crop injury at each location was correlated to several individual soil factors, no single variable accounted for the variation observed among sites (Table 9). Soil pH was the most highly correlated factor, with Pearson correlation

coefficients (r) of -0.93 and -.90 for 1985 and 1986 respectively.

Havre.

Crop injury at Havre was significantly reduced at all rates in 1986 compared to 1985 (Figure 4). The decline in injury from 1985 to 1986 was greater at the lower rates tested. Crop injury in plots treated with 1.4 kg/ha decreased 57% while injury in plots treated with 0.1 kg/ha decreased 95%. Percent injury decreased 75% from 1985 to 1986 when average percent injury was compared for all treatments and all seven crops. The only rates which caused significant injury to crops in 1986 were in plots treated with 0.8 and 1.4 kg/ha. The three lower rates of application did not cause injury.

Only lentil and sugar beet yields were reduced at Havre when planted one year after application of 1.4 kg/ha of AC 222,293 (Table 10). While the yields of yellow mustard, oats, and rape were reduced at the highest rate of application they were not significantly lower than the control because of excessive variability due to uneven stand establishment. The stand of several of the small seeded crops was erratic due to incomplete seed bed preparation and soil moisture stress at the time of planting. In addition, the experimental location at Havre was heavily invaded by grasshoppers.

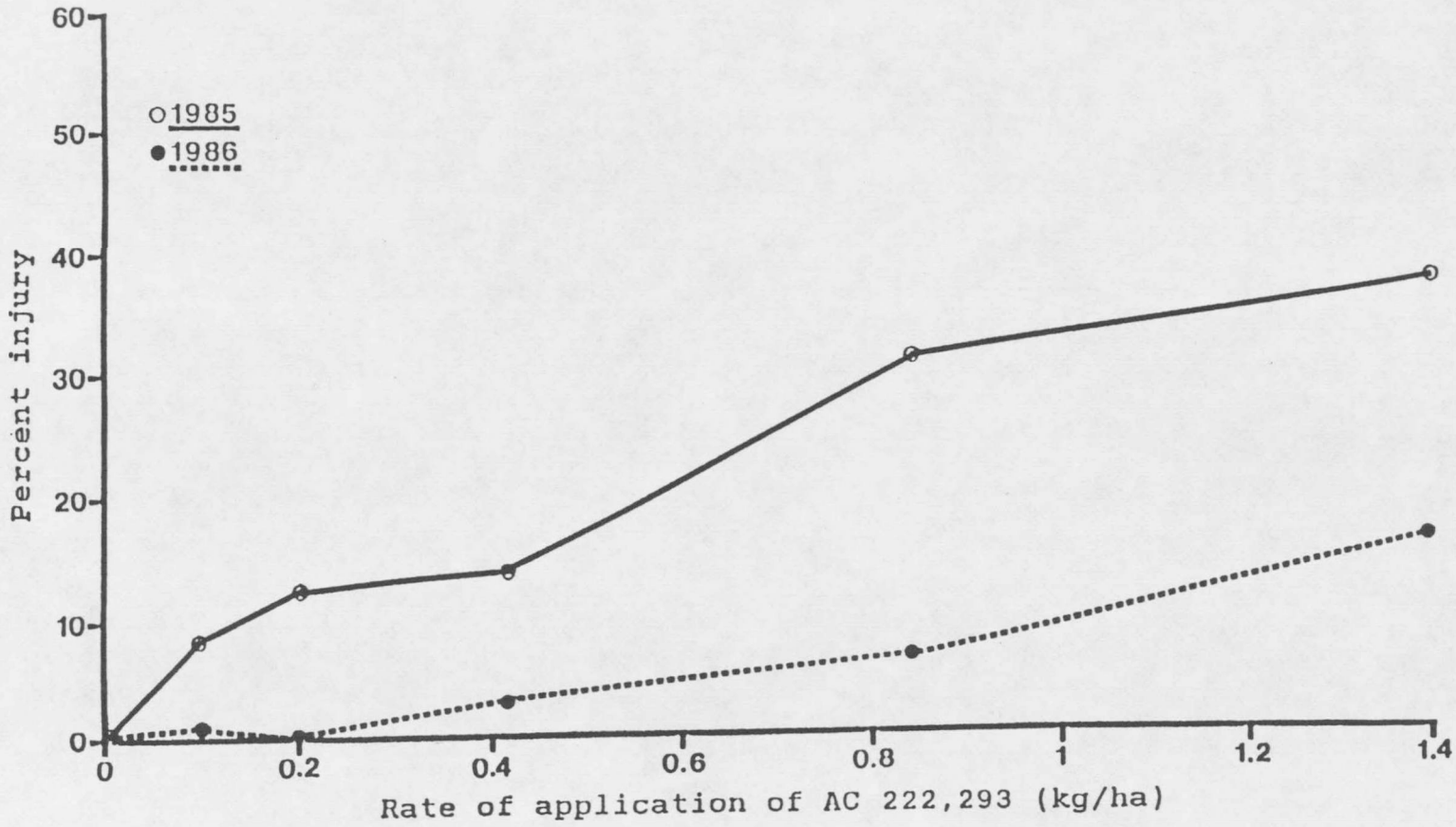


Figure 4. Average injury of alfalfa, faba bean, flax, lentils, garbanzo bean, potatoes, and sugar beet grown at Havre in 1985 and 1986 in soil treated with AC 222,293 preplant incorporated in 1985.

Table 10. Yield of 11 crops planted in 1986 in soil treated with AC 222,293 preplant incorporated in 1985 at Havre, Montana.

	Crop Yield[1]					
	AC 222,293 Rate (kg/ha)					
Crop	-0-	0.1	0.2	0.4	0.8	1.4
	% of control					
Alfalfa	100 a	112 a	112 a	104 a	127 a	121 a
Faba bean	100 a	168 a	172 a	166 a	159 a	129 a
Flax	100 a	133 a	116 a	118 a	100 a	88 a
Garbanzo bean	100 a	85 a	172 a	159 a	71 a	95 a
Lentils	100 a	58 a	173 a	188 a	74 a	19 b
Potatoes	100 a	149 a	71 a	114 a	95 a	131 a
Sugar beets	100 a	107 a	108 a	91 ab	97 a	42 b
Yellow mustard	100 a	131 a	123 a	72 ab	69 ab	37 b
Oats	100 a	123 a	134 a	108 ab	104 ab	75 b
Rape	100 a	162 a	102 a	123 a	125 a	69 a
Winter wheat	100 a	101 a	108 a	98 a	93 a	87 a

[1] Numbers in rows followed by the same letter are not significantly different at the 5% level using the LSD test.

Bozeman.

The average percent injury to the seven crops at Bozeman was significantly less in 1986 than in 1985 at all rates except the highest rate of application(Figure 5). The percent reduction in injury from 1985 to 1986 was consistent at each rate and averaged 34%. Percent injury for the seven crops in plots treated with 0.1 kg/ha, the lowest rate of application, was not significant in 1986. At the expected labeled use rate of 0.4 kg/ha the seven crops averaged 29% injury one year after application.

The yield of several crops was reduced at Bozeman in 1986(Table 11). Lentil and yellow mustard yield was lowered

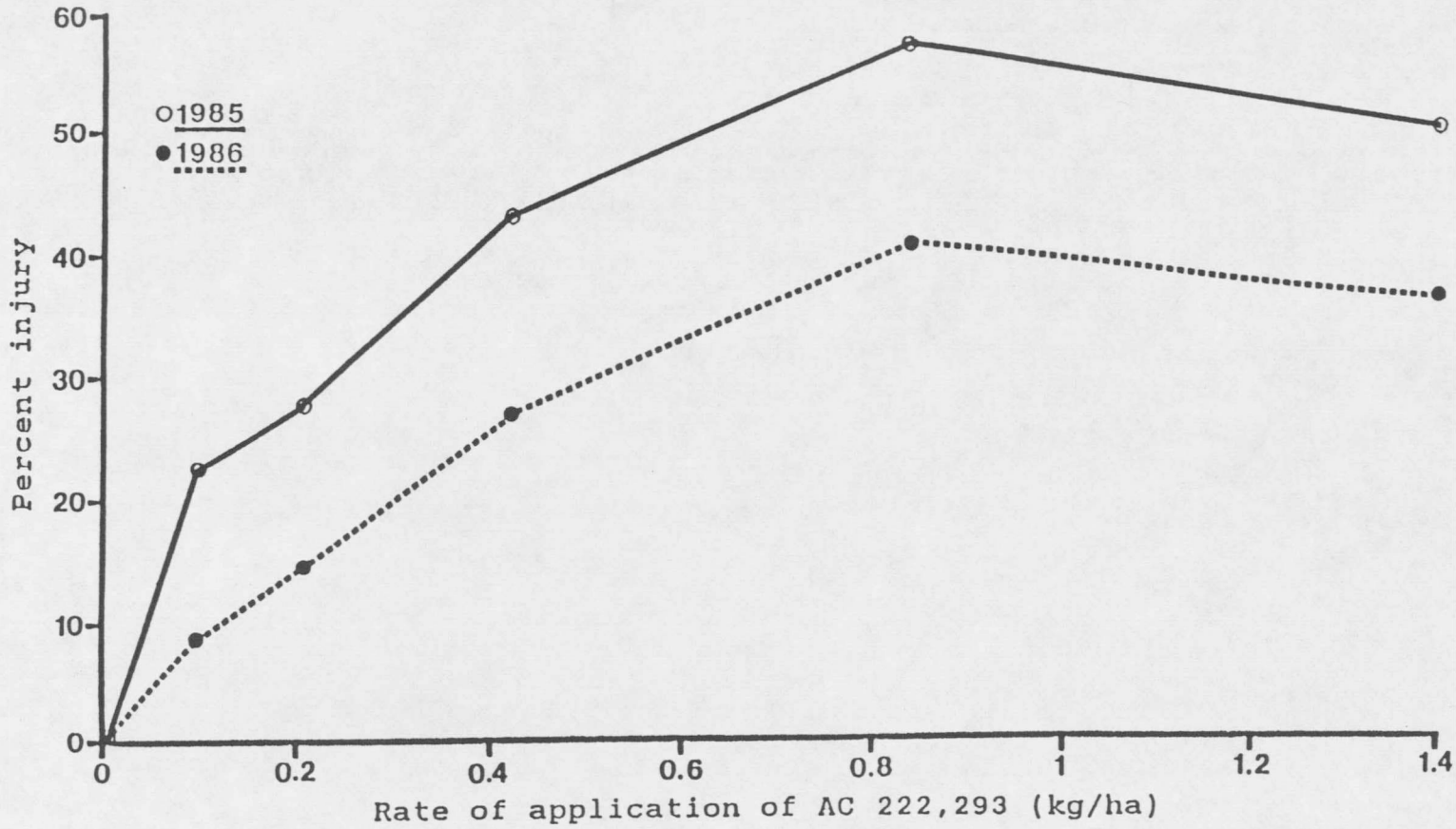


Figure 5. Average injury of alfalfa, faba bean, flax, lentils, garbanzo bean, potatoes, and sugar beet grown at Bozeman in 1985 and 1986 in soil treated with AC 222,293 preplant incorporated in 1985.

at nearly all rates of application. The yield of sugar beet was reduced in plots originally treated with rates higher than 0.2 kg/ha. Oat yield was reduced in plots treated with the two highest rates of AC 222,293 used. Rape was not harvested at Bozeman due to significant insect damage. Its sensitivity to AC 222,293 residues in soil would probably be similar to the closely related yellow mustard.

Table 11. Yield of 11 crops planted in 1986 in soil treated with AC 222,293 preplant incorporated in 1985 at Bozeman, Montana.

	Crop Yield[1]					
	AC 222,293 Rate (kg/ha)					
Crop	-0-	0.1	0.2	0.4	0.8	1.4
	% of control					
Alfalfa	100 a	124 a	113 a	118 a	126 a	127 a
Faba bean	100 a	101 a	92 a	77 a	99 a	96 a
Flax	100 ab	119 ab	131 a	124 ab	104 ab	91 b
Garbanzo bean	100 a	222 b	178 ab	160 ab	160 ab	130 a
Lentils	100 a	56 bc	73 ab	66 b	30 c	48 bc
Potatoes	100 a	103 a	92 a	90 a	85 a	99 a
Sugar beets	100 b	156 a	107 b	26 c	0 c	5 c
Yellow mustard	100 a	45 b	35 b	5 c	0 c	7 c
Oats	100 a	102 a	100 a	75 ab	26 c	69 b
Rape[2]	-	-	-	-	-	-
Winter wheat	100 a	113 a	101 a	103 a	109 a	107 a

[1] Numbers in rows followed by the same letter are no significantly different at the 5% level using the LSD test.
[2] Rape was not harvested due to insect damage.

Kalispell.

Crop injury at the 0.1 kg/ha rate was not significantly different from the control in 1985 or 1986 for 7 crops(Figure 6). Crop injury declined in 1986 compared to

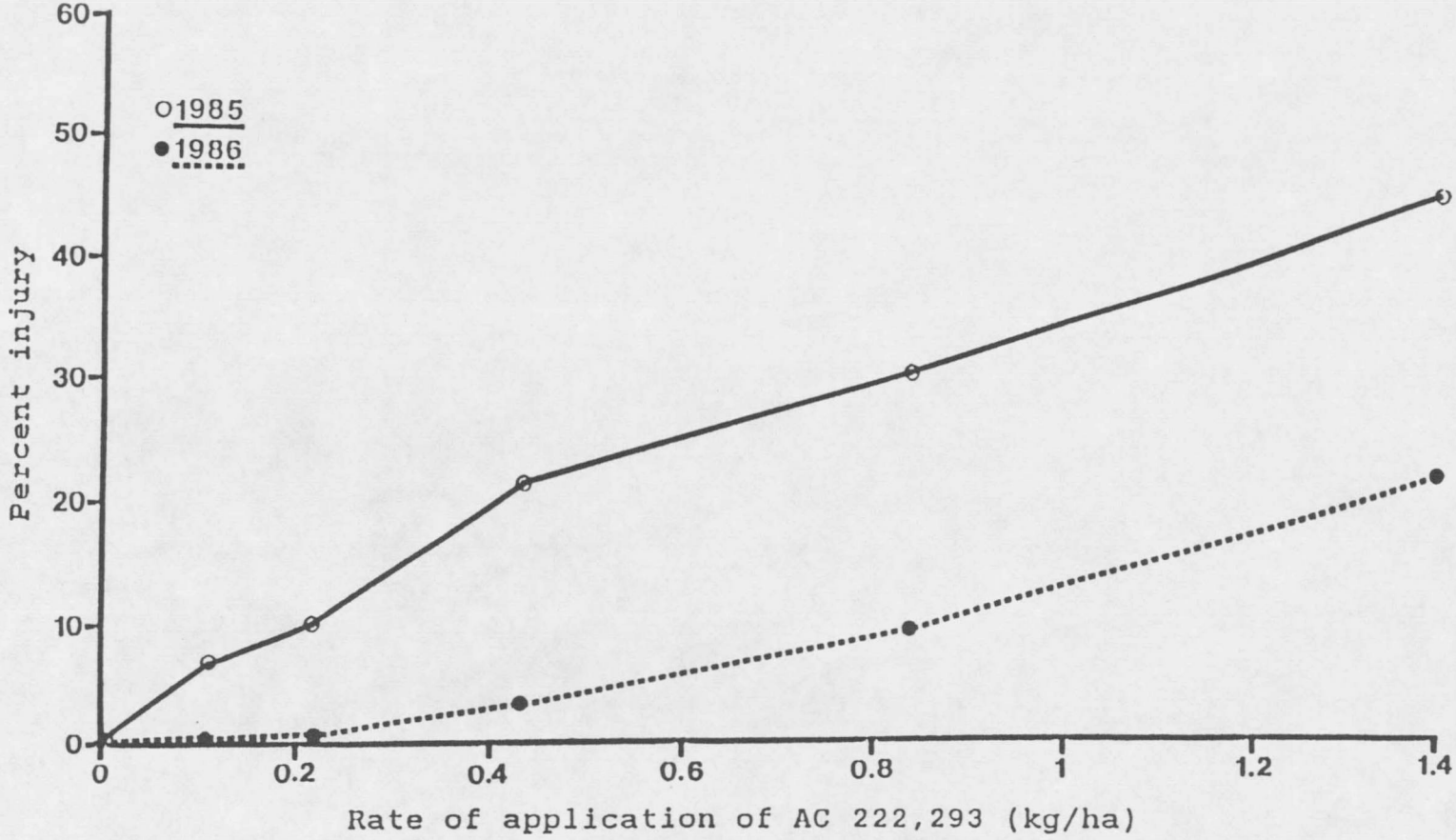


Figure 6. Average injury of alfalfa, faba bean, flax, lentils, garbanzo bean, potatoes, and sugar beet grown at Kalispell in 1985 and 1986 in soil treated with AC 222,293 preplant incorporated in 1985.

1985 at the three highest rates of application. The reduction in injury was approximately 70% which was consistent at the three highest herbicide rates. In 1986 the seven crops were not significantly injured in plots treated with 0.2 and 0.4 kg/ha.

Sugar beet yields were reduced at all rates tested at Kalispell in 1986 (Table 12). The yield of lentils was reduced only in plots treated with 1.4 kg/ha. No other crop yields were reduced despite the visual injury observed earlier in the season.

Table 12. Yield of 11 crops planted in 1986 in soil treated with AC 222,293 preplant incorporated in 1985 at Kalispell, Montana.

	Crop Yield[1]					
	AC 222,293 Rate (kg/ha)					
Crop	-0-	0.1	0.2	0.4	0.8	1.4
	% of control					
Alfalfa	100 a	97 a	98 a	99 a	108 a	98 a
Faba bean	100 a	133 a	122 a	134 a	100 a	88 a
Flax	100 a	94 a	104 a	104 a	93 a	112 a
Garbanzo bean	100 a	120 ab	143 ab	131 ab	138 ab	165 b
Lentils	100 ab	122 a	113 a	115 a	82 b	52 c
Potatoes	100 a	102 a	101 a	94 a	96 a	96 a
Sugar beets	100 a	65 bc	71 bc	74 b	52 cd	44 d
Yellow mustard	100 a	140 a	69 a	88 a	127 a	80 a
Oats	100 a	120 a	119 a	100 a	124 a	108 a
Rape	100 b	86 b	140 ab	94 b	158 a	103 ab
Winter wheat	100 ab	89 ab	102 b	99 ab	88 a	100 ab

[1] Numbers in rows followed by the same letter are not significantly different at the 5% level using the LSD test.

Summary

Sensitivity to soil residues of AC 222,293 varied among

crops. Yields of corn, lettuce, pinto beans, sunflower, and safflower was not reduced when planted into soil treated with AC 222,293 at rates as high as 1.4 kg/ha. Alternatively, lentils, yellow mustard, oats, rape, and sugar beet are sensitive to soil residues of AC 222,293.

Crop injury varied significantly by location. Crop injury was most severe at Bozeman in 1985. The difference in injury at the three locations in 1985 suggests that availability of AC 222,293 to plants varies according to soil type. Injury in 1986 followed a pattern similar to 1985 with the most severe crop injury occurring at Bozeman. Correlation of several soil factors with crop injury indicated that while no single variable could account for the variation among sites, soil pH was the most highly correlated factor. There appeared to be less crop injury on soils with a high pH.

CHAPTER 3

ADSORPTION AND LEACHING OF AC 222,293

Introduction

AC 222,293 is a promising new herbicide for the control of wild oat in small grain. The persistence of AC 222,293 in soil has been compared to that of simazine, a moderate to long term persistent herbicide (79). This extended period of soil activity may limit crop rotation alternatives.

Two important factors which govern the soil persistence of a herbicide are adsorption to soil particles and soil mobility. Soil adsorption of a herbicide effects it's mobility, biological activity, and persistence. Herbicide molecules that are adsorbed to soil constituents are normally unavailable for uptake by plants (5). While adsorption normally protects the herbicide from degradation (55), there are herbicides which are degraded by non-biological reactions while adsorbed (11).

The mobility of a herbicide in soil can influence efficacy, crop injury, and its potential for environmental contamination (105). Soil thin-layer chromatography (TLC) methods are routinely used to measure herbicide mobility in soil (47). Herbicide mobility on soil TLC plates has been used to classify herbicides into five mobility classes.

Helling and Turner (49) found that the soil TLC Rf value for 16 pesticides correlated well with their respective movement in soil measured in field studies using lysimeters and soil columns. Soil TLC is insensitive to temperature, sample size, and the removal of the sand fraction from soil (47).

The objectives of this study were to measure the soil adsorption properties of AC 222,293, to determine which soil properties influence adsorption, and to determine the mobility of AC 222,293 in several soils.

Materials and Methods

Nine agricultural soils, collected in Montana in 1985, are described in Table 13. The soils were air dried, ground, and sieved through a 0.5 mm screen before use.

Table 13. Selected properties of 9 soils used in the adsorption and leaching experiments.

No.	Soil Series and Texture	Soil pH	Organic Matter Content	Cation Exchange Capacity	Clay Content
			%	meq/100g	%
1	Bozeman silty clay loam	6.0	1.6	18.1	34.8
2	Bozeman loam	5.8	4.6	20.1	26.8
3	Scobey clay loam	7.7	1.2	16.7	28.8
4	Joplin loam	7.3	1.1	12.6	25.3
5	Creston sandy loam	6.9	3.8	12.2	10.8
6	Flathead sandy loam	7.8	4.4	32.2	17.3
7	Vanada clay loam	7.4	2.4	29.1	39.3
8	Judith-danvers clay loam	7.3	3.1	27.6	21.3
9	Pierre clay loam	7.3	2.2	31.9	55.3

Soil Adsorption of AC 222,293.

A soil slurry was formed by placing 1.0 g of soil and

10 ml of distilled water into a 25 ml plastic centrifuge tube. AC 222,293 was added to the soil slurry at soil concentrations of 0.1, 0.5, 1.0, and 1.5 ppm (w/w). Ten percent of the AC 222,293 was ^{14}C radiolabled (specific activity = 39.65 uCi/mg) on the imidazolinone ring in the #5 position. Technical grade AC 222,293 (90% purity) comprised the remaining 90%. The radiolabeled and technical grade AC 222,293 were obtained from the American Cyanamid Company. The centrifuge tubes were shaken on a mechanical shaker at room temperature for 24 hours, a period previously determined to be sufficient for herbicide adsorption to reach equilibrium. After shaking, the tubes were centrifuged for 20 minutes at 3200 x g. Five ml aliquots were taken from the supernatent and added to 15 mls of water-accepting liquid scintillation cocktail[1]. Samples were then analyzed for radioactivity by liquid scintillation counting[2] for 10 minutes. CPMs were corrected to dpms using a quench curve constructed using ^{14}C n-hexadecane (specific activity = 508 uCi/mg) as an internal standard.

Freundlich K values (15) were calculated using the log form of the Freundlich equation which forms the equation of a line:

$$\log (x/m) = \log K + 1/n \log C$$

where: x/m = soil concentration of AC 222,293 (ug/g), 1/n =

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[1] Scintiverse E., Fisher Scientific Co., Fair Lawn, N.J.
[2] Tri-carb 4430., Packard Instrument.Co., Downers Grove, IL.

slope of the line, and K = the intercept of the line. The solution concentration (C) was calculated from the amount of radioactivity present in the samples. The soil concentration of AC 222,293 was determined by subtraction of the amount in solution from the initial amount added.

The distribution adsorption constant (Kd) was calculated for each soil using the following equation:

$$Kd = (x/m) / C$$

Kd values were found at each concentration and averaged for each soil. All concentrations were replicated four times and the experiment was repeated twice.

Soil Mobility of AC 222,293.

Soil thin-layer chromatography plates were prepared by placing two layers of laboratory tape on the edge of 18 by 18 cm glass plates to act as spacers. A soil slurry was made (1:2, soil:distilled water, v/v) and spread evenly over the plates with a glass rod rolled over the tape. The plates were allowed to air dry for seven days before spotting with herbicide. Each plate was spotted with approximately 8000 dpms (0.09 ug) of ^{14}C AC 222,293 3 cm from the bottom of the plate. A separate lane was spotted on each plate with ^{14}C atrazine (specific activity = 0.005 uCi/mg) to act as a standard. The plates were placed in a glass chromatography tank at 100% relative humidity and developed with distilled water in an ascending direction to a height of 18 cm and air dried. The individual lanes on the plates were scraped in

one cm tall by 3 cm wide increments from the origin to the running front. Individual scraped samples were weighed and oxidized in a biological oxidizer[3] with the resulting ^{14}C-CO_2 trapped in CO_2 trapping scintillation cocktail[4]. Oxidizer efficiency curves were developed by weight for each soil using ^{14}C n-hexadecane. Cpms from the scintillation counting of the samples were corrected to dpms using the efficiency curves. There were three replicated soil TLC plates for each soil.

Relative mobility (Rf) values were calculated as:

$$Rf = \frac{\text{Distance traveled by the front of the band}}{\text{Distance traveled by the water front}}$$

The degree of tailing was determined by measuring the movement of the trailing edge of the herbicide streak or band (Rb) as follows:

$$Rb = \frac{\text{Distance traveled by the trailing edge}}{\text{Distance traveled by the water front}}$$

The dispersion of the herbicide band in cm was described:

$$\text{Dispersion} = Rf - Rb$$

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[3] Model OX300 Biological Oxidizer., R.J.Harvey Instrument Co., Hillsdale, N.J.

[4] Carbon 14 Cocktail., R.J.Harvey Instrument Co., Hillsdale, N.J.

Results and Discussion

Soil Mobility of AC 222,293.

Radiolabeled AC 222,293 showed limited mobility on soil TLC plates (Figure 7). There was little movement beyond 7 cm from the origin on all soils except soil 5. Rf values varied by soil ranging from 0.36 to 0.63, with an average Rf value of 0.53 for the eight soils used. Soil 9, which contained 55% clay, was not used in the soil mobility study because it fractured upon drying which prevented water movement via capillary action. AC 222,293, with an average Rf value of 0.53 is a class 3 mobile herbicide, based on the classification system of Helling and Turner (49). Other class 3 mobile herbicides include atrazine, simazine, and monuron (3-(p-chlorophenyl)-1,1-dimethylurea mono (trichloroacetate)) (46).

The Rb values for the eight soils ranged from 0.14 to 0.36 with an average value of 0.25 (Table 14). Rb values followed a pattern similar to the Rf values but were negatively correlated (r=-.93) with soil organic matter (Table 15). The AC 222,293 spot moved as a dispersed band through the soil. The range of dispersal varied significantly by soil and averaged 4.0 cm (Table 14). The mobility pattern of AC 222,293 on soil TLC plates was fairly similar to atrazine (Figure 7).

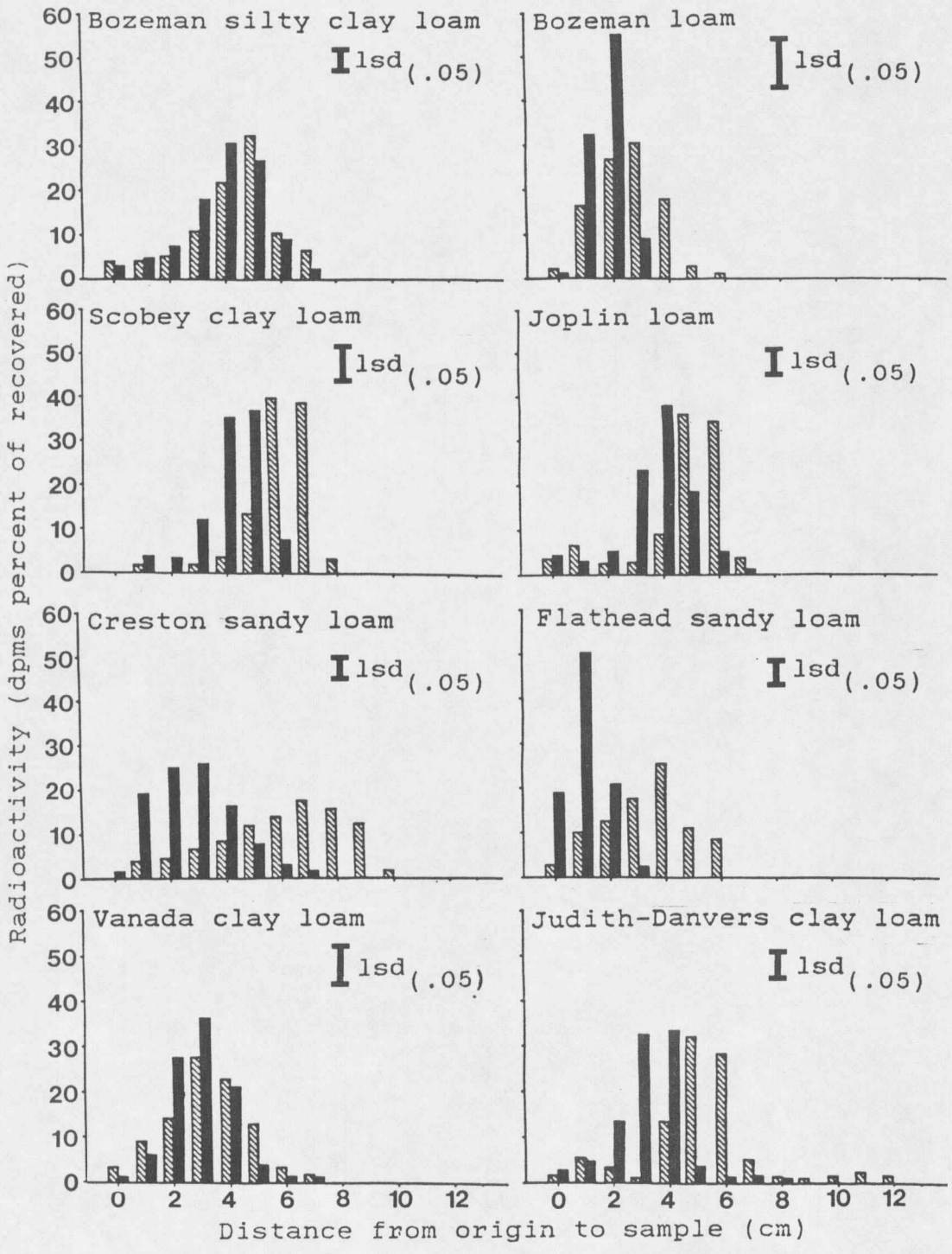

Figure 7. Distribution of ^{14}C AC 222,293 and ^{14}C atrazine in eight soils on soil thin-layer chromatography plates.

AC 222,293 atrazine

Table 14. Mobility and dispersion of AC 222,293 in eight soils on soil thin-layer chromatography plates[1].

Soil No.	Soil Mobility of AC 222,293[2]		
	Rf	Rb	Dispersion
			cm
1	.56 bc	.28 abc	3.8 ab
2	.36 a	.14 a	3.1 a
3	.56 bc	.36 c	2.7 a
4	.52 b	.30 bc	3.1 a
5	.63 c	.23 abc	5.5 c
6	.51 b	.16 ab	5.0 bc
7	.53 b	.23 abc	4.1 abc
8	.54 bc	.21 ab	4.7 bc
average	.53	.25	4.0

[1] Average of three plates per soil.
[2] Numbers in columns followed by the same letter are not significantly different at the 0.05 level using the LSD test.

Table 15. Pearson correlation coefficients (r) of Rf, Rb and dispersion values and selected soil properties of soils used in soil thin-layer chromatography study.

	Pearson correlation coefficients (r)[1]						
Factor	Rf	Rb	Dispersion	Soil pH	OM	CEC	% clay
Water flux	.53	-.03	-.17	-.31	.23	-.48	-.65
% clay	-.24	.30	-.12	-.20	-.53	.16	
CEC	-.25	-.55	.88	.34	.41		
OM	-.40	-.93	.41	-.20			
Soil pH	.42	.28	.34				
Dispersion	-.06	-.54					
Rb	.55						

[1] Correlation coefficients that are underlined are significant at the 0.05 level.

Soils 2 and 5 have the most extreme Rf values of the nine soils (Table 14). Soil 5, the Creston sandy loam soil,

has the highest Rf value of 0.63. It also has the highest water flux (WF) rate which is defined as the speed in cm/hour that the water front moves on the soil-TLC plates (Appendix b). The high water flux in soil 5 is probably due to the low clay content, 10.8%, which acts to increase the speed of water movement through of the soil by lowering the water holding capacity. Soil 2, the Bozeman loam soil, with an Rf of only 0.36, has the lowest soil pH and highest organic matter content of the soils tested (Table 13), factors that are commonly correlated with increased herbicide adsorption.

The Rf, Rb and dispersion values of AC 222,293 on soil TLC plates were correlated with selected soil factors (Table 15). Water flux (WF) had the highest correlation with the Rf values (r=-.53).

An equation was developed using multiple linear regression analysis to predict AC 222,293 mobility using selected soil properties. The equation:

$$Rf = -.6054 + .1063(pH) + .0074(\% \text{ clay}) + .0261(WF)$$

was derived which is significant at the 0.01 level (R^2=.98). Helling (49) found water flux to be significantly correlated with movement of 13 pesticides on 14 soils. However, when he removed two soils with the largest water flux rates, water flux was only correlated with movement of three of the pesticides. If soil 5 which had the highest water flux rate is not included, water flux is no longer correlated with Rf.

When multiple linear regression is then performed, the equation:

$$Rf = .4942 - .0579(OM) + .0076(CEC)$$

is derived which is significant at the 0.05 level (R^2=.86).

TLC plates provide a rapid and reproducible method of predicting soil movement. Helling (45) compared the Rf values of 37 pesticides with published observations of field and laboratory studies and found that the trends indicated by soil TLC plates were consistent with the published findings.

Soil Adsorption of AC 222,293.

Freundlich K values for AC 222,293 ranged from 0.55 to 3.45 and averaged 1.78 for the nine soils tested (Table 16). The distribution adsorption constant, Kd, averaged 0.91. The percent of AC 222,293 adsorbed was constant over the four concentrations used for each soil (Appendix C) and averaged 14.9% for nine soils (Table 16).

Soil organic matter was positively correlated with both Freundlich K values (r=.79) and percent adsorption (r=.80) at the 0.05 and 0.01 levels of significance, respectively. Soil pH was negatively correlated with the K values and percent adsorption with Pearson correlation coefficients of -0.62 and -0.64, respectively.

Table 16. Freundlich constants (K), distribution adsorption constant (Kd), and percent adsorption for AC 222,293 on nine soils.[1]

Soil Number	K	Kd	Adsorption
			%
1	1.78	1.8	15.2
2	3.45	3.6	27.0
3	0.55	1.0	8.2
4	0.76	0.8	7.6
5	2.80	2.6	19.7
6	1.96	2.0	17.1
7	0.79	0.9	9.3
8	1.80	1.4	13.0
9	2.20	2.1	17.0
mean (s.d.)	1.79(.97)	1.8(.91)	14.9(6.24)

[1] Average of two experiments per soil.

Multiple linear regression analysis was used to derive this equation:

$$K = 5.016 - .6499(pH) + .5005(\text{organic matter})$$

which is significant at the 0.01 level (R^2=.84). Therefore, as soil organic matter is increased or soil pH is decreased the adsorption of AC 222,293 is increased. It is important to note, however, that AC 222,293 was not strongly adsorbed on any of the soils tested in this study.

Soil organic matter is the soil factor most often correlated with herbicide adsorption. Grover (31) showed that the addition of organic matter reduced the availability and activity of simazine. Likewise, Harrison et al (43) found a similar relationship with five herbicides representing five herbicide families. Organic matter has the highest cation exchange capacity of all soil constituents

and a large surface area, from 300 to 800 m^2 per gram (6) making it the major site for herbicide adsorption.

Calvet (15) stated that the relationship of decreasing adsorption with increasing pH is observed when weak bases such as AC 222,293 are adsorbed on negatively charged adsorbents such as humic acids. Adsorption of atrazine, another weak base herbicide, was also found to decrease with increased pH and decreased organic matter (95).

Cohen et al (101) found that the pesticides implicated in twelve cases of groundwater contamination had water solubilities greater than 30 ppm, soil distribution coefficient (Kd) values of less than 5 (usually less than 1), and a soil half-life greater than 2 to 3 weeks. Cohen also found that pesticides found in groundwater have other characteristics: a photolysis half-life greater than 1 week, a hydrolysis half-life greater than approximately 25 weeks, a Koc value of less than 330 to 500, and a Henry's law constant less than 10^{-2} atm-m^3/mol.

Henry's law is a measure of the tendency for molecules to escape as dilute solutes from water. It is approximated by the ratio of vapor pressure to water solubility at a given temperature. The Koc value is the Kd value divided by the soil organic carbon fraction. This relates the effect of soil organic matter to herbicide adsorption. Herbicides with low Koc values are possible sources of groundwater contamination. In addition to these chemical factors certain

field conditions must exist for groundwater contamination to occur.

The water solubility of AC 222,293 is 857 and 1370 ppm for the p- and m- isomers respectively, and the herbicide has a soil half-life of 30 to 276 days (4). The Kd values for AC 222,293 averaged 1.8 for the nine soils tested, well below the upper limit found by Cohen. While AC 222,293 has several characteristics which fall within the range of values common to herbicides found in groundwater, other characteristics especially its moderate soil mobility reduce its potential for contamination.

Summary

AC 222,293 with an average Rf value of 0.53 on soil TLC plates is a moderately mobile herbicide. AC 222,293 moves as a disperse band through the soil. Soil adsorption of AC 222,293 is moderate to low with an average Freundlich K value of 1.79 on nine soils. Adsorption was positively correlated with soil organic matter. The water solubility, soil half-life, and Kd values of AC 222,293 fall well within the range of values common to herbicides that have been found to be groundwater contaminates. However, because of its limited mobility on soil TLC plates AC 222,293 will not, in my opinion, be an environmental threat to groundwater in Montana.

CHAPTER 4

DEGRADATION OF AC 222,293 UNDER CONTROLLED CONDITIONS

Introduction

AC 222,293 is a new herbicide for postemergence control of wild oat in wheat and barley. The soil half-life of AC 222,293 ranges from 30 to 276 days (4). This extended and unpredictable period of soil activity will limit crop rotation alternatives. In general, the persistence of AC 222,293 has been compared to that of simazine, a moderate to long term persistent herbicide (79).

AC 222,293 is degraded by biological and chemical pathways (64). The rate of chemical hydrolysis is slow at pH 5 and 7 however at pH 9 hydrolysis is rapid (4).

Many factors can influence the degradation rate of a herbicide. Adsorption, the binding of the herbicide to soil, can remove the herbicide from the soil solution and make it unavailable for degradation (88). Adsorption of AC 222,293 is inversely correlated with soil pH as it is more tightly adsorbed as soil pH increases (Chapter 3).

Bioassays are commonly used to determine the presence or concentration of a herbicide in soil (5). Bioassays unlike most chemical assays measure phytotoxic breakdown products in addition to the parent compound. Bioassays do

not require lengthy extraction procedures and expensive equipment needed for chemical analysis. However, bioassays measure only the amount of herbicide available to the plant. The proportion of the herbicide that is available for plant uptake can be influenced by variations in soil moisture, soil nutrient levels, soil moisture, plant density, light, and temperature.

The objective of this experiment was to measure the effect of soil type and temperature on the degradation rate of AC 222,293 using a plant bioassay.

Materials and Methods

The agricultural soils used in this study were collected in Montana in the spring, 1986 (Table 17). The soils were air dried and sieved through a 10 mm screen before use.

Table 17. Selected properties of 9 soils used in the AC 222,293 degradation experiments.

No.	Soil Series and Texture	Soil pH	Organic Matter Content	Cation Exchange Capacity	Clay Content
			%	meq/100g	%
1	Bozeman silty clay loam	6.0	1.6	18.1	34.8
2	Bozeman loam	5.8	4.6	20.1	26.8
3	Scobey clay loam	7.7	1.2	16.7	28.8
4	Joplin loam	7.3	1.1	12.6	25.3
5	Creston sandy loam	6.9	3.8	12.2	10.8
6	Flathead sandy loam	7.8	4.4	32.2	17.3
7	Vanada clay loam	7.4	2.4	29.1	39.3
8	Pierre clay loam	7.3	2.2	31.9	55.3

Soil Treatment.

A stock solution of herbicide was prepared by mixing 3.3 ml of the 2.5 EC commercial formulation of AC 222,293 with water to reach a final volume of 1000 ml. The stock solution contained 1g of AC 222,293 per liter. To prepare treatment solutions, 59 or 119 ml of stock solution was mixed with water to reach a volume of 250 ml with a final concentration of 0.19 and 0.39 mg/ml AC 222,293 respectively.

Thirty ml of water, the 0.19, or 0.39 mg/ml stock solutions were pipetted onto 6 kg of air dry soil to yield final soil concentrations of 0, 1, and 2 ppm AC 222,293 (w/w). The treated soil was placed in a 15 liter plastic container, covered tightly, and placed on a rolling mixer for 45 minutes. One hundred gram samples of the treated soil were placed in 6.5 cm diam by 4 cm deep styrofoam cups, brought to 20% moisture (w/w), covered with tightly fitting plastic lids, and stored at 4.5 or 18.5 C. Cups were placed in a freezer at -5 C after 0, 1, 2, 4, 8, 12, and 16 weeks to await the bioassay test.

A standard bioassay curve was constructed by treating 600 g of each soil with 3 ml of stock solution as described above to yield final soil concentrations of 0, 0.25, 0.5, 0.75, 1.0, 1.5, and 2.0 ppm AC 222,293 (w/w). The soil was mixed, weighed into individual cups, and watered as described above. The treated soils used for the standard

curve were frozen within 6 hours after treatment, and stored to await the bioassay. There were six replications for the standard curve and four replications for each date and temperature treatment. The experiment was repeated twice and the means pooled.

Bioassay for AC 222,293.

The cups were thawed for 24 hours, watered to field capacity, and placed in the greenhouse. Four oat (*Avena sativa* L. 'Otana') seeds were planted in each cup by pushing the seeds vertically into the soil embryo side down until the top of the seed was flush with the soil surface. The cups were watered daily with 20 ml using an automatic pipette. The greenhouse was maintained at 21 C under natural light supplemented with metalarc halide lamps which supplied 140 $uEm^{-2}s^{-1}$ artificial lighting. A completely randomized design was utilized and the cups were rerandomized every 2 to 3 days to offset environmental variation. Thirty days after planting above ground plant biomass was harvested, dried at 50 C for four days, and dry weights recorded.

A standard curve was constructed by regression analysis of the rate of AC 222,293 applied against the log of oat dry weight as a percent of the control. The rate of AC 222,293 present in treated soil was determined by comparing the log of oat dry weight as a percent of control to the standard curve. The rate of AC 222,293 remaining in the treated soil was then regressed against time in weeks. The slope of the

line represents the loss in ug of AC 222,293 per g soil per week.

Results and Discussion

Bioassay for AC 222,293.

Yellow mustard (*Brassica alba* L.), rape (*Brassica napus* L.), sugar beets (*Beta vulgaris* L.), cucumbers (*Cucumis sativus* L.), and oats were screened as bioassay plants based on their response in the plantback study (Chapter 2). Yellow mustard and rape showed differential sensitivity to AC 222,293 at 0.0, 0.25, and 0.5 ppm (w/w), but were severely injured at higher rates. Sugar beets were killed at 0.5 ppm and higher rates of AC 222,293. Cucumbers were visually injured by the AC 222,293 but survived by utilizing their cotyledon reserves so only small differences in fresh or dry weight of the true leaves were measured.

Oats were chosen as the bioassay plant because they were sensitive to the range of AC 222,293 rates tested (Figure 8). The fit of the regression lines as determined by F-tests were significant at the 0.05 level for all soils and both experiments, except soil 5 in the first test. However, the slope of each line was less than -0.2. For optimum accuracy a bioassay standard curve should not only be linear but have a reasonably large slope.

Significant visual differences were observed in oat plants harvested 30 days after planting. Untreated plants had 2 to 2.5 fully extended leaves while oats grown in soil

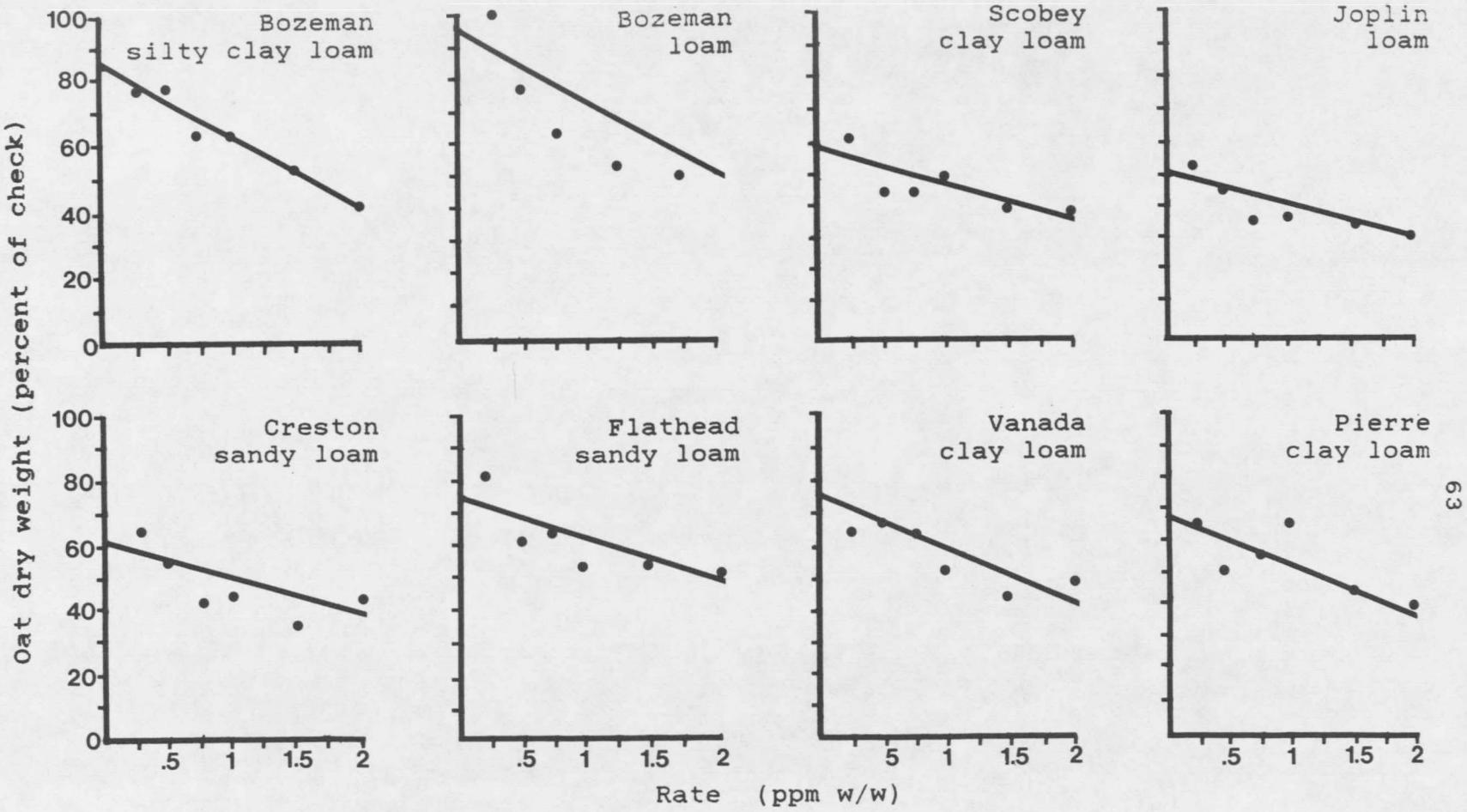

Figure 8. Standard curve for AC 222,293 degradation experiments. (Lines are derived from the equation: Log(% of check) = a + b(rate)).

treated with 2 ppm AC 222,293 had produced only one leaf. The distinction between oat plants grown at intermediate rates was not clearly discernible. Extending the harvest date beyond 30 days might intensify the differences in phytotoxicity among rates.

Degradation Rate of AC 222,293.

The degradation rate of AC 222,293 was linear over time with no initial lag phase (Figure 9). During the time course of the experiment degradation of AC 222,293 followed zero-order kinetics since the rate of degradation was independant of herbicide concentration (34). The half-life of AC 222,293 is thus dependent on the initial concentration of the herbicide.

The degradation rate of AC 222,293 was faster in soil treated with 2 ppm than at 1 ppm for all soils, except the Bozeman loam soil (Table 18). There was a twofold increase in the average degradation rate for eight soils at the higher herbicide concentration (2 ppm). However, the difference in degradation rates was not significant at the 0.05 level for any of the soils tested for reasons which will be discussed later. The trend toward more rapid degradation at higher herbicide concentrations may be due to microbial breakdown. Alexander (3) states that higher substrate concentrations may support higher levels of microbial activity causing more rapid dissipation.